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AN X-RAY DIFFRACTION INVESTIGATION OF
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SODIUM BROMIDE SOLID SOLUTIONS WITH
A NEW TYPE OF FOCUSING SPECTROMETER

DISSERTATION
Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
Graduate School of the Ohio State
University

By

GEORGE FRANCIS NEILSON, JR., B.S., M.S.

The Ohio State University
1962

Approved by

Adviser
Department of Chemistry

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The author would like to express his deep appreciation to Professor William J. Taylor, who suggested this investigation and guided it throughout its course, while giving so freely of his time and advice.

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CHAPTER I
INTRODUCTION

Distorted crystal lattices may be classified into two types, depending on whether the long-range periodicity of the lattice is or is not preserved. When the long-range periodicity of the lattice is disturbed, a broadening of the Laue-Bragg reflections may be expected. On the other hand there is evidence that certain localized defects, such as interstitial atoms or substitutional atoms of different size than the atom they replace, may distort the lattice locally without destroying its long-range periodicity or the sharpness of the Laue-Bragg reflections. However, these impurities will produce a homogenous expansion or contraction of the (mean) lattice, with a resultant shift in the position of the Laue-Bragg reflections.

The theories of the effect of lattice distortion on the diffraction intensities are reviewed in Chapter II. Emphasis is placed on the theory developed by Taylor, which treats more accurately than previously the effect of both the long-range inverse-square displacements responsible for the lattice expansion, and the relatively large displacements of neighboring atoms which depend specifically on the atomic radii and forces in a given lattice. The theory indicates that the displacement disorder will produce a decrease in the integrated intensity of the sharp Laue-Bragg reflections as well as diffuse scattering. There has been no conclusive experimental confirmation of these effects, both of which are similar to those produced by thermal vibration.

The present investigation is directed toward testing this theoretical treatment of displacement disorder by applying the theory to experimental
intensities of the Laue-Bragg reflections from solid solutions exhibiting this disorder. Three solid solutions containing 25, 50, and 75 mole percent of sodium bromide in sodium chloride were chosen for investigation. Since intensity data of the highest possible accuracy were required, a new type of x-ray powder spectrometer which makes use of a curved sample, and fulfills exactly the so-called parafocusing conditions, has been designed and constructed. The theory of this instrument, its construction, and operation are described in Chapters III and IV.

The experimental intensity data for pure sodium chloride and sodium bromide and the three solid solutions, and the calculated structure factors, are presented in Chapter VI. In Chapter VII the effective atomic scattering powers are derived and corrected for thermal vibration. The corrected values are less than the theoretical Hartree or Thomas-Fermi values. The differences must be attributed to lattice distortion, and they are interpreted in terms of the theory of Taylor. The decreases cannot be accounted for solely on the basis of the long-range inverse-square type displacements to which the entire effect is ascribed in the theory of Huang. The greater part of the decrease must be attributed to relatively large displacements of neighboring ions. Values for the magnitudes of the largest displacements are derived on the basis of the theoretical formulas of Taylor.
A. Review of X-ray Scattering from Crystals Containing Impurity Defects

When solute atoms are introduced into an otherwise perfect lattice, they may preferentially occupy either interstitial sites or lattice sites. While many examples of each defect type are known, this discussion will be concerned primarily with substitutional impurities and their effects on x-ray scattering.

To a fair degree of accuracy the x-ray scattering effects due to substitutional solute atoms can be separated into two classifications: (1) effects due to the degree of order of the soluto atoms and (2) effects resulting from a displacement of the atoms from their normal lattice positions if there is a difference in size between the solute and solvent atoms. The former effect produces sharp superlattice reflections when long-range order is present as well as diffuse scattering which depends upon the degree of short-range order. The latter effect, which causes local distortion as well as an overall lattice dilation, produces changes in the positions and intensities of the Laue-Bragg diffraction maxima and also produces diffuse maxima.

It should be pointed out that it is possible, at least in principle, to distinguish the diffuse scattering due to configurational short-range order from that due to displacement disorder since the former would give broad maxima in this diffuse background at the positions of the superlattice reflections of the ordered lattice whereas the latter
would give broad maxima at the positions of the normal Laue-Bragg reflections analogous to thermal diffuse scattering.

Scattering effects arising from an ordered distribution of atoms in a solid solution have been observed in various binary alloys, and of these the Cu₃Au alloy perhaps has been most extensively studied. Wilchinsky (1) examined this system using powder diffraction methods. He determined the degree of long-range order from the relative intensities of the superlattice reflections as well as the degree of short-range order for the first three shells around a given lattice site from a consideration of the diffuse scattering. Cowley (2) reexamined this system using single-crystal techniques and carried out a detailed analysis of the diffuse scattering by defining a short-range order parameter equivalent to the Fourier coefficients in the expansion of the diffuse intensity. Since the present investigation is mainly concerned with scattering effects due to displacement disorder, the problem of configurational order-disorder will not be discussed further.

Theoretical calculations pertaining to the x-ray scattering by a lattice containing a random distribution of localized defects are rather few. In the following review of this literature only the treatments of the problem as given by Huang (3) and Taylor (4, 5, 6) will be considered in detail.

The earliest general formulation of the effect of displacement disorder upon x-ray scattering has been clearly given by Zachariasen (7). He demonstrates that scattering from such a distorted lattice will
consist of sharp Laue-Bragg reflections at reciprocal lattice points and also diffuse maxima surrounding them. The treatments of Taylor and Huang may be considered as extensions of his results.

Ekstein (8) and Matsubara (9) have examined the case in which the lattice atoms are given small displacements from their normal sites, expressing the scattering from the distorted lattice by the first two terms in a Taylor's series. They consider only the term which pertains to the diffuse scattering at positions distant from reciprocal lattice points, relating this term to the Fourier transforms of the displacements. Unfortunately this method of approximation gives no information concerning the distortion effect upon the Laue-Bragg scattering itself. For the special case of defects which produce an elastic deformation Ekstein evaluates the transform directly and he concludes that these defects give rise to diffuse maxima surrounding the sharp Laue-Bragg reflections. Matsubara expresses the Fourier transforms in terms of the force constants between the various atoms of the lattice. In this method the atomic displacements around the defect are determined by minimizing the strain energy of the lattice with respect to the displacement thus obtaining the equation of equilibrium. The results of Matsubara are equivalent to those of Ekstein for the case of defects producing displacements over rather wide distances.

An abbreviated formulation of coherent scattering by disordered crystals has been given by Cochran (10) in terms of the Fourier transforms of the defects considered separately. General expressions for the diffuse intensity and the change in the Laue-Bragg intensity are
obtained for the case of defects which combine additively for the net displacement of a given atom. Cochran applies his equations to the specific problem of defects produced by the replacement of the lattice atom by another of different size and scattering factor and obtains results which are very similar to those of Huang (3) which will be discussed subsequently.

Warren, Averbach, and Roberts (11) obtain an expression for the total scattering by a distorted lattice which exhibits short-range substitutional order as well as displacement disorder. Their results indicate that the size effect produces modulations in the diffuse intensity similar to those produced by the short-range order. However their theory predicts no diminution of the integrated intensities of the Laue-Bragg reflections contrary to other theories. This discrepancy is probably related to their assumption that the displacements are not spherically symmetric about a given solute atom, but rather depend upon the degree of order in each shell and hence depend anisotropically on the identity of the atoms displaced.

A theoretical treatment of the x-ray effects brought about by localized lattice defects has been carried out by Huang (3) in which he considers the scattering produced by a lattice containing a random distribution of singularities which individually cause radially directed elastic displacements of the surrounding atoms. The two basic assumptions made in his treatment are (1) that the displacements due to a given solute atom are spherically symmetric and (2) that the total displacement of each lattice atom is the vector sum of the displacements produced by each defect acting separately.
For point defects in isotropic crystals the application of the classical theory of elasticity leads to displacements of the form

$$\vec{u} (\vec{A}_i^\alpha) = c \frac{\vec{A}_i}{|\vec{A}_i|} \alpha^{1/3},$$  \hspace{1cm} (2.1)$$

where $c$ is a constant, $|\vec{A}_i|$ is the distance from a defect site $\alpha$ to a lattice site $i$, and $\vec{A}_i^\alpha = \vec{A}_i^\alpha = \vec{A}_i^0$. This equation shows the displacement in the medium to be purely radial and to be of magnitude which is inversely proportional to the square of the radial distance.

The second assumption given above implies that the state of distortion around each defect may be regarded as being independent of the effects of other defect centers. The total vector displacement of the $i$th lattice atom will then be

$$\vec{u}_i = \sum_{\alpha} \vec{u} (\vec{A}_i^\alpha - \vec{A}_i^0),$$ \hspace{1cm} (2.2)$$

where $\alpha$ is summed over the $n$ sites occupied by the foreign atoms.

Equations (2.1) and (2.2) apply only to a primitive lattice containing one atom per unit cell for which all lattice atoms given by the vectors $\vec{A}_i^0$ are equivalent.

To determine the total x-ray intensity scattered by the distorted crystal, Huang begins with the expression

$$I_T = S \left\langle \left| \sum_i f_i \exp(i \vec{K} \cdot \vec{A}_i) \right|^2 \right\rangle,$$ \hspace{1cm} (2.3)$$

where $S$ is the intensity scattered by a single electron. The vector $\vec{K}$ is given by $\left( \frac{2 \pi}{\lambda} \right) (\vec{\Pi} - \vec{\Pi}_0)$, with $\vec{\Pi}$ and $\vec{\Pi}_0$ being unit vectors in the directions of the incident and scattered waves respectively.
The vector $\vec{\rho}_1$ locates the $i$th atom having the atomic scattering factor $f_1$, and it is given by

$$\vec{\rho}_1 = \vec{\mathbf{A}}_1^0 + \vec{u}_1$$

for a given configuration of the defect atoms. The summation term in Eq. (2.3) is identified as the structure factor for the entire crystal. For each configuration of the defects, the total intensity is proportional to the square of the modulus of the structure factor. However, the observed intensity will be proportional to the mean value of this square averaged over all configurations of the defects, as indicated by the angular brackets in Eq. (2.3).

Thus Huang obtains exponential factors for the diffracted intensity which depend upon the atomic displacements. Before averaging over all configurations, he expands these factors and discards terms of cubic and higher powers in the displacements. He then introduces the explicit form of the displacements as given by Eq. (2.1) and proceeds to carry out the formidable summations. His final expression for the scattered intensity will not be reproduced here because of its complexity and because more accurate expressions have been obtained by Taylor.

The calculations of Huang predict that the x-ray scattering by crystals which contain substitutional defects producing elastic distortion will consist of Laue-Bragg reflections at reciprocal lattice points surrounded by diffuse maxima. Although the calculation of the detailed nature of this diffuse scattering is difficult, Huang shows that for dilute solid solutions it should be comparable...
in intensity and extension in reciprocal space to thermal diffuse scattering at low temperatures. The term in his expression which represents the Laue-Bragg scattering can be readily interpreted and shows that these reflections will have their usual sharp form but with their positions and intensities altered. The change in position is due to a dilation of the lattice by the fractional amount \((4\pi cp)/3v\), with \(p\) the fraction of solute atoms, \(v\) the volume of the unit cell, and \(c\) the constant defined for Eq. (2.1). The intensity of the Laue-Bragg reflections are shown to be reduced by the factor \(\exp \left[-6\pi p(1-p)(\Delta d \sin \theta /\lambda)^2\right]\), where \(\Delta d\) is the difference in the lattice constants of the pure specimens of solute and solvent.

Since this expression has a form which is similar to the well known temperature factor for x-ray scattering by crystals, it is sometimes referred to as the artificial temperature factor, although it is of course temperature independent.

B. Theoretical Treatment of Lattice Distortion

In this section the theory of x-ray diffraction effects due to localized defects as developed and given by Taylor (4, 5, 6) will be considered in greater detail. Although the treatment of Huang is excellent as far as it goes, it does contain some limitations which are not present in the development by Taylor. The principal limitation is the assumption that all displacements follow the inverse square relationship predicted by elastic theory for an isotropic medium, an assumption which is unlikely to be correct for the larger displacements near a defect. A second limitation on the accuracy of Huang's theory results from the mathematical approximations made to
reduce the mean exponential factors containing the atomic displace-
ments which are directly obtained from the intensity expression as
given by Eq. (2.3). In Taylor's development these exponential
factors are averaged exactly (that is, without expanding the expo-
nentials), regardless of the magnitude or form of the displacements
about a defect. The only assumptions made are that (1) the defects
are randomly distributed among the available sites, (2) the set of
displacements about each equivalent defect site are the same,
(3) at large distances the form of the displacements asymptotically
approaches that predicted by elastic theory, and (4) the displace-
ments produced by the various defects are vectorially additive as in
Eq. (2.2).

In this general treatment a non-primitive lattice will be con-
sidered, whence the position of the \textit{i} th atom in the \textit{i} th unit cell
of the distorted lattice is given by

\[ \overline{\mathbf{r}}_{iL} = \overline{\mathbf{A}}_L^0 + \overline{\mathbf{r}}_i^0 + \overline{\mathbf{u}}_{iL}, \quad (2.5) \]

where \( \overline{\mathbf{A}}_L^0 \) and \( \overline{\mathbf{r}}_i^0 \) refer to the lattice vector and position vector
relative to the cell origin in the undistorted lattice and where

\[ \overline{\mathbf{u}}_{iL} = \sum_t^n \overline{\mathbf{u}}_{iL,t}. \quad (2.6) \]

Here \( \overline{\mathbf{u}}_{iL,t} \) is the displacement produced by the \textit{t} \textit{th} defect, and the
summation is carried out over all \( n \) occupied defect sites for a given
configuration. It has been demonstrated by Taylor that \( \langle \overline{\mathbf{u}}_{iL} \rangle \), the
mean displacement averaged over all configurations of the solute atoms,
corresponds to a uniform or homogeneous lattice dilation for which there
is a perfectly periodic lattice based on the mean lattice vectors $\overline{A}_L$ and mean position vectors $\overline{r}_i$. Consequently

$$\overline{A}_L^0 + \overline{r}_i^0 + \langle \overline{u}_{1L} \rangle = \overline{A}_L + \overline{r}_i . \quad (2.7)$$

However for any given arrangement of the defects, the displacement of a lattice atom will normally differ from its mean value $\langle \overline{u}_{1L} \rangle$. Thus there will be a displacement from the mean:

$$\overline{u}'_{1L} = \overline{u}_{1L} - \langle \overline{u}_{1L} \rangle , \quad (2.8)$$

and it is this quantity which represents the displacement disorder in a dilated lattice. In view of Eqs. (2.7) and (2.8), Eq. (2.5) can be rewritten as

$$\overline{r}'_{1L} = \overline{A}_L + \overline{r}_i + \overline{u}'_{1L} . \quad (2.9)$$

Define the structure factor for the entire crystal by

$$F_{\text{crystal}} = \sum_L \sum_i f_i \exp[i \overline{k} \cdot \overline{r}_{1L}] , \quad (2.10)$$

where $f_i$ and $\overline{k}$ are the atomic scattering factor and wave vector as defined in Eq. (2.3). Then, as shown by Zachariasen (7), the total x-ray intensity scattered by the crystal will be given by

$$I_T = S \langle |F_{\text{crystal}}|^2 \rangle , \quad (2.11)$$

whereas the Laue-Bragg scattering is given by

$$I_1 = S \left| \langle F_{\text{crystal}} \rangle \right|^2 , \quad (2.12)$$

because of the mean periodicity of the distorted lattice. In these equations the angular brackets again indicate averages over all
defect configurations. The difference, \( I_2 = I_T - I_1 \), represents the diffuse scattering. It can be established that \( \langle \exp \mathbf{k} \cdot \mathbf{u}_{1L} \rangle \) is independent of the cell index \( L \) in the interior of a crystal. In addition \( \mathbf{A}_L \) and \( \mathbf{r}_i \) do not depend upon the particular configuration of the defects by definition. In view of this, Eqs. (2.9), (2.10), and (2.12) can be combined to give for the Laue-Bragg scattering,

\[
I_1 = S \left| \langle F_{\text{cell}} \rangle \right|^2 \sum_{L,L'} \exp \left[ i \mathbf{k} \cdot (\mathbf{A}_L - \mathbf{A}_{L'}) \right], \tag{2.13}
\]

in which \( \langle F_{\text{cell}} \rangle \) is the mean structure factor for a typical unit cell in the expanded lattice and is given by

\[
\langle F_{\text{cell}} \rangle = \sum_i f_i \exp (i \mathbf{k} \cdot \mathbf{r}_i) \left\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{1L}) \right\rangle. \tag{2.14}
\]

The double sum in Eq. (2.13) is the familiar interference function, and it shows that there is no broadening of the Laue-Bragg reflections if the mean lattice is periodic as assumed.

From Eq. (2.11), the following expression for the diffuse intensity, \( I_2 \), is similarly obtained:

\[
I_2 = S \sum_{L,L'} \exp \left[ i \mathbf{k} \cdot (\mathbf{A}_L - \mathbf{A}_{L'}) \right] \sum_{i,j} f_i f_j \Phi_{ij, L-L'} \exp \left[ i \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j) \right], \tag{2.15}
\]

where

\[
\Phi_{ij, L-L'} = \left\langle \exp \left[ i \mathbf{k} \cdot (\mathbf{u}_{1L} - \mathbf{u}_{1L'}) \right] \right\rangle - \left\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{1L}) \right\rangle \left\langle \exp (-i \mathbf{k} \cdot \mathbf{u}_{1L'}) \right\rangle. \tag{2.16}
\]

In Eqs. (2.13) through (2.16), which have been formulated exactly, the Laue-Bragg scattering is seen to depend upon the mean exponential
\[ \langle \exp \left[ i \vec{k} \cdot \vec{u}_{iL} \right] \rangle, \] and the diffuse scattering in addition depends upon \[ \langle \exp \left[ i \vec{k} \cdot (\vec{u}_{iL} - \vec{u}_{jL}) \right] \rangle. \] Previous investigators have proceeded by expanding these factors before averaging, retaining only the quadratic terms in the displacements. However Taylor has shown that they can be averaged exactly, regardless of the nature of the displacements (subject to the few assumptions previously stated). In the following paragraphs his method of approach will be indicated in detail for the treatment of the Laue-Bragg scattering.

It follows immediately from Eq. (2.8) that

\[ \left| \langle \exp \left[ i \vec{k} \cdot \vec{u}_{iL} \right] \rangle \right| = \left| \langle \exp \left[ i \vec{k} \cdot \vec{u}_{iL} \right] \rangle \right| \cdot (2.17) \]

In addition it may be shown that if the distribution function for \( \vec{u}_{iL} \) is centrosymmetric, then its mean factor above is real; hence the absolute values signs can be removed on the left-hand side of this equation. Taylor (6) has pointed out that the mean exponential, \( \langle \exp \left[ i \vec{k} \cdot \vec{u}_{iL} \right] \rangle \), although entering this problem for physical reasons, is also the characteristic function of \( \vec{u}_{iL} \) from the point of view of mathematical statistics. Also, there is a standard theorem of statistics which states that the characteristic function of a sum of independent random variables is equal to the product of the characteristic function of the individual variables. Thus if the \( n \) solute atoms are distributed independently among the \( N \) defect sites as assumed, the separate displacements, \( \vec{u}_{iL,t} \), must be independent, and this theorem is applicable.

Therefore the mean value of \( \exp (i \vec{k} \cdot \vec{u}_{iL}) \), averaged over all configurations of the \( n \) solute atoms, may be set equal to the product of the \( n \) mean values of \( \exp (i \vec{k} \cdot \vec{u}_{iL,t}) \), where each of these factors is averaged
over the $n$ sites which a given defect may occupy. All defects are physically identical, however, and therefore $\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{1L,t}) \rangle$ will have the same value for each of the $n$ defect atoms. Hence

$$\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{1L}) \rangle = \left\{ \langle \exp (i \mathbf{k} \cdot \mathbf{u}_{1L,t}) \rangle \right\}^n \quad (2.18)$$

Since each defect site is equivalent, a given defect atom will have a probability of $1/n$ of being at any of the $N$ sites, and

$$\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{1L,t}) \rangle = 1/N \sum_{t=1}^{N} \exp (i \mathbf{k} \cdot \mathbf{u}_{1L,t}). \quad (2.19)$$

The sum in the last equation is initially restricted to a finite volume of the crystal, say, the interior of a sphere of radius $R$. In the final step of the calculation the limit $R \to \infty$ is considered as the concentration of defects remains constant; thus also $N \to \infty$. By an adaptation of the argument used by Holtsmark in obtaining the distribution of force between two ions in a gas (see Chandrasekhar (12)), the limit is found to yield an exponential function. Proceeding in this manner, Taylor has derived the following rigorous result for the characteristic function of $\mathbf{u}_{1L}$ for the case of a random and completely independent distribution of the $n$ defects among the $N$ sites

$$\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{1L}) \rangle = \exp \left\{ -p \sum_{t=1}^{\infty} \left[ 1 - \exp (i \mathbf{k} \cdot \mathbf{u}_{1L,t}) \right] \right\}, \quad (2.20)$$

where $p$ is interpreted as the ratio of defects to sites, $n/N$.

For the model used in the derivation of Eq. (2.20), there exists the possibility of more than one defect entering a given site. Taylor has also considered the more realistic model in which a maximum of one
defect is permitted at a site but their distribution is otherwise independent and has obtained the following rigorous result for this more difficult case by an adaptation of the Darwin-Fowler method of steepest descents:

\[
\langle \exp \left( i \vec{k} \cdot \vec{u}_{iL} \right) \rangle = \prod_t \left\{ 1 - p \left[ 1 - \exp \left( i \vec{k} \cdot \vec{u}_{iL,t} \right) \right] \right\} \cdot (2.21)
\]

In this case \( p \) may be interpreted as the fraction of sites which are occupied.

Therefore from Eq. (2.17), the characteristic function of \( \vec{u}_{iL} \) for the two types of distribution considered in Eqs. (2.20) and (2.21) becomes

\[
\left| \langle \exp \left( i \vec{k} \cdot \vec{u}_{iL} \right) \rangle \right| = \exp \left\{ -p \sum_t \infty \left[ 1 - \cos \left( \vec{k} \cdot \vec{u}_{iL,t} \right) \right] \right\} , \quad (2.22)
\]

and

\[
\left| \langle \exp \left( i \vec{k} \cdot \vec{u}'_{iL} \right) \rangle \right| = \prod_t \left\{ 1 - 2p \left( 1 - p \right) \left[ 1 - \cos \left( \vec{k} \cdot \vec{u}_{iL,t} \right) \right] \right\}^{1/2} , \quad (2.23)
\]

respectively, as reported by Taylor (4, 5).

Previous investigators evaluated the characteristic function of \( \vec{u}_{iL} \) by expanding the exponential terms before averaging, retaining only the quadratic terms in the displacements. This would be equivalent to expanding trigonometric expression \( \left[ 1 - \cos \left( \vec{k} \cdot \vec{u}_{iL,t} \right) \right] \) and the infinite product in the exact formula of Eq. (2.23), and retaining only the quadratic term, \((\vec{k} \cdot \vec{u}_{iL,t})^2/2\). It will be noted that both the exact formula and the quadratic expansion predict the maximum decrease in intensity for \( \vec{u}_{iL,t} \) parallel to \( \vec{k} \) or normal to the set of diffracting planes. However, the quadratic approximation predicts a monotonic
decrease of intensity as the magnitude of \( \mathbf{u}_{iL,t} \) increases, while the exact formula shows that the intensity is a periodic function of \( \mathbf{k} \cdot \mathbf{u}_{iL,t} \). Thus if an atom is displaced normal to the diffracting planes by an amount equal to the distance \( d_{hkl} \) between these planes, the diffracted intensity is unaffected. For high order reflections, \( d_{hkl} \) may be quite small, and there can be a significant difference between the quadratic and the exact trigonometric formulas, particularly for the largest displacements. Thus the importance of using the exact formula is obvious if it is desired to obtain information concerning these displacements.

It is interesting to note that the right-hand sides of Eqs. (2.22) and (2.23) depend on \( p \) and on \( p(1-p) \), respectively. Equation (2.22) is based on a model in which any number of defects can enter a site, and the allowed range of \( p \) is 0 to \( \infty \). With this model \( |\langle \exp (i \mathbf{k} \cdot \mathbf{u}'_{iL}) \rangle| \) decreases monotonically as \( p \rightarrow \infty \). For this more realistic model of Eq. (2.23), in which only one defect may enter a site, the permitted range of \( p \) is 0 to 1. Equation (2.23) then predicts that

\[
|\langle \exp (i \mathbf{k} \cdot \mathbf{u}'_{iL}) \rangle| \text{ is a symmetrical function of composition with its maximum value of unity occurring for } p = 0 \text{ and } p = 1, \text{ and minimum value at } p = 1/2. \text{ In the present theory the factor } p(1-p) \text{ enters as a result of the limitation of one defect to a site and the centrosymmetry of the lattice. Huang's theory also shows this dependence on } p(1-p).

For the special case of substitutional solid solution in which the defect sites possess a center of symmetry, Taylor has given the following concise derivation of Eq. (2.23). In this method of derivation an alternative viewpoint is adopted in which \( \mathbf{u}_{iL} \) in the characteristic
function refers to the displacement of the \(iL\) th lattice atom by the \(t\) th defect site, which may assume different values, depending on the occupant of this site, rather than the displacement due to a given defect, which depends on the site occupied by this defect. Let the lattice sites be occupied by \(n\) atoms of B and \((N-n)\) atoms of A, having mole fractions of \(p\) and \((1-p)\) respectively. Then

\[
\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{iL}) \rangle = \left\langle \prod_{t} \exp (i \mathbf{k} \cdot \mathbf{u}_{iL,t}) \right\rangle
\]

\[
= \prod_{t} \left\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{iL,t}) \right\rangle
\]

\[
= \prod_{\text{pairs}} \left| \left\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{iL,t}) \right\rangle \right|^2, \quad (2.24)
\]

where the last product is taken over all pairs of sites which are related by a center of symmetry. Since each product is taken over the available sites rather than over the solute atoms, the characteristic function of \(\mathbf{u}_{iL,t}\) must here refer to the probability of occupancy of the \(t\) th site.

If the distribution of solute atoms is random as assumed, then the probability that a given site will contain a B atom is \(p\), whence

\[
\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{iL,t}) \rangle = (1-p) \exp(i \mathbf{k} \cdot \mathbf{u}^{A}_{iL,t}) + p \exp(i \mathbf{k} \cdot \mathbf{u}^{B}_{iL,t}). \quad (2.25)
\]

Combining Eqs. (2.24) and (2.25),

\[
\langle \exp (i \mathbf{k} \cdot \mathbf{u}_{iL}) \rangle = \prod_{\text{pairs}} \left\{ 1-2p(1-p) \right\} \left[ 1-\cos(k \cdot \Delta \mathbf{u}_{iL,t}) \right], \quad (2.26)
\]

where \(\Delta \mathbf{u}_{iL,t} = \mathbf{u}^{B}_{iL,t} - \mathbf{u}^{A}_{iL,t}\). Equation (2.26) is equivalent to Eq. (2.23).
for this centrosymmetric case, if in Eq. (2.23) \( \overline{u}_{iL,t} \) is interpreted as the vector difference in displacement of the \( iL \) th atom when a \( B \) atom is substituted for an \( A \) atom at the \( t \) th site.

According to Eq. (2.14), the effective scattering power of an atom in the distorted lattice is the product of its atomic scattering factor and the characteristic function of its displacement from the mean position, for which an exact expression is given by Eq. (2.23). For the further evaluation of this Laue-Bragg scattering, it is assumed that defects beyond some arbitrary distance \( r_0 \) from the \( iL \) th lattice atom will displace this atom in the manner predicted by the elastic theory for a continuum. In this event the complete characteristic function of \( \overline{u}_{iL} \) will be the product of Eq. (2.21) for individual sites occurring within a sphere of radius \( r_0 \) and a similar product which is replaced by an integral approximation for sites occurring beyond this sphere. Taylor has evaluated this latter factor by taking the logarithm of Eq. (2.23), expanding the logarithms, and finally taking the antilogarithm, a procedure which is suggested by the form of Eq. (2.22). To the first degree in \( p(1-p) \) this result is

\[
\left| \exp \left( i \mathbf{F} \cdot \overline{u}_{iL} \right) \right|_{\text{ext}} \propto \exp \left\{ -p(1-p) \sum_t \left[ 1 - \cos(\mathbf{F} \cdot \overline{u}_{iL,t}) \right] \right\}. \quad (2.27)
\]

Higher order terms proportional to \( p^n(1-p)^n, n \geq 2 \), have been discarded in the exponent on the right-hand side of this equation. To this approximation Eq. (2.27) is similar to Eq. (2.22), except for the replacement of \( p \) by the factor \( p(1-p) \). The significance of this has been discussed previously. The sum in Eq. (2.27) is next approximated by an integral over all sites beyond the sphere of radius \( r_0 \), after substituting for the displacement, \( \overline{u}_{iL,t} \), the isotropic elastic theory.
approximation of Eq. (2.1). To this degree of approximation Eq. (2.23) becomes
\[
\left| \langle \exp \left( i \mathbf{F} \cdot \mathbf{u}_{\text{ext}} \right) \rangle \right|_{\text{ext}} = \exp \left[ -\frac{2\pi}{3}(\nu/v)(c^2/r_o) \right. \\
\left. \left( \frac{4\pi\sin\theta/\lambda}{\nu} \right)^2 p(1-p) E(x) \right], \quad (2.28)
\]
where \( \nu \) is the number of defect sites per unit cell \( v \), \( c \) is the constant of Eq. (2.1), and \( p \) is the fraction of solute atoms. \( E(x) \) is a function which depends in part on the Fresnel cosine integral, \( C(x) \), with \( x = 4\pi(\sin\theta/\lambda)(|c|/r_o^2) \). In practice \( r_o \) is sufficiently large for \( x \) to lie in the range 0 to 1, for which the corresponding range of \( E(x) \) is 1.000 to 0.99. Hence for most practical purposes \( E(x) \) may be set equal to unity. Furthermore the constant \( c \) can be related to the increment in volume of the crystal upon the addition of a single solute atom by the following argument. If the displacements at large distances have the form of Eq. (2.1), then the volume of the medium which is displaced across every spherical surface of radius \( r \) upon the addition of one solute atom at the center is \( \Delta V = 4\pi r^2 u(r) \). More accurately stated, this expression for \( \Delta V \) is applicable only to an infinite crystal. It has been shown by Eshelby (13) that for a finite crystal with a stress-free surface this volume increment is increased by a factor \( \gamma = 3(1-\sigma)/(1+\sigma) \), where \( \sigma \) is Poisson's ratio for the crystal. Hence from Eq. (2.1),
\[
c = \frac{\Delta V}{4\pi \gamma} \quad (2.29)
\]
A more detailed discussion will be deferred to Chapter VII as there has been some ambiguity in the literature as to whether the factor \( \gamma \) should or should not be included in Eq. (2.29). Both procedures will be considered in the interpretation of the data of this investigation.
$\Delta V$ may be identified as the partial atomic volume per defect added. If the system obeys Vegard's law over the complete range of composition, then $\Delta V = (v_A - v_B)/\nu$, where $v_A$ and $v_B$ are the unit cell volumes of the pure constituents.

It should be mentioned that if the factor $E(x)$ is omitted in Eq. (2.28), the exponential expanded, and only the first two terms retained, the resulting approximation agrees precisely with the results of Huang. However the complete characteristic function of $\bar{u}_{1L}$ is the product of Eq. (2.28) for the contribution of sites outside the sphere of radius $r_0$, and Eq. (2.23) for the larger displacements arising from sites within this sphere, and the importance of using the exact Eq. (2.23) for the large displacements has already been discussed. Furthermore, since it is the larger displacements in the immediate vicinity of each defect that produces the greatest effect upon the Laue-Bragg scattering, it may be expected that considerable error can result from the assumption that all displacements can be represented by the elastic approximation of Eq. (2.1). For instance in substitutional solid solutions which exhibit close packing the nearest-neighbor displacements produced by a defect atom larger than the original lattice atom should be nearly equal to the difference in radii of the two atoms. However this difference in radii can be more than twice as large as the corresponding elastic displacement predicted by Eq. (2.1) using Vegard's law, in which event it will certainly be necessary to consider these displacements separately, using the exact expression for the characteristic function given by Eq. (2.23). Anticipating the results of the present investigation, it will be found that in certain cases the greater part of...
the decrease in intensity is accounted for by inserting just the large nearest-neighbor displacements into the exact Eq. (2.23).

The diffuse intensity from a distorted lattice is given by Eq. (2.15), and the further evaluation of this quantity has been carried through by Taylor (6). Since no information concerning the diffuse scattering was obtained in the present investigation, only one result from his calculations will be given here without the details of the method of derivation. In the neighborhood of the Laue-Bragg reflection of indices (hkl), the diffuse intensity which arises from the influence of defects more distant than \( r_0 \) from each of a pair of lattice atoms is approximately given by:

\[
I^\text{ext}_2 = 64 \pi^4 (N \nu/v^2) p(1-p) c^2 |\vec{F}_{\text{hk}l}|^2 |F_{\text{hk}l}(2\pi \vec{E}_{\text{hk}l})|^2 \\
\left( \frac{\cos \alpha}{|\vec{b}|} \right)^2 \left( \frac{\sin r_0 |\vec{b}|}{r_0 |\vec{b}|} \right)^2
\]  

(2.30)

where \( \vec{E} = \vec{k} - 2\pi \vec{E}_{\text{hk}l} \) is \( 2\pi \) times the vector displacement from the reciprocal lattice point, and \( \alpha \) is the angle \( \vec{E} \) makes with \( \vec{k} \), or very nearly the angle \( \vec{E} \) makes with the fixed vector \( \vec{E}_{\text{hk}l} \) from the origin of reciprocal space to the lattice point. In this approximation the diffuse intensity is cylindrically symmetrical about \( \vec{E}_{\text{hk}l} \) as an axis, and it vanishes on a nodal plane which is normal to \( \vec{E}_{\text{hk}l} \) and which passes through the reciprocal lattice point. Equation (2.30) represents a refinement or correction of Huang's expression for the diffuse intensity; as a result of an incomplete evaluation of one of his integrals Huang obtained a considerably more cumbersome expression than Eq. (2.30).
To compute the diffuse scattering which will be observed when powder methods are employed, it is necessary to project the three-dimensional intensity of Eq. (2.30) onto an axis which coincides with \( E_{hkl} \). This calculation has been carried out by Taylor, and it shows that whereas the intensity of Eq. (2.30) has a nodal plane, its projection will have a single broad maximum at the Laue-Bragg reflection. However, numerical calculations indicate that the breadth of the diffuse reflection will be much greater than the observed breadth of the Laue-Bragg reflections. For the powders used in the present investigation, both the pure salts and the solid solutions, the Laue-Bragg intensity was found to have decreased to a negligible value at a displacement of about \( \Delta \theta = \pm 0.3^\circ \) from the line centers. The theory indicates that for this \( \Delta \theta \) the diffuse intensity would still have more than 90 percent of its maximum value at the line center. The observed intensity contours do not show any broad maxima separately underlying each Laue-Bragg reflection; instead the latter are superimposed on a smooth background. It has therefore been assumed in the treatment of the data that the diffuse intensity from the several Laue-Bragg reflections superimposes and combines with the other sources of continuous background (Compton scattering, white radiation, etc.) to yield the smooth background intensity observed. The Laue-Bragg intensities were thus calculated as the integrated areas of the Laue-Bragg maxima above a smoothly interpolated background curve.
C. Previous Experimental Work

In the previous sections the x-ray scattering effects due to displacement disorder which are predicted by the theories of Huang and Taylor have been considered in some detail. Both theories predict a uniform lattice dilation, but no broadening of the Laue-Bragg reflections if long range order is preserved. Moreover a decrease in the integrated intensities of the Laue-Bragg reflections is predicted, as well as the appearance of diffuse scattering.

The predicted lattice dilation and lack of line broadening are confirmed by a wide experience with solid solutions. However a systematic study of the decrease of the Laue-Bragg intensities has apparently been undertaken in only two previous investigations.

Tucker and Senio (14) studied the x-ray scattering effects in neutron-irradiated crystals of boron carbide, diamond, silicon carbide, and magnesium oxide using the Laue photographic method for obtaining the diffraction patterns. They found that the Laue-Bragg reflections of the treated crystals did suffer a decrease in intensity, and that some diffuse spots were formed. Although no estimates of the magnitude of the decrease in intensities of the Laue-Bragg reflections were given, it is probable that this experimental method (or any photographic method) is not capable of indicating the relative intensities of the reflections with the precision required for a quantitative verification of either theory. Coyle and Gale (19) seem to have carried out the only previous quantitative investigation of the effects of displacement disorder upon the intensities of the Laue-Bragg reflections. They compared the intensities of the reflections from a powder sample of pure copper with those from a copper-gold solid solution containing 10 atomic percent gold,
using a special Geiger-counter powder spectrometer for the intensity measurements. Their results indicate that the ratio of the observed intensities of the lines from the solid solution to the relative intensities computed assuming no displacement disorder is not constant for the various reflections, but shows a monotonic decline as \( \sin \theta / \lambda \) increases. Thus they conclude that the prediction of Huang concerning the decrease in scattering power from a distorted lattice is confirmed. However the actual magnitude of the intensity decrease for each reflection obtained in their results appears to be much larger than can be accounted for by the theoretical treatments of Huang and Taylor. According to these theories, and in fact any reasonable theory of displacement disorder, the decrease in intensity of the Laue-Bragg reflections due to distortion alone should vanish for \( (\sin \theta / \lambda) \rightarrow 0 \) (consider the analogy with the Debye temperature factor). Coyle and Gale's data do not satisfy this requirement even approximately, so that there is either some large systematic error in their intensities for the solid solution, or some effect other than distortion is involved.

D. Present Experimental Program

The present experimental investigation is directed toward testing the theoretical treatment of displacement disorder developed by Taylor, particularly the treatment of the larger non-elastic displacements, by applying this theory to the x-ray intensity data obtained from typical solid solutions which exhibit this disorder. Of course, it is conceivable that all displacements may have very nearly the isotropic elastic theory form of Eq. (2.1), in which case Huang's theory would be adequate, at least for the Laue-Bragg intensities. In either event, it is
The purpose of this investigation is to attempt to determine the nature of the lattice distortion near each solute atom.

The data required are the relative intensities of corresponding x-ray reflections from a series of solid solutions and pure components, and the highest possible accuracy is needed. For this purpose a new type of focusing powder x-ray spectrometer has been constructed, which is described in detail in the following two chapters.

The selection of a suitable solid solution for investigation requires some consideration. For instance, there are several apparent disadvantages in studying the copper-gold alloy used by Coyle and Gale, as well as with other alloys. In many alloys the effects of long-range and short-range ordering are very pronounced, whereas in the theoretical treatments of displacement disorder, a random distribution of solute atoms has been assumed. Also in the case of metals which are not easily ground there remains the practical problem of preparing powder samples which are sufficiently fine to eliminate primary and secondary extinction.

The ability of certain pairs of the alkali halides to form solid solutions over wide ranges of composition and temperature has long been recognized. A series of solid solutions formed from a given pair of the alkali halides containing a common ion would be well suited for the present investigation for several reasons. In a solid solution of this type, the solute ions are known to enter the lattice by substitution at lattice sites, and the substituted ions will in general be of different size and will therefore distort the lattice about them. Moreover ordering effects have never been observed in any of the mixed alkali halides (although some short-range order probably exists). There is
also the further advantage that the pure and mixed alkali halides have been thoroughly studied in other respects, and there is a variety of useful data available such as densities and heats of solution. Finally, crystals such as sodium chloride can be readily ground to a powder sufficiently fine so that the troublesome effects of primary and secondary extinction do not occur to any significant extent, as has been shown by Havighurst (16) and other workers.

In choosing a suitable alkali halide pair for investigation, the tabulation of Tobolsky (17) was found useful, in which the results of various investigations are given pertaining to the mutual solubilities of many pairs of alkali halides at various temperatures. Tobolsky observed that miscibility is incomplete at room temperature if the deviation between the respective lattice parameters is greater than about six percent. Miscibility over the complete range makes possible a more comprehensive test of the theory. It is also a practical advantage because it is found that mixed alkali halides which do not form stable solid solutions over the entire composition range tend to undergo rather rapid phase separation, especially in the presence of traces of adsorbed water.

From these considerations and after some preliminary experiments with x-ray powder photographs, the sodium chloride-sodium bromide system was chosen for investigation. It was recognized that fluorescent scattering from the bromide ion would add to the difficulties of the intensity measurements, but it was felt that the use of a pulse-height analyzer with the proportional Geiger counter would largely
overcome this problem. This system has been intensively studied over
the complete range of composition by Fineman, Wallace, and Nickels
(18, 19). These workers determined the heats of formation of the solid
solutions by calorimetric measurements, and they obtained precise
lattice parameters from x-ray powder photographs. From these sets of
experimental data, a number of derived results were obtained. Of
particular interest here is the result that the lattice constant of this
solid solution can be closely represented as a linear function of composi-
tion, or stated otherwise, that Vegard's law is closely obeyed.
CHAPTER III
THEORY OF FOCUSING X-RAY SPECTROMETER

A. Focusing Spectrometers for Powder Samples

1. Parafoocusing Principle

By making use of a focusing design, powder cameras can be constructed which give much greater resolution than Debye-Scherrer cameras of the same radius without any increase in time of exposure. Focusing cameras of this type were first devised independently by Seemann (20) and Bohlin (21). Figure 1 shows the geometrical principles involved in Seemann-Bohlin parafocusing cameras. X-rays, diverging from the point source, F, impinge on the powder sample positioned on an arc of the focusing circle and generate diffracted rays from a given set of planes (hkl) which come to a precise focus at the point S (except for certain small aberrations discussed in Section B). From the figure, $2\theta = \alpha + \beta$, the sum of the angles of incidence and reflection at the point K on the surface of the sample. Furthermore, the arcs FK and KS subtend angles $2\alpha$ and $2\beta$, respectively, at the center of the circle. Consequently the arc KFS subtends an angle of $4\theta$ at the center of the circle, and a diffraction maximum at the given Bragg angle $\Theta$ will be focused at S regardless of the point K at which it originates on the arc between F and S. It should be noted, however, that a crystallite located at a given point K on the arc cannot participate in a Laue-Bragg reflection of given $\Theta$ unless it is oriented so that the corresponding crystal planes make equal angles $\Theta$ with the incident and diffracted rays. Of primary interest is the diffracted ray KS in the plane of the focusing circle.
Fig. 1  Geometry of Optical Arrangement
In order to diffract this ray the crystallite at K must be oriented with
the normal to the given set of crystal planes in the plane of the circle
and bisecting the angle $\angle FKS$. This leads to the interesting conclusion
that regardless of the location of K on the circle the normals for all
crystallites having their diffracted rays focused at $S$ must intersect in
a common point which bisects the arc $FS$ included by the inscribed angle
$\angle FKS$. The focusing powder camera differs from the familiar bent-
crystal spectrometer in which a single-crystal is placed with a given
set of planes tangent to the circle, bent to a radius equal to the diameter
of the circle, and then ground to the radius of the focusing circle.
The bent-crystal spectrometer is capable of producing only the several
orders of reflection from the set of planes selected in the preparation
of the crystal. On the other hand the focusing powder camera (or
spectrometer, as described subsequently) is capable of simultaneously
producing and focusing all the diffraction maxima of the crystal having
$\theta$ in the range $0^\circ$ to $90^\circ$. It is clear that this is possible only
because different diffraction maxima are produced by different crystallites
in the powder sample (those properly oriented as discussed above).

2. Conventional Parafoocusing Spectrometer with Flat Sample

In the conventional x-ray powder spectrometer an approximation
to the Seemann-Bohlin parafoocusing geometry is used. Referring again to
Fig. 1, let a be the distance from x-ray source to sample, b the distance
from sample to receiving slit, and R the radius of the focusing circle.
Also $\alpha$ is the glancing angle of incidence of the primary beam on the
surface of the sample, and $\beta$ is the corresponding angle for the
diffracted beam. In the parafoocusing spectrometer the distances a and b
are equal and constant, and the receiving slit S pivots on the arm b about the sample K. The focusing circle has a variable location and radius in this case, since it must pass through the moving point S, as well as the fixed points F and K. In order to maintain the surface of the sample tangent to the focusing circle it must be rotated at K through one-half the angle of rotation of the arm bearing the slit S. However with this arrangement the curvature of the focusing circle varies continuously (increasing as θ increases), and since no practicable way to vary the curvature of the face of the powder sample has been developed, the sample surface is made plane. Thus the sample surface does not coincide with the focusing circle but is only tangent to it at a single point, and the focusing is only approximate, becoming rapidly worse as the length of the illuminated length of the sample increases. As a consequence the horizontal divergence or angular aperture of the beam incident on the sample must be kept small (about one degree) if sharp maxima and good resolution are to be obtained. This is especially the case for small values of θ or forward reflections (see the discussion in Section 8). Thus under these conditions the intensity obtainable with a flat sample is rather severely limited. This limitation on the horizontal divergence or angular aperture of the incident beam is absent in the curved-sample focusing spectrometer which has been constructed for this research and which will now be described.

3. Design of the Focusing Powder Spectrometer

In connection with this research a spectrometer which fulfills exactly the Seemann-Bohlin focusing geometry has been constructed. The suggestion that a focusing powder spectrometer of this type could be
constructed was made several years ago by P. W. Harris to W. J. Taylor, who subsequently designed the present spectrometer. The decision to construct and use this spectrometer for the present research was made because the theory indicated that it would yield more intense spectra of better quality than the conventional flat-sample spectrometer. It was important in the present study of the spectra of solid solutions to obtain intensities with the greatest accuracy possible. The performance of the instrument seems to have justified these expectations, and it is felt that the new spectrometer should be generally useful for powder work. Techniques for forming the curved powder briquet have been developed, and do not present any difficulty.

The details of construction of the spectrometer will be described in Chapter IV, and the present discussion will be confined to the manner in which the focusing geometry described in Part 1 of this section is realized. The design is based on a focal circle of fixed radius $R$, which lies in a horizontal plane, as illustrated in Fig. 1. The main shaft of the spectrometer is mounted vertically at the center of the circle and is driven by a large gear and worm. An arm, $A$, mounted on and rotating with this shaft carries at its outer end an auxiliary shaft parallel to the main shaft and bearing a platform, $B$, on which are mounted the vertical exit slit $S$ and the detector, $P$. These features are illustrated in Figs. 4 and 7. The radius of the focal circle is defined by the distance $R = 45/2\pi \approx 7.162$ inches between the axes of rotation of the two shafts. The slit $S$ is mounted on the axis of rotation of the auxiliary shaft and traverses the focal circle as the main shaft rotates. As discussed in Part 1 of this Section the angle
of rotation measured from the point on the circle is 40. The purpose of the auxiliary shaft is to permit the face of the slit S to rotate so as to remain directed at the center of the sample at K as the main shaft rotates. It is easy to establish from Fig. 1 that this objective will be achieved if the auxiliary shaft bearing the slit rotates relative to the arm in which it is mounted at one-half the rate of rotation of the main shaft and in the opposite sense (in a fixed frame of reference the auxiliary shaft rotates at one-half the rate and in the same sense as the main shaft). In the present spectrometer the necessary rotation of the auxiliary shaft is accomplished by means of two pulleys connected by a steel tape. One of these is mounted on the auxiliary shaft and another of half the diameter of the first is mounted concentric with the main shaft. The latter pulley is not connected with the main shaft, however, but is fixed to the arm, C, bearing the sample by means of a worm and gear which permit the correct initial adjustment of slit direction. The pulley system is shown clearly in Figs. 6, 7, and 8.

As the main shaft rotates, the concentric pulley, although stationary in a frame of reference attached to the sample arm, rotates at an equal and opposite rate in a frame attached to the main shaft or the arm bearing the auxiliary shaft. This causes the auxiliary shaft to rotate at one-half this rate relative to its arm and in the required sense as stated above. This device for maintaining the proper orientation of the exit slit is the most original feature of the present design and functions very satisfactorily.
The powder sample is mounted in a holder having the radius of curvature \( R \) of the focal circle and the surface of the sample is brought to this same curvature by means of a convex die of the same radius (or by leveling with a knife-edge). The sample holder is mounted on a second arm, \( C \), which can be pivoted about the center of the focal circle to bring the center of the sample to the desired point \( K \) on the circle (see Fig. 4). As previously stated the smaller pulley of the slit alignment system rotates with this arm. As a consequence the slit remains directed at the sample not only as the main shaft rotates but also as the sample is moved about the circle (or when both these rotations are made simultaneously). Appropriate translations and rotation of the sample holder are provided so that the cylindrical surface of the sample may be brought into coincidence with the focal circle.

The x-ray tube mount is provided with three mutually perpendicular translations so that the vertical line-focus on the target face may be brought accurately to the point \( I \) on the focal circle. The tube may also be rotated about a vertical axis through \( F \) to direct the x-rays at the position \( K \) of the sample.

In the present spectrometer the position of the sample arm, or the angle \( 2 \alpha \) subtended by the arc \( FK \) in Fig. 1, is adjusted manually to a suitable value. This fixes the distance, \( a \), in Fig. 1 from the source to the sample center and also the angle of incidence \( \alpha \). The spectrum is then scanned by rotating the exit slit arm, either continuously with the synchronous motor drive, or by setting small angular
increments manually. This varies the Bragg angle $\Theta$, as well as the angle of reflection, $\Phi$, measured from the sample surface and the distance $b$ from the center of the sample to the exit slit. These quantities are related by the equations:

$$\alpha + \beta = 2\Theta;$$

$$a = 2R \sin \alpha;$$

$$b = 2R \sin \beta.$$  \hspace{1cm} (3.1) \hspace{1cm} (3.2) \hspace{1cm} (3.3)

It is not necessary for focusing in the present spectrometer that $\alpha = \beta$ (or $a = b$), and it is convenient to vary $\Phi$ (and therefore also $\Theta$) while maintaining a fixed value of $\alpha$.

Since the ideal focusing geometry discussed in Part 1 of this section and illustrated in Fig. 1 applies only to rays in the plane of the focal circle (horizontal plane), it is important to limit the vertical divergence of the x-rays to a small value (not more than about 2°). This is accomplished by means of Soller slits in the incident and diffracted beams ($V_1$ and $V_2$ in Fig. 4), with the vanes of the slits horizontal (Soller's original use of his slits was with the vanes vertical to limit horizontal divergence). The Soller slits divide the x-ray beam into a number of horizontal sections, each of restricted vertical divergence. In this way the radiation from a vertical line source of considerable length may be used, while at the same time minimizing the effect of vertical divergence on line contour (see Section B).

The instrumental factors affecting the intensity distribution or contour of the Laue-Bragg lines are discussed in detail in Section B. The several aberrations are of the same general nature for the present focusing spectrometer as for the conventional flat-sample spectrometer.
with one important exception. The use of a flat-sample in the conventional spectrometer results in a line broadening which is proportional to the cotangent of the angle \( \Theta \) and to the square of the angle, \( \gamma \), measuring the horizontal divergence of the incident x-ray beam. For forward reflections \( \cot \Theta \) becomes relatively large and it is then necessary to severely restrict \( \gamma \), and therefore the total power in the beam, to prevent excessive line broadening. This aberration is entirely absent in the present spectrometer since the curved sample conforms to the focusing circle as shown at \( K \) in Fig. 4. There is therefore no need to limit the horizontal divergence of the beam \( \gamma \), or the intensity, from this cause. It is true that the requirement that the apparent width of the line source as viewed obliquely be kept small sets an upper limit on \( \gamma \), but this limit is 5 to 10 times as large as that imposed by the flat-sample aberration in the conventional spectrometer. An important feature of the Seemann-Bohlin focusing geometry, as shown in Figs. 1 and 4, is that the horizontal angle subtended at the source \( F \) by the curved face of the sample is independent of the angle \( 2 \alpha \) or the position of the sample on the focusing circle. Therefore the horizontal divergence, \( \gamma \), of the incident beam and its total power may be maintained constant as the sample is moved about the circle. Furthermore the horizontal angle subtended by the sample at the exit slit \( S \), and thus the horizontal divergence of the diffracted beam entering the detector \( P \), is not only independent of the angle \( 2 \beta \) between the sample and slit (and therefore of \( \Theta \)) but is exactly equal to the horizontal divergence \( \gamma \) of the beam incident on the sample. Therefore the same region of the detector is used in measuring the intensities of all the diffraction maxima.
B. Theory of Line Contours

Although the shape of the line contour is not of major importance in this investigation since only integrated line intensities are needed, an examination of this contour is important when evaluating the performance of any spectrometer. Also it is of interest to compare the effects of the geometrical properties of the flat-sample and curved-sample spectrometers upon the widths of the observed diffraction profiles under typical conditions of operation. An analysis of the effects of instrumental factors in modifying a pure diffraction maximum has been given by Alexander (22, 23, 24) for the parafocusing flat-sample spectrometer.

In accordance with the superposition principle which applies if the several factors may be regarded as independent, the overall line contour is obtained by the repeated convolution of the true intensity contour with various weighting functions which depend on instrumental factors. Each of the weighting functions as well as the true contour may be expressed as a function of the variable $\epsilon$ which measures the angular deviation of $\theta$ from the theoretical Bragg angle, $\theta_0$.

The weighting functions which are important in either the conventional or the focusing spectrometer are (23): (1) x-ray source profile; (2) width of the receiving slit; (3) penetration of the sample by the beam; (4) vertical divergence of the beam; and (5) the flat-sample correction. Each of these factors will be considered individually, but the overall contour will not be calculated because an accurate calculation would involve a great deal of labor, and the exact theoretical contour is not required for this research. However, it is worth
noting that if the several weighting functions individually yield mean
values of the angular displacement of $\bar{\epsilon}_1$, $\bar{\epsilon}_2$, ..., $\bar{\epsilon}_k$, where $\bar{\epsilon}_1$ is related
to the weight function $I(\epsilon_1)$ by
\[
\bar{\epsilon}_1 = \frac{\int_{-\infty}^{\infty} \epsilon_1 I(\epsilon_1) \, d\epsilon_1}{\int_{-\infty}^{\infty} I(\epsilon_1) \, d\epsilon_1}, \tag{3.4}
\]
then the mean overall displacement of intensity from $\Theta_0$ (defined
similarly) will be given by
\[
\bar{\epsilon} = \bar{\epsilon}_1 + \bar{\epsilon}_2 + \cdots + \bar{\epsilon}_k. \tag{3.5}
\]
Furthermore, if $\sigma_1^2$ is the mean value of $(\epsilon_1 - \bar{\epsilon}_1)^2$, or the square of
the standard deviation of $\epsilon_1$ from its mean value, etc., then the
overall standard deviation or mean value of $(\epsilon - \bar{\epsilon})^2$ is
\[
\sigma^2 = \sigma_1^2 + \sigma_2^2 + \cdots + \sigma_k^2. \tag{3.6}
\]
Thus the mean displacements or first moments, and the squares of the
standard deviations or the second moments about the mean, and also the
third moments about the mean (but not in general higher moments) are
strictly additive for independent variables. These statements are
equivalent to well-known theorems of mathematical statistics, and their
application to the present problem has been discussed by R. C. Spencer
(25). The mean displacement of course measures the displacement of the
centroid of the weighting function from $\Theta_0$, and in several cases this
will vanish so that this factor will make no contribution to the dis-
placement of the centroid of the line from $\Theta_0$. The standard deviation is
a measure of the width or dispersion of the function, and from Eq. (3.6)
each instrumental factor necessarily makes a positive contribution to the overall width of the line. The third moments are measures of asymmetry or skewness.

1. X-ray Source Profile

The focal line on the target face of the x-ray tube used in this investigation (North American Philips Company, Cat. No. 32113) is stated by the manufacturer to have approximate dimensions 1 x 10 mm. The x-ray incident on the sample were those emerging laterally or perpendicular to the long dimension of the focal line, and at a mean angle of approximately 5.5° to the target face. Thus the apparent width of the focal line as viewed from the sample is approximately \( w_a = 0.096 \) mm. Since the source to sample distance is \( 2R \sin \alpha \) the corresponding interval in \( \Theta \) (half the interval in \( 2\Theta \)) is, in degrees,

\[
\Delta \Theta = 57.3 \frac{w_a}{4R \sin \alpha}
\]  

(3.7)

The form of the intensity distribution is not known and it will, therefore, be assumed to be a rectangular function of width \( \Delta \Theta \). The mean deviation \( \overline{\epsilon} \), vanishes when referred to the center of the line focus, and it may be shown that the standard deviation for the rectangular function is

\[
\sigma = 4.135 \left( \frac{w_a}{R \sin \alpha} \right)
\]  

(3.8)

Inserting the values applicable to the present measurements, \( w_a = 0.0037 \) inches, \( R = 7.162 \) inches, and \( \alpha = 22.5^\circ \), yields \( \sigma = 0.006 \) degrees. This value is so small that the focal spot may for most purposes be regarded as a line of negligible width.

2. Width of Exit Slit

The weighting function due to the exit slit is clearly a rectangular function. The present spectrometer is equipped with a set of General
Electric SPG slits (Cat. No. A4954X), having linear widths, \( w_b \), of 0.02, 0.01, 0.005, and 0.002 inches. The angular slit width in degrees is

\[
\Delta \theta = 57.3 \frac{w_b}{4R \sin \phi} \tag{3.9}
\]

The mean displacement (referred to the slit center) vanishes, \( \bar{e} = 0 \).

The standard deviation for the rectangular function is easily shown to be (in degrees):

\[
\sigma = 4.135 \left( \frac{w_b}{R \sin \phi} \right) \tag{3.10}
\]

In the present investigation integrated intensities were required, and in order to obtain the maximum intensity the widest slit, \( w_b = 0.02 \) inches, was used. It will be shown subsequently that even though the use of a wide slit affects the intensity contours it does not lead to any error in the determination of integrated intensities. Inserting the value \( R = 7.162 \) inches in Eqs. (3.9) and (3.10) we obtain for the present measurements:

\[
\Delta \theta = 0.04/\sin \phi, \tag{3.11}
\]

and

\[
\sigma = 0.0115/\sin \phi \tag{3.12}
\]

The value of \( \phi \) in the present measurements varied from 8° for the most forward reflections to about 38°. The corresponding values for the angular slit width are \( \Delta \theta = 0.29 \) to 0.065 degrees, and for the standard deviation, \( \sigma = 0.083 \) to 0.019 degrees.

3. Penetration of Sample by Incident Beam

The intensity distribution due to penetration of the beam into the sample, with resultant absorption of the incident and scattered rays will be calculated in this section. It is assumed that the surface of the
sample is on the focal circle, so that rays diffracted at the surface are focused at the point on the focal circle corresponding to the Bragg angle $\Theta_o$. This is the point $S$ in Fig. 1, with $\Theta = \Theta_o$. Now consider a ray incident at $K$ at the angle $\alpha$ which penetrates the sample to a distance $s$ (measured in the direction of incidence). Let this ray then be diffracted and consider the diffracted ray emerging from the sample in the plane of the circle. This diffracted ray also makes an angle $2\Theta_o$ with the incident ray, and therefore is parallel to the ray $KS$ diffracted from the surface, but is displaced to the right in Fig. 1 by a distance $s \sin 2\Theta_o$ (measured normal to $KS$). Denote the point at which this parallel ray strikes the focal circle by $S'$, and let the arc $SS'$ subtend the angle $-4\epsilon$ at the center of the circle. This ray will then appear to have been diffracted at an angle $\Theta = \Theta_o + \epsilon$, where $\epsilon$ is a negative angle. The perpendicular distances of the rays striking at $S$ and $S'$ from the center of the circle are $R \cos \beta$ and $R \cos (\beta + 4\epsilon)$, respectively. Setting the difference of these two distances equal to the expression given previously for the separation of the two rays yields the following relation between $s$ and $\epsilon$:

$$s \sin 2\Theta_o = R \left[ \cos (\beta + 4\epsilon) - \cos \beta \right] = -R \left[ 4\epsilon \sin \beta + 8 \epsilon^2 \cos \beta + \ldots \right], \quad (3.13)$$

if the right-hand side is expanded in powers of $\epsilon$. For the relatively high absorption coefficients under consideration the values of $s$ and $\epsilon$ for which the diffracted intensity is appreciable are small, and it is sufficient to retain only the first term on the right side of Eq. (3.13), so that:

$$s = -4R (\sin \beta / \sin 2\Theta_o) \epsilon. \quad (3.14)$$
The ratio of the intensity of the ray received at $S'$ to that at $S$, or the ratio of the intensity at $\Theta = \Theta_0 - \epsilon$ to that at $\Theta_0$, will be

$$\exp \left[ -\mu(s + t) \right], \quad (3.15)$$

where $s$ and $t$ are the path lengths of the incident and diffracted beams in the sample and $\mu$ is the linear absorption coefficient. A straightforward but tedious calculation yields the following expansion of $t$ in powers of $s$:

$$t = \left( \frac{\sin \alpha}{\sin \beta} \right) s + \left( \frac{1}{2k \sin \beta} \right) \left[ 1 + \left( \frac{\sin \alpha}{\sin \beta} \right) \left( \frac{\sin \alpha}{\sin \beta} + 2 \cos 2\Theta_0 \right) \right] s^2 + ... \quad (3.16)$$

Since $s \ll R$, the terms of second and higher degree in $s$ on the right-hand side of Eq. (3.16) may be neglected. This amounts to neglecting the curvature of the surface of the sample in computing $t$. The ratio of intensities, (3.15), now becomes

$$\exp \left[ -\mu \left( 1 + \frac{\sin \alpha}{\sin \beta} \right) s \right]. \quad (3.17)$$

Finally, we substitute $s$ from Eq. (3.14) into Eq. (3.17), and normalize the resulting expression to unity by integration over the range $\epsilon = -\infty$ to $0$ (the formal extension of the range of integration to $\epsilon = -\infty$ produces no significant error for the values of $\mu$ of interest because of the exponential decrease of the intensity). This yields the following expression for the intensity distribution due to penetration of the beam into the sample, as a function of the displacement from the Bragg angle, $\epsilon = \Theta - \Theta_0$:

$$I(\epsilon) = k \exp (k \epsilon) \quad (3.18)$$

where

$$k = 4 \mu R (\sin \alpha + \sin \beta) / \sin 2\Theta_0. \quad (3.19)$$
Equation (3.18) is applicable only for negative values of $€$; the intensity is zero for $€$ positive. For the parafocusing arrangement, $\alpha = \beta$, and Eq. (3.19) reduces to

$$k = \frac{8 \mu R \sin \beta}{\sin 2 \theta_o} = 4 \mu b / \sin 2 \theta_o. \quad (3.20)$$

This is equivalent to the result obtained by Alexander (22) for the conventional flat-sample spectrometer. It is now an elementary matter to evaluate the mean displacement, $\overline{\varepsilon}$, and the standard deviation about the mean, $\sigma$, from Eq. (3.18). Expressed in degrees the results are:

$$\overline{\varepsilon} = -\frac{(57.3/k)}{} \quad (3.21)$$

and

$$\sigma = \frac{(\varepsilon - \overline{\varepsilon})^2}{(57.3/k)} \quad (3.22)$$

The extreme values of the angles used in the major part of the present investigation were approximately: (i) $\alpha = 21^\circ$, $\beta = 8^\circ$, and $\theta_o = 14.5^\circ$; and (ii) $\alpha = 22.5^\circ$, $\beta = 37.5^\circ$, and $\theta_o = 30^\circ$. The linear absorption coefficients of NaCl and NaBr are 18.2 and 208.2 cm$^{-1}$, respectively, for MoK$\alpha$ radiation, and $R = 18.19$ cm. Substitution of these values into the preceding equations yields the following range of values for $\overline{\varepsilon}$ and $\sigma$: for NaCl, $\overline{\varepsilon} = -0.042$ to $-0.038$, and $\sigma = 0.042$ to 0.038 degrees; and for NaBr, $\overline{\varepsilon} = -0.0037$ to $-0.0033$, and $\sigma = 0.0037$ to 0.0033 degrees.

4. Vertical Divergence of the Beam

As has been stated previously, it is only those rays which are parallel to the plane of the focal circle in Fig. 1 which are perfectly focused at the point $S$, or more accurately on a vertical line through $S$. In practice the incident and diffracted rays will diverge to a greater or lesser extent from a horizontal plane. Let the angles of vertical divergence of particular incident and diffracted rays from the horizontal...
plane (measured in the vertical plane containing the ray) be $\delta_a$ and $\delta_b$, respectively. These angles are positive if the slope in the direction of the ray is upward, and negative if the slope is downward. In accordance with Bragg's law the angle measured from the incident to the diffracted ray in the plane of the two rays will be $2 \Theta_0$. However, when the rays diverge from the horizontal plane the angle between their perpendicular projections on the horizontal plane will not be $2 \Theta_0$, in general, but $2 \Theta = 2(\Theta_0 + \epsilon)$. It is this projected angle which determines the angular setting, $\Theta = \Theta_0 + \epsilon$, of the vertical exit slit of the spectrometer when these particular rays are detected. Eastabrook (26) has given the exact relation between the $\delta_a$, $\delta_b$, $\Theta_0$, and $\epsilon$, which becomes in our notation:

$$\cos 2(\Theta_0 + \epsilon) = (1 + \tan^2 \delta_a)^{1/2} (1 + \tan^2 \delta_b)^{1/2} \cos 2 \Theta_0 - \tan \delta_a \tan \delta_b.$$  
(3.23)

In spectrometers with horizontal slits $\delta_a$ and $\delta_b$ are held to small values. It is then an adequate approximation to expand the left-hand side of Eq. (3.23) in powers of $\epsilon$ and retain only the linear term in $\epsilon$, and to expand the right-hand side in powers of $\delta_a$ and $\delta_b$ and retain only the quadratic terms. This leads to the following relation valid for $\delta_a$ and $\delta_b$ small and $2 \Theta_0$ not too close to the values $0$ or $\pi$:

$$\epsilon = 1/2 \delta_a \delta_b \csc 2 \Theta_0 - 1/4 (\delta_a^2 + \delta_b^2) \cot 2 \Theta_0.$$  
(3.24)

Let $\Delta_a$ and $\Delta_b$ be the maximum absolute values of $\delta_a$ and $\delta_b$, respectively, as determined by the horizontal vanes of the Soller slits in the incident and diffracted beams. If the separation of two adjacent vanes of the Soller slit is $2h$, and the length of the vanes is $L$, then
\( \Delta = \arctan \left( \frac{2h}{L} \right) \). Inserting the extreme values \( \delta_a = \pm \Delta_a \) and \( \delta_b = \pm \Delta_b \) in Eq. (3.24) yields for the two extreme values of \( \epsilon \):

\[
\epsilon = \pm \frac{1}{2} \Delta_a \Delta_b \csc 2 \theta_0 - \frac{1}{4}(\Delta_a^2 + \Delta_b^2) \cot 2 \theta_0. \tag{3.25}
\]

The upper and lower signs in Eq. (3.25) represent \( \epsilon_{\text{max}} \) and \( \epsilon_{\text{min}} \), respectively. For forward reflections, \( 0 < 2 \theta_0 < \pi/2 \), \( \cot 2 \theta_0 \) is positive, so that \( |\epsilon_{\text{max}}| < |\epsilon_{\text{min}}| \), and the intensity distribution is spread toward lower \( \theta \). For back reflections, \( \pi/2 < 2 \theta_0 < \pi \), and \( \cot 2 \theta_0 \) is negative, and thus the situation is reversed; \( |\epsilon_{\text{max}}| > |\epsilon_{\text{min}}| \) and the intensity is spread more to the high \( \theta \) side of \( \theta_0 \). For the particular value \( 2 \theta_0 = \pi/2 \), \( \cot 2 \theta_0 = 0 \), and the intensity distribution is symmetric about \( \theta_0 \), with \( |\epsilon_{\text{max}}| = |\epsilon_{\text{min}}| \). However, in all these cases the total width of the intensity distribution is given by the formula:

\[
\epsilon_{\text{max}} - \epsilon_{\text{min}} = \Delta_a \Delta_b \csc 2 \theta_0. \tag{3.26}
\]

The total width is a minimum for \( \theta_0 = \pi/4 \) and increases markedly as \( \theta_0 \) approaches 0 or \( \pi/2 \).

Eastabrook (26) has also given an approximate treatment of the distribution of the intensity as a function of \( \epsilon \) for the case \( \Delta_a = \Delta_b = \Delta \). It would be possible by a straightforward generalization to treat the case \( \Delta_a \neq \Delta_b \). However, this will not be done here because his method is not exact in any case. An exact calculation would have to take detailed account of the average effective apertures of the Soller slits which are treated in Section C, Part 4. The detailed calculation given there of the effect of the Soller slits on the integrated intensity is justified by its importance for the present research, but an equally
accurate calculation of the intensity contour would be even more laborious and is scarcely justified. We will therefore conclude this section with a summary of Lastabrook's approximate calculation for the case \( \Delta_a = \Delta_b = \Delta \). In this case Eqs. (3.25) and (3.26) become

\[
\epsilon_{\text{max}} = \frac{1}{2} \Delta^2 (\csc 2 \vartheta_o - \cot 2 \vartheta_o) = \frac{1}{2} \Delta^2 \tan \vartheta_o, \quad (3.27)
\]

\[
\epsilon_{\text{min}} = -\frac{1}{2} \Delta^2 (\csc 2 \vartheta_o + \cot 2 \vartheta_o) = -\frac{1}{2} \Delta^2 \cot \vartheta_o, \quad (3.28)
\]

\[
\epsilon_{\text{max}} - \epsilon_{\text{min}} = \Delta^2 \csc 2 \vartheta_o. \quad (3.29)
\]

The intensity vanishes at \( \epsilon_{\text{max}} \) and at \( \epsilon_{\text{min}} \) but has a logarithmic infinity at \( \epsilon = 0 \). That is, as \( \epsilon \to 0 \) from either the positive or negative side, the intensity approaches proportionality to \( \ln |\epsilon| \). The detailed expressions for the intensity are quite complicated. However, the mean value of \( \epsilon \), or the displacement of the centroid of the distribution from \( \vartheta_o \), is

\[
\bar{\epsilon} = -\frac{\Delta^2}{12} \cot 2 \vartheta_o, \quad (3.30)
\]

and the standard deviation from the mean is

\[
\sigma = \frac{\Delta^2}{12} \left[ 1 + \frac{17}{10} \cot^2 2 \vartheta_o \right]^{1/2}. \quad (3.31)
\]

The displacement of the centroid is to values of \( \vartheta \) lower than \( \vartheta_o \) for forward reflections \( (\vartheta_o < \pi/4) \), and to higher values of \( \vartheta \) for back reflections. The standard deviation is a minimum for the intermediate case, \( \vartheta_o = \pi/4 \), for which \( \bar{\epsilon} = 0 \). However \( \sigma \) increases rapidly as \( \vartheta_o \) approaches 0 or \( \pi/2 \).

In the present investigation \( \Delta_a = 0.0275 \) radians and \( \Delta_b = 0.0157 \) radians. The form of Eq. (3.25) suggests that \( \Delta^2 \) in Eqs. (3.27) to
(3.31) be approximated by either $\Delta_a \Delta_b = 4.32 \times 10^{-4}$ or $(\Delta_a^2 + \Delta_b^2)/2 = 5.01 \times 10^{-4}$, for the case $\Delta_a \neq \Delta_b$. It is not clear which choice will give the better approximation, so the average value $\Delta^2 = 4.7 \times 10^{-4}$ will be used. On substituting this value in Eq. (3.30) and (3.31) the following formulas, approximately applicable to this investigation, are obtained:

$$\xi \approx -0.0022 \cot 2 \Theta_o,$$  \hspace{1cm} (3.32)

$$\sigma \approx 0.0022 (1 + 1.70 \cot^2 2 \Theta_o)^{1/2}$$  \hspace{1cm} (3.33)

The extreme values of $\Theta_o$ in the present research were approximately $14.5^\circ$ and $30^\circ$. The corresponding values of the displacement of the centroid of the line are $\xi = -0.0085$ and $-0.0038$ degrees, and of the standard deviation, $\sigma = 0.0113$ and $0.0054$ degrees, respectively.

5. Effect of Horizontal Divergence with a Flat Sample

The instrumental effects discussed in the preceding parts of this section have the same qualitative form in the present focusing spectrometer as in the conventional para-focusing spectrometer. The only advantage of the present instrument is that its design is based on the focusing circle illustrated in Fig. 1, with the source, exit slit, and curved sample all lying on the focal circle. In contrast to this, as has been pointed out in Part 2 of Section A of this chapter, the radius of the focal circle of the para-focusing spectrometer varies continuously as $\Theta_o$ is varied. It is therefore impracticable in the conventional instrument to have the face of the sample coincident with the focal circle, and the best that can be done is to use a flat sample which is tangent to the focal circle for all values of $\Theta_o$. The departure of the flat sample from the focal circle produces relatively serious aberrations in focusing in the
conventional instrument of a kind which are totally absent in the present spectrometer with its curved sample. This aberration becomes particularly large if the angular aperture or horizontal divergence of the incident x-ray beam is large. This angle, which is measured in the plane of the focal circle, will be denoted by $\gamma$. For a given x-ray tube and operating voltage the total intensity in the incident beam is approximately proportional to $\gamma$. If it is desired to obtain spectra of good quality with the conventional flat-sample spectrometer the value of $\gamma$ and consequently the total intensity must be rather severely limited. No limitations on the value of $\gamma$ exist in the present spectrometer other than those imposed by the construction of x-ray tube and the size of the sample. In the present investigation an incident beam of relatively large horizontal divergence, $\gamma = 5.5$ degrees, was used. It will be shown that the use of this value of $\gamma$ in the conventional flat-sample spectrometer would result in line displacement and broadening effects equaling or exceeding the combined effects of all the other aberrations discussed in this section.

The intensity distribution, $I(\epsilon)$, resulting from the use of a flat sample and parafocusing geometry ($\alpha = \beta = \theta_0$) has been treated by Alexander (23). $I(\epsilon)$ vanishes except in the range $\epsilon_m \leq \epsilon \leq 0$, or $\theta_0 + \epsilon_m \leq \theta \leq \theta_0$. In this interval the intensity function, normalized to unity, has the form:

$$I(\epsilon) = \frac{1}{2} |\epsilon_m\epsilon|^{-1/2}$$

(3.34)

The value of $\epsilon_m$, or the maximum displacement, is

$$\epsilon_m = -\frac{\gamma^2}{229.2} \cot \theta_0,$$

(3.3b)
with both $\varepsilon_m$ and $\gamma$ expressed in degrees. From Eq. (3.34) the mean displacement or position of the centroid of the distribution is calculated to be

$$\overline{\varepsilon} = (1/3) \varepsilon_m.$$  

(3.36)

Note that $\varepsilon_m$ and $\overline{\varepsilon}$ are both negative. Similarly, the standard deviation or the square root of the second moment about the mean is

$$\sigma = \left(\frac{2}{3} \sqrt{5}\right) |\varepsilon_m| = 0.2981 |\varepsilon_m|.$$  

(3.37)

For $\gamma = 5.5$ degrees and for the extreme values of $\Theta_0$ in the present investigation, the preceding equations yield the following results:

For $\Theta_0 = 14.5^\circ$, $\varepsilon_m = -0.511$, $\overline{\varepsilon} = -0.170$, and $\sigma = 0.152$ degrees; and for $\Theta_0 = 30^\circ$, $\varepsilon_m = -0.229$, $\overline{\varepsilon} = -0.076$, and $\sigma = 0.068$ degrees. These aberrations are of course absent in the present measurements using a curved sample, but represent the additional aberration that would have been present if a flat sample had been used. They will be compared with the other aberrations in the summary which follows.

6. Summary of the Instrumental Aberrations

In the preceding parts of this section there has been calculated the mean displacement of the centroid, $\overline{\varepsilon}$, and the standard deviation from the mean, $\sigma$, for aberrations due to the following instrumental effects: (1) x-ray source profile; (2) width of exit slit; (3) penetration of sample by incident beam; (4) vertical divergence of the beam; and (5) effect of horizontal divergence with a flat sample. The results for the approximate extreme values of $\Theta_0$ used in this research, $\Theta_0 = 14.5^\circ$ and $30^\circ$, are summarized in Table 1. The aberration of type (1) depends on the angle $\alpha$, which was $21^\circ$ for the three reflections having the
**TABLE 1**

Mean Displacement, $\bar{e}$, and Standard Deviations, $\sigma$, for the Instrumental Aberrations

<table>
<thead>
<tr>
<th>Type of Aberration</th>
<th>$\Theta_0$(deg)</th>
<th>$\bar{e}$(deg)</th>
<th>$\sigma$(deg)</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Source profile</td>
<td>14.5</td>
<td>0</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>0</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>(2) Exit slit width</td>
<td>14.5</td>
<td>0</td>
<td>0.083</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>0</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>(3) Penetration of Sample</td>
<td>14.5</td>
<td>-0.042</td>
<td>0.042</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>-0.038</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.5</td>
<td>-0.004</td>
<td>0.004</td>
<td>NaBr</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>-0.003</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>(4) Vertical Divergence</td>
<td>14.5</td>
<td>-0.009</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>-0.004</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>(5) Flat Sample</td>
<td>14.5</td>
<td>-0.170</td>
<td>0.152</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>-0.076</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>Total, (1) to (4)</td>
<td>14.5</td>
<td>-0.051</td>
<td>0.094</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>-0.042</td>
<td>0.043</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.5</td>
<td>-0.013</td>
<td>0.084</td>
<td>NaBr</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>-0.007</td>
<td>0.021</td>
<td></td>
</tr>
</tbody>
</table>

The smallest $\Theta_0$, and $22.5^\circ$ for the other reflections, but $\sigma$ is constant to the accuracy given. The sample is indicated for the aberration of type (3), which depends on the absorption coefficient. The values of $\bar{e}$ and $\sigma$ are all in degrees. The values of $\bar{e}$ are either zero, indicating no displacement of the centroid of the line, or negative, indicating a shift from the theoretical Bragg angle, $\Theta_0$, to a smaller angle.

It has been pointed out previously that, to the approximation in which these aberrations can be treated as independent of one another, the total displacement, $\bar{e}_T$, of the centroid of the line will be the sum
of the mean displacements, \( \bar{\varepsilon}_t \), due to the individual aberrations,

\[
\bar{\varepsilon}_t = \sum \varepsilon_i .
\]

(3.38)

Similarly,

\[
\sigma_t = \left( \sigma_o^2 + \sum \sigma_i^2 \right)^{1/2} .
\]

(3.39)

where \( \sigma_o \) is the standard deviation from its mean, \( \theta_o \), that would be exhibited by the intensity distribution in the absence of instrumental aberrations (a measure of natural line width), \( \sigma_i \) is the standard deviation about its mean for the \( i \)th type of aberration, and \( \sigma_t \) is the observed standard deviation of the intensity distribution from its mean, \( \theta_o + \bar{\varepsilon}_t \).

In the present spectrometer, with a curved sample lying on the focusing circle, only the first four types of aberration in Table 1 occur. The total displacement, \( \bar{\varepsilon}_t \), computed from Eq. (3.38), and the root-mean-square standard deviation computed from the expression

\[
\left( \sum \sigma_i^2 \right)^{1/2} ,
\]

(3.40)

with the sums in both cases extending over only the aberrations (1) to (4), are given at the foot of Table 1 in the columns labeled \( \varepsilon \) and \( \sigma \), respectively. It is clear that the cumulative effect of all the aberrations present in the focusing instrument is considerably less than the single flat-sample aberration which would result from the use of the large horizontal divergence employed in the present investigation with a conventional spectrometer.
Table 2 shows the approximate half-width, w (at half the peak height above background) of several reflections of NaCl and NaBr as observed with the present spectrometer. The form of the peaks is approximately Gaussian, and the following relation applicable to a Gaussian curve has been used to estimate the values of the standard deviations in Table 2:

$$\sigma_t = 0.425 w$$  \hspace{1cm} (3.41)

These observed values of $\sigma_t$ are larger than the calculated values at the foot of Table 1, since they include the effect of the natural line width as well as any other aberrations or broadening effects not accounted for in the preceding calculation. Possible effects of this type are imperfect geometry and alignment of the spectrometer (source, sample, or slit displaced from focal circle), rough or non-cylindrical sample surface, non-random orientation of crystal grains in sample, and effect of the unresolved Kα doublet (for the larger $\Theta_o$ values the doublet is resolved and is not included in the estimated width). The final column of Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>hkl</th>
<th>$\Theta_o$(deg)</th>
<th>w(deg)</th>
<th>$\sigma_t$(deg)</th>
<th>$\sigma_o$(deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>400</td>
<td>14.55</td>
<td>0.33</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>16.33</td>
<td>0.27</td>
<td>0.11</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>22.18</td>
<td>0.26</td>
<td>0.11</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>640</td>
<td>26.98</td>
<td>0.21</td>
<td>0.09</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>642</td>
<td>28.09</td>
<td>0.19</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>NaBr</td>
<td>400</td>
<td>13.75</td>
<td>0.38</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>15.45</td>
<td>0.26</td>
<td>0.11</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>20.92</td>
<td>0.22</td>
<td>0.09</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>622</td>
<td>23.26</td>
<td>0.15</td>
<td>0.06</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>642</td>
<td>26.43</td>
<td>0.12</td>
<td>0.05</td>
<td>0.04</td>
</tr>
</tbody>
</table>
gives the apparent value of \( \sigma_0 \) due to natural line width calculated from \( \sigma_t \), the theoretical widths in Table 1, and Eq. (3.39), for the extreme values of \( \Theta_0 \). It should be pointed out that the 400 reflection of NaBr is much broader than any of the other lines of NaBr for which measurements were carried out, and is not typical. Thus, it can be stated that with this exception the apparent values of \( \sigma_0 \) for both NaCl and NaBr are equal to or less than 0.10 degree. According to Klug and Alexander (27) the rocking angles for typical rock salt single crystals, are 0.08 to 0.25 degrees, although much smaller values have been observed for exceptionally perfect single crystals. The natural widths observed with powders which have been subjected to extreme stresses in the grinding process would be expected to be at least as great as for relatively imperfect single crystals. Since \( \sigma_0 \) should be approximately half as great as \( \Delta \Theta \), the values of \( \sigma_0 \) calculated in Table 2 are quite reasonable.

From Table 1 it may be seen that small displacements of the centroid of the line from the theoretical Bragg angle \( \Theta_0 \) are predicted. For the aberrations operative in the present instrument the total displacement is given by \( \overline{E}_t \) and is negative. It would be very difficult to align the spectrometer with sufficient accuracy to detect these small displacements on an absolute basis. However a check may be obtained by comparing the differences between the theoretical \( \overline{E}_t \) predicted for NaCl and NaBr with the observed differences. These differences should be essentially independent of small errors in the alignment of the instrument. It is seen from Table 1 that the theoretical value \( (\overline{E}_t)_{\text{NaCl}} - (\overline{E}_t)_{\text{NaBr}} \) is -0.038 degrees at \( \Theta_0 = 14.5^\circ \) and -0.035 degrees at \( \Theta_0 = 30.0^\circ \). This
agrees very well with the average value of the observed difference of
the reflections studied which was $-0.04 \pm 0.01$ degrees and appeared not
to depend significantly on $\Theta_o$.

C. Integrated Intensities

The various factors required for the interpretation of the integrated
intensities and in particular the calculation of the crystal
structure factors from the intensities will be considered in this section.

1. Integrated Intensity from a Small Crystallite

In this section the formulas will be given for the integrated
intensity produced when x-rays are diffracted by a crystal whose volume
is large enough to contain many unit cells so that it yields sharp
diffraction maxima, but of small enough volume so that absorption and
extinction within the crystallite may be ignored. Consider a particular
set of crystal planes of interplanar spacing $d$, and Bragg angle $\Theta_o$.
Let the crystal be oriented so that the incident beam makes an angle
$\Theta$ with this set of planes, or so that the angle between the normal to
the planes and the incident beam is ($\pi/2$) - $\Theta$ (the probability that a
crystallite has the proper orientation will be considered subsequently).
If the crystallite is irradiated with a beam of intensity $I$ (energy per
unit area per unit time), then both theory and experiment indicate that
the total power (energy per unit time) in the scattered beam has the form:

$$P(\Theta) = I \cdot R(\Theta), \quad (3.42)$$

where $R(\Theta)$, the reflecting power of the given set of planes, has a sharp
maximum at $\Theta = \Theta_o$. The scattered radiation will lie in a narrow angular
interval making angles of very nearly $2 \Theta_o$ with the incident beam. The
form of the function $R(\Theta)$, or the intensity distribution for the reflection, depends on the dimensions of the crystallite through the Laue interference function. However, the integrated intensity of the reflection, defined by

$$\int P(\Theta) \, d\Theta$$  \hspace{1cm} (3.43)

can be shown to be proportional to the volume, $dv$, of the crystallite, and to have the form:

$$\int P(\Theta) \, d\Theta = I \int R(\Theta) \, d\Theta = I \, Q \, dv, \hspace{1cm} (3.44)$$

where, for unpolarized incident radiation of wavelength $\lambda$,

$$Q = \left( \frac{e^2}{mc^2} \right)^2 \left( \frac{N^2 \lambda^3}{\sin 2 \Theta_0} \right) |F|^2 \cdot \left( 1 + \cos^2 2 \Theta_0 \right)/2. \hspace{1cm} (3.45)$$

In Eq. (3.45), $e$ and $m$ are the charge and mass of the electron, $c$ is the velocity of light, $N$ is the number of unit cells of the crystal per unit volume, and $F$ is the familiar structure factor of the unit cell.

The final factor, $(1 + \cos^2 2 \Theta_0)/2$, in Eq. (3.45) is the polarization factor for unpolarized radiation. For a derivation and discussion of the preceding equations, reference is made to the treatment of James (28).

It is perhaps worth pointing out that the integrated intensity from a set of crystal planes is unaffected by rotation of the crystal about an axis normal to the planes, so that it is sufficient to specify the single angle $\Theta$ in the preceding discussion.

2. The Integrated Intensity from a Small Volume of Powdered Crystal

We now make use of the results of Part 1 of this section to obtain the integrated intensity from a small volume, $dV$, of crystalline powder. We assume that $dV$ is small enough so that absorption of radiation within $dV$ may be neglected. On the other hand $dV$ must be of sufficient size to
contain a large number, \( n \), of crystallites; this is equivalent to stating that \( dV \gg d\bar{v} \), where \( d\bar{v} \) is the mean volume of a crystallite. We assume also that the \( n \) crystallites in \( dV \) have random rotational orientations. We first compute the fraction of crystallites in \( dV \) for which the incident beam makes an angle \( \Theta - \kappa \) to \( \Theta \) with the plane of Miller indices \((hkl)\). For this to be the case the normal to this crystal plane must make an angle \((\pi/2) - \Theta \) to \((\pi/2) - \Theta + \kappa \) with the incident beam. This is illustrated in Fig. 3a, where the incident and diffracted beams are indicated by \( IK \) and \( KS \), respectively, and the crystallite at \( K \) is so oriented that the normal to the given set of planes lies along the line \( KP \). In the figure a sphere of unit radius has been described about \( K \) as a center and there has been indicated the annular area within which the normal \( KP \) must intersect the sphere if it is to make an angle within the specified interval with the incident beam \( FK \). The total area of the annular strip is \( 2 \pi \sin(\pi/2 - \Theta) d\Theta = 2 \pi \cos \Theta d\Theta \), and the fractional part of the total solid angle \( 4\pi \) that it subtends at \( K \) is \((1/2)\cos \Theta d\Theta \). Therefore if the crystals are randomly oriented there is a probability \((1/2) \cos \Theta d\Theta \) that the normal to the crystal plane under consideration will make the required angle with the incident beam. It should be noted that the complete specification of the rotational orientation of the crystallite requires not only the specification of the direction of the normal to the set of planes but also the angle of rotation of the crystallite about the normal as an axis (one of the three Eulerian angles). However, as previously stated the integrated intensity is independent of the latter angle and it may be disregarded.
We now make two modifications in the preceding probability. The first is the insertion of the familiar multiplicity factor $p$ such that $p-1$ is the number of sets of crystal planes equivalent to the set $(hkl)$. Equivalent planes have the same interplanar spacing, Bragg angle, and integrated intensity of reflection. The minimum value of $p$, even for a general reflection in the triclinic system, is two, corresponding to the planes $(hkl)$ and $(hkar{l})$ for which the normals coincide but are oppositely directed (note that in the preceding discussion the normal was treated as uni-directional). The maximum value of $p = 48$ occurs in the cubic system for $h \neq k \neq l \neq 0$, and arises from the six possible permutations and $2^3$ choices of positive and negative signs possible for the indices $(hkl)$. The probability that the normal to the set of planes $(hkl)$ or an equivalent set of planes will make an angle with the incident beam within the range specified is clearly $(p/2) \cos \Theta \, d\Theta$.

If $\Theta$ is nearly equal to the Bragg angle $\Theta_0$ these crystallites will diffract radiation into a thin cone making angles in the neighborhood of $2 \Theta_0$ with the forward extension of the incident beam. For example, in Fig. 3a KS is a diffracted ray lying in this cone. The second modification of the probability which is necessary is connected with the fact that in a spectrometer, whether of the conventional parafocusing type or the true focusing type constructed for this research, the only part of the diffracted radiation actually detected is that lying approximately in the plane of the focal circle of Fig. 1, or the plane FKS of Fig. 3a. Since the normal to the crystal planes (KP in Fig. 3a) lies in the plane of the incident and diffracted rays, the radiation will be detected only if the normal KP intersects the sphere in Fig. 3a in a small section of
the annular strip such as the shaded area in this figure. We will denote by \( g \) the ratio of the shaded area to the total area of the annular strip, or the ratio of the corresponding solid angles. The value of \( g \) for a particular experimental arrangement depends upon the angular divergences from the plane of the focal circle permitted for the incident and diffracted rays by the Soller slit system of the spectrometer. Since the focal plane is horizontal, the divergences in question are in a vertical direction, and \( g \) will be called the vertical divergence factor. The calculation of this factor for the present spectrometer is considered in Part 4 of this section, but we do not need its detailed form at this point. It is now obvious that

\[
(\frac{pg}{2}) \cos \Theta \, d\Theta
\]

(3.46)
is the probability that the normal to the plane \((hkl)\) or an equivalent plane will make an angle within the specified range of \(\Theta\) with the incident beam, and will have a vertical divergence within the permitted range.

If the volume element, \(dV\), of the crystalline powder, containing a total of \(n\) crystallites, is irradiated with an incident beam of intensity \(I\) it follows from Eq. (3.42) and (3.46) that the total power diffracted by the crystallites having the orientations just specified is given by

\[
n \left(\frac{pg}{2}\right) I \bar{R}(\Theta) \cos \Theta \, d\Theta,
\]

(3.47)

where \(\bar{R}(\Theta)\) is the mean reflecting power of the crystallites. On integrating with respect to \(\Theta\) over an interval about \(\Theta_0\) sufficiently broad to contain virtually all the intensity associated with the reflection,
and using Eq. (3.44), we now obtain for the integrated intensity within the permitted range of vertical divergence (hereafter this restriction on the term integrated intensity will be understood) the following results:

\[ n \left( \frac{pg}{2} \right) I \cos \Theta_0 \int R(\Theta) d\Theta = n\left( \frac{pg}{2} \right) I Q \cos \Theta_0 \cdot \overline{dv}. \quad (3.48) \]

Since \( \cos \Theta \) is a slowly-varying function compared to \( R(\Theta) \), it may be removed from under the integral sign and replaced by \( \cos \Theta_0 \), with no significant error. The same comment applies to \( g \), which is also a slowly varying function of \( \Theta \). In Eq. (3.48) \( \overline{dv} \) is the mean volume of a crystallite, and the total volume of the crystallites in the volume element \( dV \) is therefore \( n \overline{dv} \). It follows that

\[ n \overline{\varphi \overline{dv}} = \overline{\varphi' \overline{dv}}, \quad (3.49) \]

where \( \varphi \) is the true density of the crystal, and \( \varphi' \) is the apparent density of the powder (including the interstices between the crystallites).

From Eqs. (3.48) and (3.49) the integrated intensity may be written in the convenient form

\[ \left( \frac{pg}{2} \right) I Q \cos \Theta_0 \cdot \left( \frac{\varphi'}{\varphi} \right) \overline{dv}. \quad (3.50) \]

\( \left( \frac{\varphi'}{\varphi} \right) \) may conveniently be termed the packing fraction. As previously indicated, Eq. (3.50) is based on the assumption that \( dV \) is sufficiently small so that the absorption within this volume element is negligible.

However, because of the finite thickness of the sample and the penetration of the radiation into the sample, the expression (3.50) must be integrated over the sample. The effect of absorption by the sample on the incident intensity \( I \) and on the diffracted intensity is then important, and is considered in the next part of this section.
3. Absorption by the Sample

In the focusing spectrometer as used in this investigation the x-ray beam is incident on the face of the compacted powder sample at an angle $\alpha$, and diffracted radiation emerges from the sample at an angle $\varphi$, where $\alpha + \varphi = 2 \theta_0$. The sample is sufficiently thick so that essentially all of the radiation which is not diffracted out of the sample is absorbed in the sample, and in the following treatment the sample may with negligible error be taken to be infinitely thick. Although the face of the sample is curved as required for the focusing of the diffracted rays, it will be seen subsequently that the curvature has only a minor affect on the absorption correction. Therefore the problem involved is very similar to the familiar problem of the diffraction of a parallel beam of x-rays by a flat sample of infinite thickness. This case is illustrated in Fig. 2a and reference may be made to James (28) for the standard treatment. However, one difference that should be considered is that in the present spectrometer the incident beam is a divergent beam originating at the line focus on the target of the x-ray tube, as illustrated in Fig. 2b. In order to show the relation to the standard treatment the two cases will be developed in a parallel manner. We assume that in both cases the beams are of unit height, so that the element of scattering volume $dV$ is equal in magnitude to its projected area, which is shaded in Fig. 2. Let the path length within the sample traversed by the beam incident on $dV$ be $s$, and let the thickness of $dV$ in the direction of the beam be $d\alpha$. Then if the parallel beam in Fig. 2a is of unit width (therefore also of unit cross-sectional area), $dV = ds$. 
Fig. 2. Reflection of x-rays from interior of powder sample: (a) by parallel beam; (b) by divergent beam
Let $A_0$ be the intensity (energy per unit time per unit area) of the beam before entering the sample. Then the intensity, $I$, of the beam incident on $dV$ is $A_0 \exp(-\mu's)$, where $\mu'$ is the effective linear absorption coefficient of the sample. Thus the product $I\,dV$ which occurs in Eq. (3.50) assumes the form

$$I\,dV = A_0 \exp(-\mu's)\,ds \quad (3.51)$$

for the case of a parallel beam.

In the case of a divergent beam it will be assumed that the incident beam of angular aperture $d\alpha$, and unit height, as illustrated in Fig. 2b, contains power $P(\alpha)\,d\alpha$ (energy per unit time). The cross-sectional area of this beam at $dV$ is $(a+s)\,d\alpha$, where $a$ is the distance from the line source to the sample surface, and $s$ the distance from the surface to $dV$ (in the direction of the beam). It follows that the intensity of the beam incident on $dV$ is

$$I = \left[\frac{P(\alpha)}{(a+s)}\right] \exp(-\mu's). \quad (3.52)$$

The volume element in this case is

$$dV = (a+s)\,d\alpha\,ds. \quad (3.53)$$

Therefore the product $I\,dV$ becomes

$$I\,dV = P(\alpha) \exp(-\mu's)\,d\alpha\,ds. \quad (3.54)$$

This differs from Eq. (3.51) for the case of a parallel beam only in the replacement of the intensity $A_0$ by the power $P(\alpha)\,d\alpha$. It is particularly worth noting that although $I$ and $dV$ depend on the radial distance $(a+s)$ in the divergent case, the product $I\,dV$ does not. This is of
interest because in the present spectrometer a depends on $\alpha$ through Eq. (3.2). It will be necessary subsequently to consider an average over the face of the sample, covering a finite range of $\alpha$, and we see that $I\,dV$ depends on $\alpha$ only through the angular power distribution, $P(\alpha)$, characteristic of the tube, not on the tube to sample distance. It should perhaps be mentioned to avoid confusion that $P(\alpha)$ depends fundamentally on the angle which the beam incident on the sample at angle $\alpha$ makes with the face of the target of the x-ray tube, and $P(\alpha)$ is thus indirectly a function of $\alpha$.

The integrated intensity diffracted by the sample in volume element $dV$ is obtained by substitution of Eq. (3.54) into (3.50). However, the diffracted radiation travels an additional distance $t$ within the sample as shown in Fig. 2b, so that the integrated intensity emerging from the sample is

$$\frac{p_0}{2} Q \cos \theta_0 \cdot P(\alpha) \cdot \left( \rho' / \rho \right) \exp \left[ -\mu'(s + t) \right] \, d\alpha \, ds.$$  \hspace{1cm} (3.55)

The relation between $t$ and $s$ for the sample of radius of curvature $R$ has been given in Eq. (3.16). We abbreviate this as

$$t = \left( \frac{\sin \alpha}{\sin \beta} \right) s + z \, s^2 + \cdots,$$  \hspace{1cm} (3.56)

where $z$ is the coefficient of $s^2$ on the right-hand side of Eq. (3.16).

As pointed out previously, retention of only the first term on the right-hand side of Eq. (3.56) is equivalent to the assumption of a flat sample in computing the absorption correction. We now substitute Eq. (3.56)
into the exponential factor in Eq. (3.55), and expand the part containing the correction for curvature, \( z_s^2 \), to obtain:

\[
\exp \left[ -\mu' (s + t) \right] = \exp \left[ -\mu' \left( 1 + \frac{\sin \alpha}{\sin \beta} \right) s \right] \cdot \left( 1 - \mu' z_s^2 + \cdots \right), \quad (3.57)
\]

Substitution of Eq. (3.57) into (3.55) and integration over \( s \) now yields for the total integrated intensity diffracted by and emerging from the sample (out of the incident beam of angular aperture \( \alpha \) and power \( P(\alpha) \) \( d\alpha \)) the expression:

\[
I(\alpha) \, d\alpha = \left( \frac{pg}{2} \right) \cos \Theta_0 \cdot \frac{\rho'}{\rho} P(\alpha) \, d\alpha \int_0^\infty \left( 1 - \mu' z_s^2 + \cdots \right) \exp \left[ -\mu' \left( 1 + \frac{\sin \alpha}{\sin \beta} \right) s \right] \, ds
\]

\[
= \left( \frac{pg}{2} \right) \cos \Theta_0 \cdot \frac{\rho'}{\rho} P(\alpha) \, d\alpha \left[ -\mu' \left( 1 + \frac{\sin \alpha}{\sin \beta} \right) \right]^{-1} \cdot \left\{ 1 - 2\mu' z_s^2 \left[ -\mu' \left( 1 + \frac{\sin \alpha}{\sin \beta} \right) \right]^{-2} + \cdots \right\}. \quad (3.58)
\]

But if \( \mu \) is the linear absorption coefficient of solid crystal, the effective absorption coefficient of the powder sample is

\[
\mu' = \left( \frac{\rho'}{\rho} \right) \mu, \quad (3.59)
\]

where \( \left( \frac{\rho'}{\rho} \right) \) is the packing fraction defined in connection with Eq. (3.50). Equations (3.58) and (3.59) now yield

\[
I(\alpha) \, d\alpha = \left( \frac{pg}{2} \right) \cos \Theta_0 \cdot P(\alpha) \, d\alpha \cdot \left[ \mu \left( 1 + \frac{\sin \alpha}{\sin \beta} \right) \right]^{-1} C(\mu', \alpha, \beta) \quad (3.60)
\]

where

\[
C(\mu', \alpha, \beta) = 1 - \left( \frac{2\mu}{\mu'} \right) \left( 1 + \frac{\sin \alpha}{\sin \beta} \right)^{-2} + \cdots \quad (3.61)
\]
The factor \( \left[ \mu(1 + \sin \alpha / \sin \beta) \right]^{-1} \) in Eq. (3.60) is of the same form as the absorption factor for an infinitely-thick flat sample. The factor \( C(\mu', \alpha, \beta) \) on the right-hand side of Eq. (3.60) corrects the absorption factor for the curvature of the face of the sample. This factor is close to unity but its effect is not negligible under all conditions. However, at the time the data of this investigation were treated the correction for curvature had not been derived and its possible importance was not appreciated. As a result this factor was ignored and only the flat-sample factor \( \left[ \mu(1 + \sin \alpha / \sin \beta) \right]^{-1} \) was used. The effects of this omission on the calculated integrated intensities will be considered after the presentation of these intensities in Chapter VI.

The calculation leading to Eq. (3.60) has not yet taken into account the absorption of the x-ray beam by the air. This is a small correction for the MoK\( \alpha \) radiation used in this investigation, but would be much more important with CuK\( \alpha \) radiation, for example. The absorption by the windows on the x-ray tube and counter and the filter may be ignored as they are constant in all measurements. Let \( a \) and \( b \) be the source to sample and sample to exit slit distances as shown in Fig. 1. Then the total air path is

\[
(a - a') + (b + b'),
\]

(3.62)

where \( a' \) is the distance the beam travels within the evacuated x-ray tube and \( b' \) is the air path from the exit slit to the counter. On using Eqs. (3.2) and (3.3) the air absorption factor now becomes

\[
A_{\text{air}} = \exp \left[ \mu_{\text{air}}(a' - b') \right] \exp \left[ -2R \mu_{\text{air}}(\sin \alpha + \sin \beta) \right],
\]

(3.63)

where \( \mu_{\text{air}} \) is the absorption coefficient of air. In measurements with a
a given type of radiation, x-ray tube, and counter, the first exponential factor on the right-hand side of Eq. (3.63) is constant and may be ignored in the calculation of relative intensities. If, in addition, \( \alpha \) is constant in a given series of measurements, the variable part of the air absorption factor becomes simply

\[
\exp(-2R\mu_{\text{air}} \sin \theta).
\]  

(3.64)

The appropriate form of the air absorption factor is to be inserted on the right-hand side of Eq. (3.60).

4. Vertical Divergence Factor

In Part 2 of this section it was pointed out that if the radiation diffracted by a crystallite located at \( K \) in Fig. 3a is to pass through the Soller slits and reach the detector, then the normal to the set of diffracting planes must intersect the unit sphere in the small shaded area shown in the figure. The ratio of this area to the total area of the annular strip was designated by \( g \) and called the vertical divergence factor. The evaluation of this factor will now be considered.

Figure 3b is a vertical section through the Soller slits and illustrates the manner in which the effective aperture of the slits is determined as viewed from a point on the sample. The distance from the sample to the near end of the slits is denoted by \( D \) and the length of the Soller slits by \( L \). It is convenient to designate the vertical distance between adjacent vanes of the slits by \( 2h \) (for purposes of illustration the ratio of \( 2h \) to \( L \) is greatly exaggerated in the figure). The relative height of the point on the sample under consideration is measured by the coordinate \( \xi \), with \( \xi = 0 \) corresponding to the height at the middle of the slit opening directly opposite. The part of the
Fig 3 Effect of vertical divergence on x-ray intensity due to
(a) random orientation of crystal fragments
(b) total vertical aperture of Soller slits
sample opposite the given opening then lies in the ranges $5 = -1$ to $5 = 1$, but as a result of the symmetry of the slit system with respect to reflection in a horizontal plane at $5 = 0$ it is sufficient to consider the range $3 = 0$ to $3 = 1$ on the sample face. The effective apertures of successive openings of the slits as viewed from a point at height $5$ on the sample are denoted by $\ldots, l_{-2}, l_{-1}, l_0, l_1, l_2, \ldots$, in Fig. 3b. These are linear apertures measured vertically at a distance $D + L$ from the sample. It will be noted that the opening opposite the point under consideration on the sample has its maximum value, $l_0 = 2h$, for all values of $5$ in the range $-1 \leq 5 \leq 1$, but that the effective apertures of the other openings is reduced by the shadowing effect of the slit vanes as indicated by the shaded regions. This is, of course, the principle by means of which the Soller slits restrict the vertical divergence of the beam. The following explicit expressions for the apertures are readily obtained:

$$l_0 = 2h ;$$

$$l_i = h \left[ 2 - \frac{L}{D} (2|1| - 1 \mp 5) \right], \ i \neq 0. \quad (3.66)$$

In Eq. (3.66) and subsequent equations the upper sign is to be used if $i$ is a positive integer, and the lower sign if $i$ is a negative integer. The values of $i$ permissible in Eq. (3.66) are also restricted by the condition that $l_i \geq 0$, or:

$$|i| \leq \frac{(D/L) + (1 \mp 5)}{2} \quad (3.67)$$

Whenever the right-hand side of Eq. (3.67) is a positive integer, $n$, the upper limit of $|i|$ may be taken to be either $n$ or $n-1$, whichever is most convenient, since then $l_n = 0$ or $l_{-n} = 0$, as the case may be.
The problem may be simplified by considering the particular sample to Soller slit distances:

\[ D = nL; \quad n = 0, 1, 2, \ldots; \quad (3.68) \]

or

\[ D = \left[ n + \left( 1/2 \right) \right] L; \quad n = 0, 1, 2, \ldots. \quad (3.69) \]

For \( D = nL \), the relation \((3.67)\) becomes

\[ |i| \leq n + \left( 1/2 \right) \pm \left( \delta /2 \right); \quad (3.70) \]

while for \( D = \left[ n + \left( 1/2 \right) \right] L \),

\[ |i| \leq n + 1 \pm \left( \delta /2 \right). \quad (3.71) \]

As previously stated, the restriction \( 0 \leq \delta \leq 1 \) may be imposed without loss of generality. Therefore, keeping in mind the comment following Eq. \((3.67)\), the range of \( i \) may be taken to be:

\[-n \leq i \leq n, \quad D = nL; \quad (3.72)\]

and

\[-n \leq i \leq n + 1, \quad \delta = \left[ n + \left( 1/2 \right) \right] L. \quad (3.73)\]

These two relations may be consolidated in the form:

\[-n \leq i \leq n + \delta; \quad D = \left[ n + \left( \delta /2 \right) \right] L, \quad \delta = 0 \text{ or } 1. \quad (3.74)\]

It should be noted that the range of \( i \) for these particular values of \( D \) is independent of \( \delta \); this is not true for general values of \( D \).

The preceding treatment must be modified for a real Soller slit having a finite number, \( \nu \), of openings. Suppose the point on the sample which is under consideration is opposite the \( j \)th opening reckoned
from the bottom of the slit, where \( j \) may assume any value from 1 to \( \nu \). Then it is clear that, in addition to the restriction of the range of \( i \) by Eq. (3.74), the following restriction must also be considered:

\[-j + 1 \leq i \leq \nu - j.\]  

(3.75)

We will denote the maximum and the minimum of two numbers \( a \) and \( b \) by \( M(a,b) \) and \( m(a,b) \), respectively. Thus, if \( a > b \), \( M(a,b) = a \) and \( m(a,b) = b \). Then it is clear that the combined effect of Eq. (3.74) and Eq. (3.75) is to restrict the range of \( i \) to

\[M(-n,-j+1) \leq i \leq m(n+\delta,\nu-j), \quad D = \left[ n + \left( \delta/2 \right) \right] L, \quad \delta = 0 \text{ or } 1. \]  

(3.76)

The total vertical aperture for a point on the sample face at height \( \delta h \) above the mid-point of the \( j \)th slit opening may now be written as

\[I_{n\delta,\nu j} = \sum_{i=M(-n,-j+1)}^{m(n+\delta,\nu-j)} l_i, \]  

(3.77)

where \( l_i \) is given by Eq. (3.65) and (3.66). The average value of \( I_{n\delta,\nu j} \) for points on the sample face at heights between 0 and \( h \) above the mid-point of the \( j \)th slit opening, or for all points on the sample face opposite the upper half of the slit opening, is now obtained by integrating \( \delta \) over the range 0 to 1:

\[I_{n\delta,\nu j} = 2h + h \sum_{i=M(-n,-j+1)}^{m(n+\delta,\nu-j)} \left\{ 2- \left[ n + \left( \delta/2 \right) \right]^{-1} \left[ 2\lfloor 1 \rfloor - 1 + (1/2) \right] \right\}. \]  

(3.78)

The prime on the summation sign indicates that \( i = 0 \) is to be excluded. The upper sign before \( 1/2 \) on the right-hand side of Eq. (3.78) is to be
used for \( i > 0 \), and the lower sign for \( i < 0 \). The summation indicated in Eq. (3.76) may be carried out explicitly to obtain:

\[
T_{n_{\xi},\nu} = 2h \left\{ 1 + \left[ 1 + (4n + 2\xi)^{-1} \right] \left[ m(n+\xi,\nu-j) + m(n, j-1) \right] \right. \\
\left. - (2n + \xi)^{-1} \left[ \{m(n+\xi,\nu-j)\}^2 + \{m(n, j-1)\}^2 \right] \right\} . \tag{3.79}
\]

In this reduction we have used the relation \( m(a,b) = -m(-a,-b) \), and also the familiar formula for the sum of the first \( n \) integers.

The average of the total vertical aperture for all points on the sample face is now obtained by averaging \( T_{n_{\xi},\nu} \) over all slit openings:

\[
T_{n_{\xi},\nu} = \frac{1}{\nu} \sum_{i=1}^{\nu} T_{n_{\xi},\nu} . \tag{3.80}
\]

It will be noted that in arriving at Eq. (3.80) the averaging has been carried out only for points on the sample opposite the upper half of the Soller slit openings, but from symmetry considerations the average for the lower half of the openings has the same value, so that Eq. (3.80) yields the overall average as stated. Substitution of Eq. (3.79) into Eq. (3.80), followed by a transformation of indices in two of the resulting sums yields

\[
T_{n_{\xi},\nu} = 2h + (2h/\nu) \left\{ \left[ 1 + (4n + 2\xi)^{-1} \right] \left[ S_1(n) + S_1(n + \xi) \right] \right. \\
\left. - (2n + \xi)^{-1} \left[ S_2(n) + S_2(n + \xi) \right] \right\} , \tag{3.81}
\]

where \( S_1(k) \) and \( S_2(k) \) are defined for positive integral \( k \) by
\[ S_1(k) = \sum_{j=1}^{\nu} m(k, j-1) = (1/2)\nu(\nu - 1), \quad (k \geq \nu - 1) \] (3.82)

\[ = k\left[\nu - (1/2)k - (3/2)\right], \quad (k < \nu - 1) \] (3.83)

\[ S_2(k) = \sum_{j=1}^{\nu} \left[m(k, j-1)\right]^2 = (1/6)\nu(\nu - 1)(2\nu - 1), \quad (k \geq \nu - 1) \] (3.84)

\[ = \frac{1}{6}k(k+1)(2k+1) + k^2(\nu - k - 2), \quad (k < \nu - 1). \] (3.85)

Also, \( S_1(0) = S_2(0) = 0 \) for all \( \nu \), and \( S_1(k) = S_2(k) = 0 \) for all \( k \) for \( \nu = 1 \). To recapitulate, in these formulas \( \nu \) is the number of openings in the Soller slit, \( 2h \) is the height of each, and the formulas yield the value of the average total aperture, \( \bar{I}_{n\delta, \nu} \), for \( D = \left[n + (\delta/2)\right]L \) with \( n = 0, 1, 2, \ldots \), and \( \delta = 0 \) or 1.

Although the preceding analysis is exact for the idealized case of a Soller slit with horizontal vanes of zero thickness, real Soller slits must of course have vanes of some finite thickness, \( t \), separating the openings. Let \( 2h \) then be the distance between the middle of two adjacent vanes, so that the openings are of height \( 2h - t \). Then a modification of the preceding analysis valid for \( t \ll 2h \) shows that the following expression should be added to the right-hand side of Eq. (3.81) to correct for the finite thickness of the vanes:

\[ \Delta I_{n\delta, \nu} = t - (t/\nu) \left[1 + (2n + \delta)^{-1}\right] \left[S_1(n) + S_1(n + \delta)\right]. \] (3.86)

This correction is given for future use, but was not applied in the present investigation. It is doubtful if it would have had a significant effect on the determination of relative intensities.
Hereafter, \( l_{n,v,j} \), \( \bar{l}_{n,v,j} \), and \( \bar{l}_{n,v} \) of Eqs. (3.77), (3.79), and (3.81), will be abbreviated as \( l \), \( \bar{l} \), and \( \bar{\bar{l}} \), respectively. That is, \( l \) will denote the total vertical aperture for a point on the sample face at given \( j \) and \( \delta \), \( \bar{l} \) represents an average of \( l \) over \( \delta = 0 \) to \( l \), and \( \bar{\bar{l}} \) represents the average of \( \bar{l} \) over all \( j \), or the overall average total vertical aperture. From Eqs. (3.81) to (3.85) it is clear that \( \bar{\bar{l}} \) has a different functional form for the two cases \( n < \nu - 1 \) and \( n \geq \nu - 1 \).

Since \( D = nL \) (for simplicity it will be assumed throughout the present discussion that \( \delta = 0 \)) these two cases correspond to relatively small and large sample to Soller slit distances, respectively. It is clear from (3.75) that on increasing \( D \) the transition occurs at the distance at which an observer located at an arbitrary point on the sample face is able for the first time to see through (at least partially) each of the \( \nu \) openings of the Soller slit. Prior to reaching this critical distance the observer is able periodically to see through openings which were previously closed, and this produces a relatively rapid rate of increase in \( \bar{l} \). On the other hand for distances greater than the critical distance there are no additional openings to open up, and the rate of increase of \( \bar{l} \) becomes smaller. In fact, as is readily verified from the preceding equations as \( D \to \infty \) (or \( n \to \infty \)), \( \bar{\bar{l}} \) approaches asymptotically the constant value \( 2h\nu \), which is the total height of the Soller slit. This is clearly a result of the fact that at \( D = \infty \) each of the \( \nu \) openings of the slit would appear fully open to our hypothetical observer, with its maximum aperture, \( l_0 = 2h \). Thus, as \( D \to \infty \) the vanes of the Soller slit lose their function of limiting the vertical divergence of the beam, and the Soller slit behaves as
though it were simply a single horizontal slit of height $2h\nu$. The range in which a Soller slit exhibits its characteristic properties most strongly, and is most useful, is therefore that of distances less than the critical distance, or $D < (\nu-1)L$. The distances used in the present investigation fall within this range.

The preceding analysis has given \( T \) only for values of $D$ which are integral or half-integral multiples of $L$. However, qualitative consideration of the problem for general values of $D$ shows that \( T \) is a continuous function of $D$ (even at the point of transition), and that within each of the two ranges discussed above at least the first derivative of \( T \) with respect to $D$ is continuous (in fact it is easily shown that for the outer range, $D \geq (\nu-1)L$, \( T \) and all its derivatives are strictly continuous). This suggests that for numerical applications it should be quite satisfactory to calculate \( T \) for values of $D$ which are integral and half-integral multiples of $L$ ($n = 0, 1, 2, \ldots; \delta = 0$ or 1) from Eqs. (3.81) to (3.8b), and to obtain \( T \) for other values of $D$ by interpolation from a smooth curve drawn through these points. A numerical investigation for the inner range required in this research ($n < \nu-1$) showed that the points for both $\delta = 0$ and 1 fall on a smooth curve within an accuracy of about 0.1 percent, any alternation of the values for $\delta = 0$ and 1 being undetectable. These interpolated values were used in the treatment of the data of this research. The numerical values of \( T \) will not be given directly, but rather the values of the factor \( T/(D+L) \) which enters into the vertical divergence factor, \( g \). These values, which will be given subsequently, were calculated by
numerical summation of the apertures of the individual slit openings as given by Eqs. (3.65) and (3.66), followed by integration over $S$. The more explicit Eqs. (3.79) and (3.81) to (3.85) were obtained subsequently by W. J. Taylor. However, the two treatments are entirely equivalent.

The dependence of $g$ on $\overline{I}$ will now be considered. In Fig. 3a let $K$ represent a particular point on the sample surface, and let the far end of the Soller slit be located at $S$. Thus, $\overline{KS}$ is the distance $D + L$ illustrated in Fig. 3b. It should be noted that this differs from the distance $\overline{KS}$ in Figs. 1 and 4, which represents the distance from the sample to the vertical exit slit. The total vertical aperture of the Soller slit as defined by Eq. (3.77) for the point $K$ on the sample is indicated by a vertical line of length $l_b$ at $S$ in Fig. 3a. The subscripts $b$ or 2 are used to denote instrumental components and associated quantities for the diffracted beam, and subscripts $a$ or 1 for the incident beam. It has been seen that $l_b$ is composed of segments determined by the apertures of the individual Soller slit openings, but the following argument is unaffected (to the third order in the small quantities involved) if the aperture for point $K$ is regarded as being determined by a single opening of height $l_b$ at $S$. The direction of the incident beam in Fig. 3a is denoted by the line $FK$ and its extension $KH$, the diffracted beam by $KS$ and the normal to the diffracting planes of the crystal by $KP$. All these lines lie in a common plane, the plane of diffraction. Also, from the figure $\overline{RS} = \overline{KS} \sin 2 \Theta_o = (D_b + L_b) \sin 2 \Theta_o$. The existence of a finite vertical aperture $l_b$ at $S$ permits a rotation of
the plane of diffraction about the line FKR through an angle
\[ \Delta \phi_b = \frac{l_b}{(D_b + L_b)} \sin 2 \theta_o . \] (3.87)

Here as before we have neglected the difference between the angle \( \Delta \phi_b \) and its tangent; the error of this approximation is \((\Delta \phi)^3/3\) and does not exceed 0.1 percent of \( \Delta \phi \) for either of the Soller slits employed.

As a result of the rotation of the plane of diffraction through the angle \( \Delta \phi_b \) the normal, KP, to the crystal planes may intersect the unit sphere anywhere in the small shaded area shown in Fig. 3a. In Part 2 of this section the ratio of this shaded area to the total area of the annular strip is denoted by \( g_b \), and called the vertical divergence factor. It is now clear that this ratio is
\[ \Delta \phi_b / 2\pi . \] (3.88)

However, this value refers only to the particular point K on the sample. If we now substitute Eq. (3.87) into the expression (3.88), and successively average \( l_b \) over \( S \) and the index j to obtain \( \bar{l}_b \) as given by Eq. (3.81), the average vertical divergence factor for the diffracted beam becomes
\[ g_b = \frac{\bar{l}_b}{2\pi} (D_b + L_b) \sin 2 \theta_o . \] (3.89)

An exactly equivalent analysis can be given for the Soller slit in the incident beam. This is most easily seen by reflecting Fig. 3a in a vertical plane through KP, which carries the vertical aperture \( l_b \) into \( l_a \). The angle 2 \( \theta_o \) enters in the same way. Thus, the average vertical divergence factor for the incident beam is
\[ g_a = \frac{\bar{l}_a}{2\pi} (D_a + L_a) \sin 2 \theta_o . \] (3.90)

In order to see how to combine these two vertical divergence factors we consider the vertical component, \( \Delta z \), of the displacement of the point P where the normal to the crystal planes intersects the unit sphere where simultaneous rotations \( \Delta \phi_a \) and \( \Delta \phi_b \) are performed. For
definiteness let \( \Delta \phi_b \), the rotation about FK in Fig. 3a, be positive when in the sense of a left-handed screw advancing from F to K. \( \Delta \phi_a \) is the rotation into which \( \Delta \phi_b \) is carried under the reflection referred to previously and is thus a rotation about SK, positive when in the sense of a right-handed screw advancing from S to K. Then it is easily shown that the leading terms in the expansion of \( \Delta z \) in powers of \( \Delta \phi_a \) and \( \Delta \phi_b \) are of the form:

\[
\Delta z = c_1 \Delta \phi_a + c_1 \Delta \phi_b + c_2(\Delta \phi_a)^3 + c_2(\Delta \phi_b)^3 + c_3(\Delta \phi_a)^2 \Delta \phi_b \\
+ c_3 \Delta \phi_a (\Delta \phi_b)^2 + \cdots,\quad (3.91)
\]

where \( c_1 = \cos \theta_o \), and \( c_2, c_3, \text{ etc.} \), are also functions of \( \theta_o \). The absence of terms \( (\Delta \phi_a)^2 \) and \( (\Delta \phi_b)^2 \) in Eq. (3.91) follows from the fact that \( \Delta z \) is an odd function of \( \Delta \phi_a \) if \( \Delta \phi_b = 0 \), and vice versa. The absence of a term \( (\Delta \phi_a)(\Delta \phi_b) \) may be inferred from the fact that \( \Delta z = 0 \) for \( \Delta \phi_a = -\Delta \phi_b \). It follows from Eq. (3.91) that \( \Delta z \) is linear in \( \Delta \phi_a \) and \( \Delta \phi_b \) to a high degree of accuracy when these angles are sufficiently small, the error in this approximation being due to the neglect of terms of cubic and higher degree. The percentage error in \( \Delta z \) as calculated from only the linear terms in Eq. (3.91) is less than 0.1 percent for the values of \( \Delta \phi_a \) and \( \Delta \phi_b \) occurring in this investigation.

In the linear approximation Eq. (3.91) yields

\[
(\Delta z/2 \pi \cos \theta_o) = (\Delta \phi_a/2 \pi) + (\Delta \phi_b/2 \pi). \quad (3.92)
\]

For a given point on the sample \( \Delta \phi_b \) is given by Eq. (3.87) and \( \Delta \phi_a \) by a similar equation. If we now average over all points on the sample
(indicated by a double bar as before) and use Eqs. (3.89) and (3.90), we obtain

\[
\left( \Delta \frac{x}{2} \pi \cos \theta_o \right) = g_a + g_b .
\]  

(3.93)

But from the discussion in Part 2 of this section the left-hand side of Eq. (3.93) is clearly the overall average vertical divergence factor, \( g \), resulting from divergence in both the incident and diffracted beams (on multiplying both numerator and denominator by \( d\theta \) these become the areas of the shaded region and of the annular strip, respectively, in Fig. 3a). Thus,

\[
g = g_a + g_b .
\]  

(3.94)

Equations (3.89) and (3.90) show that \( g_a \) and \( g_b \) are functions of \( D_a \) and \( L_b \), the distances from the sample to the near ends of the Soller slits in the incident and diffracted beams, respectively, as shown in Fig. 3b. But from Figs. 1 and 4 (where the Soller slits are designated by \( V_1 \) and \( V_2 \), and Eqs. (3.2) and (3.3),

\[
D_a = 2R \sin \alpha - D'_a ,
\]  

(3.95)

\[
D_b = 2R \sin \beta + D'_b .
\]  

(3.96)

Here \( D'_a \) is the fixed distance from the line-focus \( F \) to the end of the Soller slit \( V_1 \) nearest the sample \( K \), and \( D'_b \) is the fixed distance from the vertical exit slit \( S \) to the end of the Soller slit \( V_2 \) nearest it. The lengths of the Soller slits \( V_1 \) and \( V_2 \) have been designated by \( L_a \) and \( L_b \), respectively, and the vertical separation of the vanes in
these two slits may be designated by $2h_a$ and $2h_b$. The values of these parameters are given in Table 3.

**TABLE 3**

**Soller Slit Parameters (in inches)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_a$</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>$L_b$</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>$D_a$</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>$D_b$</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>$2h_a$</td>
<td>0.0340</td>
<td></td>
</tr>
<tr>
<td>$2h_b$</td>
<td>0.0192</td>
<td></td>
</tr>
</tbody>
</table>

$K = 7.162$

It is convenient to factor out the parts of $g_a$ and $g_b$ that depend on $\alpha$ and $\beta$, respectively. Thus, from Eqs. (3.89) and (3.90),

$$g_a = A(\alpha)/2\pi \sin 2 \theta_o ,$$

$$g_b = B(\beta)/2\pi \sin 2 \theta_o ,$$

where

$$A(\alpha) = \frac{\overline{I}_a}{(D_a + L_a)} ,$$

$$B(\beta) = \frac{\overline{I}_b}{(D_b + L_b)} .$$

It should be noted that $\overline{I}_a$ and $\overline{I}_b$ are functions of $D_a$ and $D_b$, and therefore of $\alpha$ and $\beta$, respectively. Finally, from Eq. (3.94),

$$g = \frac{1}{2\pi \sin 2 \theta_o} \left[ A(\alpha) + B(\beta) \right] .$$

The values of $\overline{I}_a$ and $\overline{I}_b$ have been calculated as discussed previously, and the values of $A(\alpha)$ and $B(\beta)$ interpolated from the smooth curves.
These dimensionless quantities are tabulated in Tables 4 and 5 for several values of $\alpha$ and $\beta$. The overall vertical divergence factor $g$, as calculated from these tables and Eq. (3.101) is to be inserted in Eq. (3.60) for the integrated intensity.

**TABLE 4**

(Values of $A(\alpha)$)

<table>
<thead>
<tr>
<th>$\alpha$ (deg)</th>
<th>$A(\alpha) \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.0</td>
<td>2.530</td>
</tr>
<tr>
<td>22.5</td>
<td>2.568</td>
</tr>
<tr>
<td>37.5</td>
<td>2.312</td>
</tr>
<tr>
<td>52.5</td>
<td>2.129</td>
</tr>
</tbody>
</table>

**TABLE 5**

(Values of $B(\beta)$)

<table>
<thead>
<tr>
<th>$\beta$ (deg)</th>
<th>$B(\beta) \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.524</td>
</tr>
<tr>
<td>10</td>
<td>1.495</td>
</tr>
<tr>
<td>15</td>
<td>1.465</td>
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<tr>
<td>20</td>
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<tr>
<td>25</td>
<td>1.410</td>
</tr>
<tr>
<td>30</td>
<td>1.383</td>
</tr>
<tr>
<td>35</td>
<td>1.358</td>
</tr>
<tr>
<td>40</td>
<td>1.334</td>
</tr>
<tr>
<td>45</td>
<td>1.311</td>
</tr>
</tbody>
</table>
In conclusion it must be admitted that with regard to the form of the vertical divergence factor, g, in the expression for integrated intensities the new focusing spectrometer described here is at a disadvantage relative to the conventional spectrometer. In the conventional spectrometer described in Section A-2 of this chapter the line source and exit slit remain at a constant distance from the sample, and it is therefore possible to maintain the Soller slits also at a constant distance from the sample. The vertical divergence factor g is a function of the distance as shown by the preceding calculation, but since the distance is constant, g is also constant and may be ignored.

The design of the present spectrometer based on the focal circle yields true focusing but also makes it almost inevitable that the sample to Soller slit distance be variable. As it is impracticable to construct geometrically precise Soller slits with widths of more than several millimeters they must be placed in the narrow parts of the incident and diffracted beams as shown in Fig. 4. However, it is felt that if the slits are constructed and aligned horizontally with sufficient accuracy and the accurate theory developed in this section is used to calculate g, then this feature of the present spectrometer is not a serious handicap. This conclusion is reinforced by the fact that $A(\omega)$ and $B(\phi)$ are rather slowly varying functions of $\theta_0$, as shown by Tables 4 and 5. It is believed that in the present investigation $g$ has been evaluated with an accuracy of one percent, except for the neglect of the correction for the thickness of the slit vanes, Eq. (3.86), which was obtained after the treatment of the data had been completed. The
The thickness of the vanes is \( t = 0.0026 \) inches, and it may be seen from Eqs. (3.81) and (3.86) that \( \overline{I} \) should be reduced approximately in the proportion of \( t \) to \( 2h \). Therefore it may be estimated that this correction will reduce \( A(\alpha) \) by about 7.6 percent, and \( B(\beta) \) by about 13.5 percent. In the main series of measurements of this investigation \( A(\alpha) = 0.0257 \) and \( B(\beta) \) varied from 0.0151 to about 0.0134. Thus, in view of Eq. (3.101) the thickness correction would reduce the absolute value of \( g \) about 9.7 ± 0.1 percent over the entire range of \( \theta \). Since this correction is constant to a few tenths of one percent, the effect on the relative intensities is unimportant.

5. Vertical or Exit Slit Factor

We have now obtained in Eq. (3.60) with the inclusion of the air absorption factor of Eq. (3.63), the complete expression for the total power (energy per unit time) diffracted by the sample out of the beam incident on it between angles \( \alpha \) and \( \alpha + d\alpha \). This total power, also called the integrated intensity, has been denoted by \( I(\alpha) \, d\alpha \) because it depends in part on \( \alpha \) (as well as \( \Theta_0 \)) and is proportional to the power, \( P(\alpha) \, d\alpha \), in the incident beam. This diffracted power will be distributed in some manner in the neighborhood of the Bragg angle, \( \Theta_0 \). We therefore introduce an intensity function, \( I(\alpha, \theta) \, d\alpha \, d\theta \), equal to the power diffracted out of the beam incident between \( \alpha \) and \( \alpha + d\alpha \) and into angles between \( \theta \) and \( \theta + d\theta \). In the present discussion \( \theta \) is understood to represent not necessarily the true angle of diffraction but the apparent value of this angle as determined by the position (projected vertically) on the focal circle at which the ray falls. The precise form of the intensity contour, \( I(\alpha, \theta) \, d\alpha \), will depend in
part on the natural line shape but also on the instrumental aberrations discussed in Section B of this chapter. However, it should be noted that \( I(\alpha, \Theta) \, d\alpha \) represents the intensity distribution falling on the exit slit, not that passing through it, so that the exit slit width plays no part in the determination of \( I(\alpha, \Theta) \). In view of its definition, \( I(\alpha, \Theta) \) must satisfy the relation

\[
I(\alpha) \, d\alpha = d\alpha \int_{-\infty}^{\infty} I(\alpha, \Theta) \, d\Theta,
\]

from which the suitability of the description of the total power, \( I(\alpha) \, d\alpha \), as the integrated intensity becomes evident. The extension of the limits of integration in Eq. (3.102) to infinity is convenient and formally permissible as virtually the entire contribution to the integral comes from a small region of \( \Theta \) in the neighborhood of \( \Theta_o \). That is, after correction for background radiation \( I(\alpha, \Theta) \) vanishes rapidly as \( |\Theta - \Theta_o| \to \infty \).

In the present investigation the quantity of primary interest is the integrated intensity, \( I(\alpha) \, d\alpha \), rather than the intensity distribution function \( I(\alpha, \Theta) \), but this may not always be the case. If it were not for the problem of eliminating background radiation the simplest method of obtaining \( I(\alpha) \, d\alpha \) would be to use a slit wide enough to accept at a single setting essentially all of the diffracted power. This method of obtaining integrated intensities is often used with single crystals for which the background is negligible. However, with powder samples there is nearly always a continuous background due to radiation of other than the characteristic wave length, and incoherent
and diffuse scattering, and in order to separate the Laue-Bragg scattering from this background it is essential to obtain an intensity contour. The most direct method of accomplishing this is, in principle, to scan the line with an exit slit so narrow that it does not introduce any significant falsification of the form of the intensity distribution. In this way the sum of the true intensity function $I(\alpha, \theta)\, d\alpha$ and the background could be measured as a function of $\theta$, a background curve drawn, and $I(\alpha, \theta)\, d\alpha$ obtained by subtraction of the background. However, this procedure is seldom practicable because of the low intensities or counting rates which would be obtained with such a narrow slit. Thus, as discussed in Chapter IV, Section D-2, there is a lower limit to the number of counts which may be recorded at each slit setting if the percentage error due to random fluctuations in the counting rate is to be kept below any given figure. It is therefore usually necessary in practice to use an exit slit of intermediate width representing a compromise between the two extremes discussed above. For example, in the present investigation the exit slit width contributed a large part of the overall width of the recorded contours, as shown by Tables 1 and 2. Under these circumstances the measured intensity contour will not be the true contour, $I(\alpha, \theta)\, d\alpha$, of the intensity reaching the slit, but will represent a modified contour, $I'(\alpha, \theta')\, d\alpha$, the total power passing through the slit when the center of the slit is set at $\theta'$. That is, if $\Delta \theta$ is the range of $\theta$ intercepted by the exit slit, as given by Eq. (3.9),

$$I'(\alpha, \theta')\, d\alpha = d\alpha \int_{\theta'-(\Delta \theta/2)}^{\theta'+(\Delta \theta/2)} I(\alpha, \theta)\, d\theta.$$  (3.103)
Another way of formulating this is to represent \( I'(\alpha, \Theta') \, d\alpha \) as the convolution of \( I(\alpha, \Theta) \, d\alpha \) and a rectangular function of \( \Theta \) equal to unity in the range \( \Theta'-(\Delta \Theta/2) \) to \( \Theta'+(\Delta \Theta/2) \) and zero outside this range. This is the point of view adopted in Section B of this chapter and a general theorem given there shows that the square of the standard deviation, \( (\sigma')^2 \), of \( I'(\alpha, \Theta') \, d\alpha \) from its mean will exceed the corresponding quantity, \( \sigma^2 \), for \( I(\alpha, \Theta) \, d\alpha \) by an amount equal to \( \sigma^2_b \), where \( \sigma^2_b \) is the standard deviation for the rectangular slit function as given by Eq. (3.10). Thus, \( I'(\alpha, \Theta') \, d\alpha \) is necessarily a broader distribution than \( I(\alpha, \Theta) \, d\alpha \) and its qualitative form may be different (for example the resolution of the \( \alpha_1 \alpha_2 \) doublet will be poorer for the first than for the second function). In spite of this, in practice \( I'(\alpha, \Theta') \, d\alpha \) represents the only approximation to \( I(\alpha, \Theta) \, d\alpha \) one has available.

The procedure followed in this research was the customary one of plotting the observed intensity, drawing a smooth background curve, and subtracting the background intensity to obtain the observed line contour, \( I'(\alpha, \Theta') \, d\alpha \). The area or integral of the line contour was then calculated by numerical integration using Simpson's rule. The integrated intensities obtained in this way may be represented as

\[
I'(\alpha) \, d\alpha = d\alpha \int_{-\infty}^{\infty} I'(\alpha, \Theta') \, d\Theta', \quad (3.104)
\]

cr, using Eq. (3.103),

\[
I'(\alpha) \, d\alpha = d\alpha \int_{-\infty}^{\infty} d\Theta' \int_{\Theta'-(\Delta \Theta/2)}^{\Theta'+(\Delta \Theta/2)} I(\alpha, \Theta) \, d\Theta. \quad (3.105)
\]
It is not immediately obvious how the integrated intensity, $I'(\alpha) \, d\alpha$, obtained by this procedure is related to the integrated intensity reaching the exit slit, $I(\alpha) \, d\alpha$, as given by Eq. (3.60) or (3.102). This is a problem which arises in all measurements of intensities using a finite slit width but in spite of this the solution to the problem does not seem to be given in the standard sources or to be widely known. The formulation and solution of the problem given here is due to W. J. Taylor, and is a special case of a more general theorem for the convolution of two or more functions.

In order to evaluate the double integral in Eq. (3.105), introduce the transformation $\Theta = \Theta' + x$. Since $\Theta'$ is constant in the first integration over $\Theta$, $d\Theta = dx$, and

$$ I'(\alpha) \, d\alpha = d\alpha \int_{-\infty}^{\infty} d\Theta' \int_{-\Delta\Theta/2}^{\Delta\Theta/2} I(\alpha, \Theta' + x) \, dx \quad (3.106) $$

The variables of integration no longer occur in the limits of integration, and the order of integration may be interchanged to yield

$$ I'(\alpha) \, d\alpha = d\alpha \int_{-\infty}^{\infty} dx \int_{-\Delta\Theta/2}^{\Delta\Theta/2} I(\alpha, \Theta' + x) \, d\Theta' $$

$$ = \int_{-\Delta\Theta/2}^{\Delta\Theta/2} dx \int_{-\infty}^{\infty} I(\alpha, \Theta) \, d\Theta $$

$$ = I(\alpha) \, d\alpha \Delta\Theta, \quad (3.107) $$
from Eq. (3.102). We, therefore, obtain the surprisingly simple
result that in spite of the modification of the intensity contour by
the finite slit width $\Delta \theta$, the observed integrated intensity,
$I'(\alpha)\,d\alpha$, passing through the slit is simply $\Delta \theta$ times as great
as the integrated intensity, $I(\alpha)\,d\alpha$, reaching the exit slit.
That is, the factor to be introduced into the expression for the
integrated intensity to allow for the width of the vertical exit slit
is simply $\Delta \theta$ as given by Eq. (3.9). In this treatment we have
neglected the slight variation of $\Delta \theta$ in the neighborhood of $\theta_0$. It
should also be noted that the $\Delta \theta$ required here does not include any
contribution from the width of the line source as given by Eq. (3.7). The
latter influences the intensity contour reaching the exit slit,
$I(\alpha, \theta)\,d\alpha$, but does not alter the integrated intensity reaching
the slit, $I(\alpha)\,d\alpha$, in terms of which the problem has been
formulated. This is an important point because the width and contour
of the line source is not accurately known.

6. Total Integrated Intensity

It has now been shown that the integrated intensity, $I'(\alpha)\,d\alpha$, scattered out of the beam incident between $\alpha$ and $\alpha+d\alpha$ and reaching
the detector is obtained by multiplying the power, $I(\alpha)\,d\alpha$ as given
by Eq. (3.60), by $A_{air}$ of Eq. (3.63) and $\Delta \theta$ of Eq. (3.9). The
question of units may be somewhat confusing. In Eq. (3.60) both
$P(\alpha)\,d\alpha$ and $I(\alpha)\,d\alpha$ have dimensions of power (erg sec$^{-1}$) by
definition. It may be verified from Eq. (3.45) that $Q$ has dimensions
of reciprocal length (cm$^{-1}$), and since $\alpha$ has also dimensions of
reciprocal length Eq. (3.60) is dimensionally consistent. From Eq. (3.107) it is clear that I'(α) dα, the integrated intensity calculated in practice, has the dimensions power times angular measure. This is consistent with the fact that I'(α) dα is calculated as an area on a plot of power versus angle. Equation (3.9) gives Δθ in practical units of degrees, and thus I'(α) dα will be expressed in units of erg sec⁻¹ deg.

In Eq. (3.60) we also substitute for g from Eq. (3.101) and for Q from Eq. (3.45). It is convenient to replace N in Eq. (3.45) by 1/v, where v is the volume of the unit cell of the crystal. The expression for the integrated intensity obtained in this way is conveniently written

\[ I'(\alpha) d\alpha = k(p \lambda^{3/2} \mu v^2) \left( \frac{w_b}{R} \right) |F|^2 G(\theta_o) H(\alpha, \beta) R(\alpha) d\alpha, \]  

(3.108)

where

\[ k = \left( \frac{45}{32} \pi^{2} \right) \left( \frac{e^2}{m_0^2} \right)^2 = 1.1313 \times 10^{-26} \text{ cm}^2 \text{ deg} , \]  

(3.109)

\[ G(\theta_o) = \left( 1 + \cos^2 2\theta_o \right)/\sin^2 \theta_o \cos \theta_o , \]  

(3.110)

\[ H(\alpha, \beta) = \left[ \frac{A(\alpha) + B(\beta)}{\sin \alpha + \sin \beta} \right] C(\mu', \alpha, \beta) A_{air} . \]  

(3.111)

In computing k the approximate factor 57.3 in Eq. (3.9) has been replaced by 180/π and the values of the fundamental constants given by DuMond and Cohen (29) have been used. Of course, the numerical value of k is required only for the calculation of absolute
intensities or absolute structure factors. The quantities in Eq. (3.108) with their c.g.s. units are the wave length of the radiation, \( \lambda \) (cm); the linear absorption coefficient of the solid crystal, \( \mu \) (cm\(^{-1}\)); the volume of the unit cell, \( v \) (cm\(^3\)); the width of the vertical exit slit, \( w_0 \) (cm); the radius of the focal circle, \( R \) (cm); and the incident power, \( P(\alpha) d\alpha \) (erg sec\(^{-1}\)). The multiplicity factor, \( p \), and the functions \( G(\theta_0), H(\alpha, \beta), A(\alpha), B(\beta), C(\mu, \alpha, \beta) \) and \( \Lambda_{air} \) are all pure numbers.

To obtain the total integrated intensity, \( I_{int} \), scattered by the entire sample and received at the detector \( I'(\alpha) d\alpha \) must be integrated over \( \alpha \). Let the horizontal divergence of the x-ray beam be \( \gamma \), so that the illuminated part of the sample subtends an angle \( 2\gamma \) at the center of the focal circle in Fig. 1. Let also \( \alpha_o \) and \( \beta_o = 2\theta_o - \alpha_o \) be the values of \( \alpha \) and \( \beta \) at the midpoint of the arc of the focal circle covered by the sample. Then it is easily seen that the values of at the two ends of the illuminated part of the sample are

\[
\alpha_1 = \alpha_o - (\gamma/2), \quad (3.112)
\]

and

\[
\alpha_2 = \alpha_o + (\gamma/2). \quad (3.113)
\]

Thus,

\[
I_{int} = k(p \lambda^3/\mu v^2) (w_0/R) |F|^2 G(\theta_o) H(\alpha, \beta) Po, \quad (3.114)
\]

where \( P_o \) is the total power incident on the sample,

\[
P_o = \int P(\alpha) d\alpha, \quad (3.115)
\]

and the weighted average of \( H(\alpha, \beta) \) is

\[
\overline{H(\alpha, \beta)} = P_o^{-1} \int H(\alpha, \beta) P(\alpha) d\alpha. \quad (3.116)
\]
Figure 1 shows the relation between the angle $\gamma$ at which a ray leaves the face of the target of the x-ray tube at F and the angle, $\alpha$, at which it is incident on the sample at K. It is evident that

$$\alpha = (\pi/2) - \gamma' - \gamma,$$  \hspace{1cm} (3.117)

where $\gamma'$ is the angle the radius of the focal circle drawn to F makes with the target face. In the present investigation the beam used covered approximately the range $\gamma = 2.75$ to $8.25$ degrees ($\gamma = 5.5$ degrees). As has been pointed out previously, $P(\alpha)$ is primarily a function of $\gamma$, and only indirectly a function of $\alpha$ through Eq. (3.117). Theoretical considerations indicate that $P(\alpha)$ is a slowly varying function of $\gamma$ in the range involved, so that it should be a good approximation to replace $P(\alpha)$ by $P(\alpha_0)$, where

$$\alpha_0 = (\alpha_1 + \alpha_2)/2,$$  \hspace{1cm} in Eqs. (3.115) and (3.116). In this approximation

$$P_0 \approx P(\alpha_0),$$  \hspace{1cm} (3.118)

$$H(\alpha, \beta) \approx (\Delta \alpha)^{-1} \int_{\alpha_1}^{\alpha_2} H(\alpha, \beta) d\alpha,$$  \hspace{1cm} (3.119)

$$\Delta \alpha = (\alpha_2 - \alpha_1) \approx \gamma.$$  \hspace{1cm} (3.120)

The form of $H(\alpha, \beta)$ is known and a numerical investigation indicated that a negligible error (0.1 percent or less) is introduced by making the further approximation

$$H(\alpha, \beta) \approx H(\alpha_0, \beta_0).$$  \hspace{1cm} (3.121)

Equations (3.121) and (3.111) were used in evaluating $H(\alpha, \beta)$ in Eq. (3.114) in this investigation.
All the present measurements were performed with MoKα radiation, for which \( \lambda = 0.7076 \times 10^{-3} \text{ cm} \), and with \( w_o = 0.020 \text{ inches} \). The latter is a nominal value but the precise value is not important for relative measurements. Substituting \( k \) from Eq. (3.109) and \( R = 7.162 \text{ inches} \), and expressing \( v \) in units of \( (k)^3 \) or \( 10^{-24} \text{ cm}^3 \), Eq. (3.114) assumed the following form for this investigation:

\[
I_{\text{int}} = k' \left( P/\mu v^2 \right) / F^2 \frac{G(\theta_p)}{H(\alpha', \beta')} P_0,
\]  

(3.122)

where

\[
k' = k \lambda^3 \left( w_o/R \right) \times 10^{48} = 1.12 \times 10^{-5} \text{ cm}^5 \text{ deg}.
\]  

(3.123)

If the units of \( P_0 \) are \( \text{erg sec}^{-1} \) then those of \( I_{\text{int}} \) are \( \text{erg sec}^{-1} \text{ deg} \). Of course, in all these equations other units of power or intensity may be used if used consistently. For example, in the present investigation counts per second, or x-ray quanta per second, were recorded. In any case the intensity measurements in the present investigation were on a relative rather than an absolute basis. Absolute measurements would require the determination of \( P_0 \), the power incident on the sample, and also the efficiency of the detector, as \( I_{\text{int}} \) in the preceding analysis is the integrated intensity received at the detector. The recorded intensity is the product of \( I_{\text{int}} \) and the efficiency. It was assumed that \( P_0 \) and the counting efficiency were constant over the period of a few hours required for comparison of the intensities of the unknown reflection and the (422) reflection of NaCl, which was taken as the standard. In a series of measurements in which \( P_0 \), the counting efficiency, and \( k' \) of Eq. (3.123) are all constant
the ratio of the intensities of an unknown and the standard reflection is given by

\[
\frac{I_{\text{int}}}{(I_{\text{int}})^{\text{stand}}} = \frac{(p/\mu v^2) |F|^2 G(\theta_o) H(\alpha_o, \beta_o)}{(p/\mu v^2) |F|^2 G(\theta_o) H(\alpha_o, \beta_o)^{\text{stand}}}.,
\]

(3.124)
in view of Eq. (3.122).

Equation (3.124) may be solved for the ratio of the magnitudes of the structure factors for the unknown and standard reflections,

\[
\frac{|F|}{|F|^{\text{stand}}} = \sqrt{\left\{\frac{(p/\mu v^2) G(\theta_o) H(\alpha_o, \beta_o)^{\text{stand}}}{(p/\mu v^2) G(\theta_o) H(\alpha_o, \beta_o)} \right\}} \cdot \frac{I_{\text{int}}}{(I_{\text{int}})^{\text{stand}}}. \quad (3.125)
\]

In order to bring all intensity measurements to the same basis it is convenient to assign a fixed though arbitrary value to the standard reflection; denote this by \((I_{\text{int}}^0)^{\text{stand}}\). Then the intensity of the unknown reflection on the same scale is calculated from the relation

\[
I_{\text{int}}^0 = (I_{\text{int}}^0)^{\text{stand}} \left\{ \frac{I_{\text{int}}}{(I_{\text{int}})^{\text{stand}}} \right\}, \quad (3.126)
\]

the experimentally determined ratio of integrated intensities appearing within the brackets. From Eqs. (3.125) and (3.126) we now obtain

\[
|F| = \left\{ \frac{I_{\text{int}}^0}{K (p/\mu v^2) G(\theta_o) H(\alpha_o, \beta_o)} \right\}^{1/2},
\]

(3.127)

where the constant \(K\) is defined by

\[
K = \frac{(I_{\text{int}}^0)^{\text{stand}}}{\left\{ (p/\mu v^2) G(\theta_o) H(\alpha_o, \beta_o) |F|^2 \right\}^{\text{stand}}}. \quad (3.128)
\]
As will be discussed in more detail subsequently, the values for the standard \((422)\) reflection of NaCl were

\[
\begin{align*}
I_\text{int}^\text{stand} &= 100.85; \\
|F| &= 9.50; \\
p &= 24; \\
\mu &= 18.21 \text{ cm}^{-1}; \\
v &= 178.34 (\AA)^3; \\
G(\theta_0) &= 18.34; \\
H(\alpha_0, \beta) &= 0.06492.
\end{align*}
\]

Thus,

\[
K = 2.2650 \times 10^4 \text{ cm}^{-1} (\AA^6).
\] (3.129)

This section will be concluded with a description of a test of the functional dependence of \(I_\text{int}\) on \(\alpha_0\) and \(\beta_0\). From Eq. (3.122) the ratio \(I_\text{int}/H(\alpha_0, \beta)\) should be independent of \(\alpha_0\) and \(\beta_0\) in observations on a given reflection at fixed \(\theta_0 = (\alpha_0 + \beta)/2\).

In order to obtain a wide range of variation of \(\alpha_0\) and \(\beta_0\), it was necessary to have \(\theta_0\) large, and the NaCl reflection at \(\theta_0 = 31.25\) degrees was chosen. This is a superposition of the \((820)\) and \((644)\) reflections. The observed intensities at \(\alpha_0 = 22.5, 37.5,\) and \(52.5\) degrees, were \(I_\text{int} = 5.00, 4.61,\) and \(4.55\) counts sec\(^{-1}\) deg, respectively. The corresponding values of \(H(\alpha_0, \beta)\) computed from Eq. (3.111) are \(0.03574, 0.03371,\) and \(0.03468,\) respectively. This yields the ratios \(I_\text{int}/H(\alpha_0, \beta) = 139.9, 136.8,\) and \(131.2\), respectively. Unfortunately these ratios are not as constant as they should be, the trend being \(-6.2\) percent as \(\alpha_0\) varies from 22.5 to 52.5 degrees. However, the trend may be accidental rather than real, in view of the relatively low accuracy of the measurements, which were carried out in April 1958 before the techniques for calibration of the x-ray beam intensity described in Section E of Chapter 4, and the accurate numerical integration procedure of Chapter 6, Section B, were perfected. In addition, this high index reflection is weak (2.6 percent of the intensity of the strongest line studied), and has a complicated contour as
a result of the resolution of the $\alpha_2$ doublet and overlap with the 
(733) reflection. There was also a pronounced change in the line 
contour in going from $\alpha'_o = 22.5$ to 52.5 degrees, with a decrease of 
peak height above background by 34 percent, an increase of 10 percent 
in line width, and much decreased resolution of the $\alpha_2$ doublet. As a 
result of these factors it is doubtful if an accuracy of greater than 
5 percent can be assigned to these early measurements at $\alpha'_o = 22.5$ and 
37.5 degrees, and perhaps 8 percent at 52.5 degrees in view of the 
marked change in contour (the final measurement of the intensity of 
this reflection are regarded as accurate to 3 percent). The average 
deviation of the three values of the ratio given above from their mean 
is only $\pm 2.3$ percent, which is considerably less than the estimated 
uncertainty of the measurements. It may also be noted that the new or 
novel factors entering into $H(\alpha'_o, \varphi'_o)$ are the Soller slit factor, 
$A(\alpha'_o) + B(\varphi'_o)$, and the curvature correction to the absorption factor, 
$C(\mu'_o, \alpha'_o, \varphi'_o)$. If these factors are omitted from $H(\alpha'_o, \varphi'_o)$, the 
trend in the value of $I_{int}/H(\alpha'_o, \varphi'_o)$ becomes more than twice as large, 
-13.7 percent instead of -6.2 percent. Further measurements of this 
type should be carried out, but there was insufficient time for this 
after the development of the theory necessary for their interpretation, 
as given in the present chapter.

In the main series of measurements in the present investigation 
$\alpha'_o$ had a fixed value of 22.5 degrees and only $\theta'_o$ was varied (with the 
exception of the measurements for a few reflections occurring at small 
values of $\theta$ for which it was necessary to decrease $\alpha'_o$ to 21 degrees).
In spite of their preliminary nature and relatively low accuracy, the preceding results raise the question of the possible existence of a systematic trend with Bragg angle $\theta$ of the intensities and structure factors measured in the main series of measurements on sodium chloride, sodium bromide, and their solid solutions reported in Chapter VI. This question is considered in Section E-3 of the latter chapter, where a detailed comparison is made of the structure factors obtained for sodium chloride in the present investigation and in the four other investigations reported in the literature. It is concluded that there is little evidence for such a trend, except possibly at the smallest values of $\theta$ where somewhat higher relative intensities are observed in the present investigation.
A. Construction of Spectrometer

The principles of the present focusing spectrometer have been discussed in Section A-3 of Chapter III and illustrated in Fig. 1. A partially schematic drawing of the spectrometer is shown in Fig. 4 (letters in the text indicating spectrometer components refer to this figure). Radiation is emitted from the line focus, F, on the target face of the x-ray tube, the point F being positioned on the focal circle. The horizontal divergence of the incident beam is limited by the vertical slits, H₁ and H₂, and its vertical divergence by the Soller slit collimator, V₁. The diverging incident beam impinges on the powder packed in the front face of the curved sample holder, K, which is positioned on the focal circle. The sample holder and sample table, T, are supported on the sample arm, C. The diffracted beam for each line is focused at the appropriate point on the focal circle. The detector slit, S, which is mounted on a motor-driven slit arm A, traverses the focal circle as the slit arm rotates. The detector slit and platform B, are directed toward the center of the sample by means of an alignment mechanism consisting of the pulleys, P₁ and P₂, which are connected by a steel tape. The portion of the diffracted beam which passes through the detector slit traverses a second Soller slit, V₂, and then enters the proportional counter, P.
Fig 4 Focusing X-Ray Spectrometer (partially schematic drawing)
A photograph of the spectrometer together with the detector circuit components is shown in Fig. 5. Photographs of the spectrometer alone taken from several angles are shown in Figures 6, 7 and 8. It should be especially useful to compare the top view in Fig. 7 with the drawing in Fig. 4.

1. X-ray Tube Housing and Support

An essential requirement for a spectrometer based on the principles discussed above is the provision of means for bringing the line-focus on the target of the x-ray tube accurately and reproducibly to a point, $F$, on the focal circle, as illustrated on Fig. 4. This problem is not as simple as it may appear, because the precise location of the line-focus is not directly observable. In contrast to optical grating spectrometers using the closely related Rowland circle geometry, or to the very similar focusing x-ray diffraction camera of Guinier, which have real entrance slits that are readily located on the focal circle, the line-focus itself acts as the entrance slit in the present spectrometer. Of course, the latter feature also characterizes some other designs of x-ray spectrometers using a line-focus source, but in general there is no requirement that the line-focus be located precisely on a specified curve in space such as the focal circle of the present spectrometer. The position of the focal circle relative to the spectrometer proper is fixed by the radial distance at which the exit slit, $S$, is positioned, and it is impractical to vary this distance because of the necessity for an auxiliary shaft for precise rotation of the slit and detector platform, $B$. It is, therefore, clear that
Fig. 5  Focusing X-Ray Spectrometer and Detector Components
Fig. 7 Focusing X-Ray Spectrometer (Top View)
there must be provision for precise and reproducible translations of
the x-ray tube and housing relative to the spectrometer proper in the
plane of the focal circle over a range sufficient to bring the line-focus
for different x-ray tubes to the focal circle (the technique for carrying
out this adjustment is described in Section B-4 of this chapter).
In addition, provision must be made for rotation of the x-ray tube to
direct the beam at different points on the focal circle, without
disturbing the positioning of the line-focus on the circle. Because
of the considerable bulk and weight of the x-ray tube, housing, and
associated high-voltage cable, this is a problem of no mean
proportions. However, a highly satisfactory solution was obtained by
converting an old shaper to the support of the spectrometer and x-ray
tube housing.

The shaper is equipped with a side arm and table capable of precise
translation in a horizontal plane and rotation about a vertical axis.
The x-ray tube housing was mounted on this table, and the spectrometer
proper on the main column of the shaper, offset as shown in Figures 5
and 6. The side arm may be translated vertically by means of a
relatively coarse screw, and rotated about a vertical axis coincident
with the center of the main column of the shaper. The vertical line
defined by this axis of rotation can be located precisely in space
because of the size and excellence of the bearing for this rotation,
and serves as the primary fiducial line for the spectrometer. In
particular, it defines the point F on the focal circle at which the
line-focus of the x-ray source is to be positioned (the offset of the
spectrometer proper is such that the focal circle passes through the
fiducial line). The table of the side arm, upon which is secured the support for the x-ray tube mount, is equipped with heavy V-ways and high quality screws which allow for precise horizontal translations of the x-ray tube in directions parallel and normal to its axis. These horizontal translations may be reproduced with a precision of 0.001 inch by means of the scales provided on the shaper. Thus the line-focus on the target face of the tube may be accurately set to a point on the focal circle coincident with the fiducial line. Once this adjustment has been achieved the x-ray tube may be rotated without disturbing the positioning of the line-focus on the focal circle, since the axis of rotation coincides with the fiducial line.

The tube housing and high voltage connector, most clearly visible in Fig. 6, are of standard design for use with a Philips Norelco, short-anode x-ray tube. An insulating sleeve, supplied by the tube manufacture, fits within the housing. The input high-voltage electrode assembly was also supplied by the tube manufacturer. The tube and its housing are mounted horizontally. The head of the housing to which the x-ray tube is bolted is machined from a 3.67 inch O.D. brass cylinder. The target face of the tube anode is located 1.25 inches from the inner face of the base of the tube which seats on the housing. A flat vertical face is machined on one side of the outside surface of the head at an angle of six degrees to the tube axis opposite the tube window from which the x-ray beam is emitted. Thus the normal to the flat face of the head is directed six degrees from the plane of the anode face, which is the take-off angle recommended by the tube
manufacturer. A circular window 0.50 inches in diameter is cut in the flat face for passage of the x-ray beam. The knurled circular plate attached to the flat surface of the head, which can be seen in Fig. 8, is a 1/8 inch thick brass filter wheel that can be rotated to bring any one of five holes (for x-ray filters) or a shutter opposite the window of the tube.

2. Entrance Slit Assembly

The support and housing for the entrance slit assembly can be seen in Figures 7 and 8. Essential details are shown in Fig. 4. The top and front of the housing, normally in place for shielding purposes, have been removed for these photographs so that the slit mechanism and the arrangement of the slit components can be seen. The brass base plate of the housing upon which the assembly is mounted has the shape of a sector of an annulus, and is rigidly fixed to a supporting arm which is mounted so that it rotates with the x-ray tube housing but does not share in the horizontal and vertical translations of the latter (see Fig. 6). A second brass plate also having the shape of a sector of an annulus is mounted on the base plate. The accurately machined inner and outer arcs of this sector serve as tracks to define the motion or the slit carriages which ride upon it. The radii of curvature of the concentric inner and outer arcs (shown as dashed curves in Fig. 4) are 2.172 and 3.577 inches, respectively, and they subtend an angle of 55 degrees. The plate is positioned so that the common center of curvature of these arcs coincides with the primary fiducial line at F within an accuracy of 0.001 inch. This adjustment
is easily verified at any time by placing a pressure-type gauge against the inner arc and rotating the arm supporting the slit assembly and tube housing on its vertical axis, in which case the gauge should not register any movement. Each of the rolling carriages $G_1$ and $G_2$, is also an annular sector having outer radii of curvature of 3.94 inches, and subtending arcs of 20 degrees. Each carriage tracks by means of attached $1/4$ inch O.D. ball-bearing rollers, one at the inner end and two at the outer end, which ride against the vertical edges of the inner and outer arcs of the main sector or tracking plate, as shown in Fig. 4. The carriages and their outer rollers are also shown quite clearly in Fig. 8. The slit edges limiting the horizontal divergence of the x-ray beam are mounted at the front and back of each carriage flush with the inner edges of the carriages, so that the slits are closed when the carriages are in contact. The position of the carriages may be independently set by means of two screws which can be seen at the sides of the housing in Fig. 7. Because of the construction which has been described, the projected surfaces through the front and back vertical slits on each side always intersect at the fiducial line at which the line-focus on the anode of the x-ray tube is positioned. A jig is provided for the initial alignment of these slits in this fashion. This arrangement of two pairs of vertical slits allows a continuous adjustment of the horizontal divergence of the incident beam from 0 degrees to the maximum permitted by the window of the x-ray tube, or about 8 degrees. This divergent slit assembly is an important component of the focusing x-ray spectrometer,
the optics of which are essentially dependent on the use of a divergent incident beam.

The Soller slit, $V_1$, in the incident beam consists of a series of closely spaced horizontal vanes, and serves to limit the vertical divergence of the beam incident on the sample. It is mounted between the front and back horizontal divergence slits on a step-shaped bracket which in turn is secured to the tracking plate (the carriage plates have rectangular sections cut from their inner edges to accommodate the bracket). The slits employed for this assembly were taken from a General Electric SPG standard slit set. The dimensional parameters of the particular Soller slit unit used in this research are given in Table 3. The housing of the Soller slit was modified to allow an angle of horizontal divergence up to 8 degrees (as originally constructed the maximum angle of divergence was only 3 degrees).

3. Main Casting, Drive Gear, and Motors

The main casting of the spectrometer is of bronze, and is secured to a heavy (one inch thick) steel plate mounted on the main column of the shaper, as shown in Fig. 6. It is positioned so that the axis of the main drive shaft of the spectrometer at the center of the housing is precisely 7.162 inches from the primary fiducial line previously defined. Thus the focal circle passes through the fiducial line as required. The lower portion of the casting, which houses the main drive gear, has an outer diameter of 11.75 inches and a height of 3 inches. There is also an upper portion or neck on the casting (which cannot be seen except in Fig. 7 because of the
cylindrical sleeve of the sample arm surrounding it) that extends 3 inches above the lower portion and is 3 inches in diameter. The outer surface of this neck is accurately machined concentric with the bearing mounts for the main shaft of the spectrometer. The sleeve of the sample arm is bored to fit closely around this portion of the casting, which thus serves as the bearing for the rotation of the sample arm. The outer rim of the lower portion of the casting is graduated on one side from 0 to 180 degrees for the positioning of the sample arm, and its upper surface has holes drilled at 15 degree intervals to allow the sample arm to be locked by means of a heavy ground pin at accurately reproducible positions, as can be seen in Fig. 8. The scale marker on the sample arm is positioned so that the angle $\theta$ of Fig. 1, is read directly from the scale.

The center of the casting is bored with a 1.5 inch hole to accommodate the main drive shaft. This center shaft supports the large drive gear which is housed in the lower portion of the casting, and it also supports the rotating slit arm, A. The main drive shaft was machined from a steel rod of nominal 1.25 inch diameter, and it is mounted in two SKF preloaded single-row super-precision type ball bearings. The outer races of the upper and lower bearings, which are 2.0472 inches in diameter, are tightly fitted in recesses machined at the top and bottom of the hole for the main drive shaft. The shaft has a collar 1.25 inches in diameter and 7/16 inch in length, which seats on the top of the inner race of the upper ball bearing and resists the vertical thrust of the shaft. The shaft is machined for
a length of 4.125 inches below the bottom of the collar to fit tightly the 0.9843 inch inside diameter of the main ball bearings. A section of the shaft 1.000 inch in diameter extends three inches above the top of the collar for mounting of the slit arm and slit alignment pulley. There is an extension at the top of the shaft, which is 0.750 inches in diameter and 1.5 inches in length, to serve as a spindle for the radius gauge which is used to correctly position the sample holder, as described in Section B-2 of this chapter. The main drive gear is mounted at the lower end of the shaft by means of a key and slot (to prevent rotation), and a heavy 3/4 inch I.D. nut that threads onto the shaft. Tightening this nut exerts pressure (through a sleeve) on the inner race of the lower bearing and, in conjunction with the collar resting on the inner race of the upper bearing, further loads the ball bearings. As a result, the mounting of the main shaft is extremely firm in its bearings, with no perceptible play. This is important because of the considerable weight of the slit and detector arms.

The main drive gear is a brass worm gear having 300 teeth. It was cut in the Chemistry Department instrument shop with a cutter adapted from a specially hardened duplicate of the steel worm used to drive the gear (see below). Since this is a single-thread worm of 0.100 inch linear pitch, the ideal pitch diameter of the main gear would be \( (360 \times 0.100 / 3.1416) = 11.46 \) inches. The gear was cut to a pitch diameter about 2 percent less than this in order to fit it into the main casting. There is no reason to believe this affected
the angular accuracy of the gear. The scale on this gear, which is read through the window on the lower side of the casting visible in Fig. 6, is graduated to indicate degrees and 1/4 degrees in $\Theta$, and is marked at 5 degree intervals. It should be noted that each 1/4 degree interval in the Bragg angle, $\Theta$, corresponds to one degree of actual rotation, or an advancement of the gear by one tooth, as explained in Section A of Chapter III. The main gear is driven by a single-thread hardened steel worm of 0.500 inch pitch diameter and 11/16 inch length. The shaft through the worm terminates in a disc and knurled knob on the outside of the gear box which is mounted alongside the main casting. A scale is marked on this disc at intervals of one minute and 1/5 minute in $\Theta$, with one complete revolution of the worm corresponding to a 15 minute or 1/4 degree increment in $\Theta$. These features can be seen in Fig. 6. The worm is mounted firmly against the main worm gear, and its shaft has a thrust screw and nut at one end which can be tightened to eliminate play. As a result, there is no detectable backlash of the worm and gear system, and settings are reproducible to at least 0.1 minute in $\Theta$. The procedure for setting the zero of the $\Theta$-scale is given in Section B-1 of this chapter.

Within the gear box are two synchronous 60 cycle per second motors, having reduction gears such that their output shafts rotate at precisely 2 and 60 RPM, respectively. Either of these can be coupled, through a gear shift mechanism and gear trains, to the shaft of the worm which drives the main worm gear and slit arm.
Since both motors are of a reversing type, they can be energized to rotate the main shaft in either a forward or backward direction (or turned off) by means of three-way switches. The gear trains are visible on the left-hand face of the gear box in Fig. 6. The output shafts and gears of the 60 and 2 RPM motors are at the lower left and lower right, respectively. The shaft of the worm which drives the main gear, together with its scale and input gear, are at the upper left, and a change gear for the 2 RPM motor at the upper right (additional change gears to give various scanning rates as described below are stored on top of the gear box). The shift mechanism and idler gear for connecting to either the 2 or 60 RPM system is visible at the bottom center. With the 60 RPM motor connected and energized, the slit arm scans at a rate of 15 degrees per minute. This rapid scanning speed is used only to advance the slit arm to approximately the desired position. The final precise adjustment to any given value of \( \Theta \) may be made manually by means of the knurled knob and scale on the worm shaft after disconnecting the motor. With the 2 RPM motor connected and energized, scanning rates of 2.5, 1.5, 1.0, 0.5, 0.25, 0.167, or 0.10 degrees per minute can be obtained, depending upon the ratio chosen for the two change gears (manual adjustment of should never be attempted when the 2 RPM motor is in gear because of the high reduction factor in the gear box of the latter). This continuous scanning facility was used in the present investigation only to locate the positions of the diffraction maxima, and the actual intensity data which was obtained was measured by stationary
counting at suitable intervals of $\Theta$ over the diffraction profiles.

Two limit switches, located on the upper surface of the casting and on the sample arm, respectively, as can be seen in Fig. 7, deactivate either motor when the slit arm approaches the tube housing or the sample arm, preventing possible damage to the main gear or slit arm mechanism.

4. Sample Arm, Table, and Holder

The mechanisms for supporting and adjusting the sample in the present spectrometer have been made exceptionally sturdy, not only to obtain great rigidity, but also with the possibility in mind that rather heavy or bulky sample arrangements such as furnaces or cryostats may be necessary for some investigations. The design of the cast bronze sample arm, C, which rotates about the neck of the main casting, is best seen by referring to Figures 4, 7, and 8. The nominal outer diameter of the sleeve at the inner end is 4.25 inches, and it is accurately bored to fit the 3 inch neck of the main casting. The length of the arm is 8.7 inches from the center of the sleeve to the outer end. The horizontal V-way on the arm is 3 inches in length and provides for radial translation of the sample table with a reproducibility of 0.001 inch, so that the face of the sample can be brought to the 7.162 inch radius of the focal circle. The cast bronze L-bracket that rides on the horizontal V-way is 3 inches square at its base, and 5.75 inches in height, and is provided with V-ways 3 inches in length and a screw for vertical translation of the sample. The cast bronze block which slides in the vertical V-way has an integrally
cast hub, 1.25 inches in diameter at the upper end, which is bored to contain the shaft of the sample table, T. Rotational adjustment of the sample table about the vertical axis of this shaft is provided by a sector cut from a worm gear having originally 72 teeth of 0.1 inch linear pitch. This worm gear, which is secured to the sample table, is driven by a single-thread worm of 0.1 inch pitch. The shaft has a thrust screw and nut at one end to eliminate play. A knob on the shaft through the worm is graduated so that a rotation of the knob by one division is equivalent to a 1/6 degree rotation of the sample table. The sample holder, K, seats firmly in a 1.5 inch slot cut into the top of the approximately 2 inch diameter circular sample table. The holder is positioned by means of a pin accurately located at the center of the sample table which engages a hole on the bottom of the holder, and is further secured in place by means of a knurled screw. With this arrangement the sample holder can be removed from the spectrometer and either exchanged for another holder or returned quickly and accurately to the same position on the table. The sample holders are all interchangeable with their front rims machined to the 7.162 inch radius of the focal circle of the spectrometer. The curved rim of the holder is brought into coincidence with the focal circle by means of the rotational and radial translation adjustments previously described, using the procedure given in Section B-2 of this chapter.
5. Exit Slit Arm, Detector Platform, and Slits

The main slit arm, A, was cast of bronze, with an I-beam cross-section for rigidity, and a 2 inch diameter hub at each end. Details of its construction are shown in Figures 4, 6, 7, and 8. Both ends are accurately bored with the hole centers separated by a distance of 7.162 inches, which establishes the radius of the focal circle. The inner end is bored with a 1.000 inch hole to fit the main center shaft of the spectrometer. The hub at this end is split, and is pulled tight on the shaft by means of two heavy Allen screws after the slit arm has been properly positioned relative to the main drive gear. The outer end of the arm is bored to accommodate the bearings and shaft which support the detector platform, B, and its alignment pulley, P₂. This hole is recessed at the top and bottom to accommodate two SKF, preloaded, single-row, super-precision ball bearings having outside and inside diameters of 1.2598 and 0.4724 inches respectively. The portion of the shaft extending above the arm which supports the detector platform is 1.5 inches in length and 0.7500 inches in diameter, while the lower end of the shaft is turned down to fit closely within the inner races of the two ball bearings.

The detector platform, B, is machined of aluminum, and has the shape as shown in Figures 4, 7, and 8. Holes are bored in it to fit the supporting shaft and the 1.00 inch outer diameter of the proportional counter tube which is placed vertically. Each hole is slotted and provided with two Allen screws for tightening on the shaft and counter, respectively. A description of the proportional counter will be given
in Section C-2 of this chapter. The exit slit and Soller slits are mounted by Allen screws to the side of an L-shaped bracket, which in turn is secured to the side of the detector platform. They are, therefore, easily interchangeable. The detector slit is mounted precisely over the axis of the shaft, as shown in Fig. 4, so that it remains on the focal circle when the shaft is rotated by means of the pulley system to keep the slits and detector platform directed toward the center of the sample. The front window of the counter has a width of 1/4 inch and is approximately 1.9 inches from the exit slit, allowing a maximum horizontal divergence of about 7.5 degrees with this particular counter. The Soller slit assembly, \( V_2 \), which limits the vertical divergence of the diffracted beam, is mounted on the platform between the vertical exit slits and the counter. The detector slits and Soller slit assembly were taken from a General Electric SPG standard slit set. The Soller slit assembly has horizontal vanes with 1/2 millimeter vertical spacing, and its dimensional parameters are given in Table 3. The detector slits in this set are 3/8 inches in height and have widths of 0.02, 0.01, 0.005, and 0.002 inches. The resolving width and aperture of these slits as used in the present spectrometer are a function of the position of the slit, as has been discussed in detail in Sections B-2 and C-5 of Chapter III.

6. Alignment System for Exit Slit and Detector Platform

The principle and method of operation of the pulley system employed for directing the slit platform toward the sample have been described in A-3 of Chapter III. The details of its construction will
now be given. The system is shown best in Figures 6 and 7, and is illustrated schematically in Fig. 4. The smaller pulley, \( P_1 \), which is concentric with the main or central shaft of the spectrometer, has an outer diameter of 1.500 inches. Below the pulley and attached to it is a worm gear having 96 teeth and a pitch diameter of 5.05 inches. The gear and pulley are driven by a single-thread worm mounted on the sample arm. The worm shaft is equipped with a thrust screw and nut to eliminate play. Both pulley and gear are mounted concentrically with the main shaft, between the sleeve of the sample arm and the main slit arm, with a needle bearing of 1.25 inch O.D. and 1 inch I.D., so that the shaft can rotate freely inside the pulley and gear. As has been previously noted, this pulley remains stationary relative to the sample arm, except when it is rotated with the worm and worm gear to properly align the detector arm. The larger pulley, \( P_2 \), has a diameter of 3.000 inches, exactly twice that of the smaller pulley, and is mounted on the lower end of the auxiliary shaft at the end of the slit arm. A steel tape 1/4 inch wide connects the pulleys. Tension on the tape is maintained by a third pulley as shown in Fig. 8. With this arrangement rotation of the slit arm relative to the sample arm by a given angle produces a rotation of the detector platform by half this angle in the opposite sense relative to the slit arm, and, therefore, by half the angle in the same sense relative to the sample arm. These statements remain valid if the relative rotation of the slit and sample arms is produced by rotation of the latter. As a result, once the exit slit and detector platform are directed toward
the center of the sample by the procedure of Section B-3 of this chapter, they remain so directed as the slit arm or sample arm is rotated. This is perhaps the most original design feature of the present focusing spectrometer.

B. Alignment of Spectrometer

The mechanical alignment of the spectrometer involves four steps, namely, the setting of the scale for the Bragg angle $\Theta$, the positioning of the sample holder on the focal circle, the adjustment of the pulley system for the alignment of the detector platform, and the setting of the line-focus of the source on the focal circle. The procedures for making these adjustments will now be considered.

1. Setting of Scale for Bragg Angle $\Theta$

The scales for the measurement of the Bragg diffraction angle, $\Theta$, are described in Section A-3 of this chapter. These consist of the scale on the main gear reading to $1/4$ degree, and a fine scale reading to $1/5$ minute in $\Theta$. The first and relatively trivial step is the setting of the fine scale so that it reads zero when the main scale is set at an integral number of degrees, by rotating the disc on which the fine scale is ruled relative to the worm shaft and then tightening a set screw. The second and more important step is the setting of the angle of the main slit arm, $A$, relative to the main gear and drive shaft. This is accomplished by loosening the two Allen screws holding the split hub of the slit arm on the drive
shaft (as shown in Fig. 6), adjusting the position of the slit arm as described below, and then tightening the screws.

As Fig. 1 shows, the angle measured along the arc of the focal circle from the primary fiduciary line, F, to the exit slit, S, is equal to $4 \theta$. However, the $\theta$-scales are graduated to indicate $1/4$ of this angle, or $\theta$ directly. The simplest procedure, in principle, would be to set the scale to a reading $0^0 0.0'$ and then set the slit arm so that the exit slit is at the position, F, of the fiduciary line. However, this procedure is somewhat difficult because the fiduciary line is defined by the axis of rotation of the x-ray tube housing and is not readily located physically. Advantage was, therefore, taken of the fact that the zero of the angular scale for the sample arm (described in Section A-3 of this chapter) is set as accurately as feasible by mechanical means on the plane containing the fiduciary line, F, and the axis of rotation of the slit arm, A. Furthermore, the setting of the sample arm is very accurately reproducible at intervals of 15 degrees by means of the pin previously described. The sample arm was, therefore, set at the convenient angle of 90 degrees, and the slit arm was loosened and set diametrically opposite to the sample arm, so as to bring the following three points into line: (1) the center of the exit slit; (2) the center of the main spectrometer shaft, as indicated by the small hole at the bottom of conical centering hole visible on top of the shaft in Fig. 7; and (3) the center of the sample table, as indicated by the center of the 1/8 inch diameter ground steel pin which positions
the sample holder. When the two arms are set in this manner, then as shown by Fig. 1, \(2\alpha = 90^\circ, 2\beta = 180^\circ\), and \(\theta = (\alpha + \beta)/2 = 67.5^\circ\).

The \(\theta\)-scale was set to this value, and the slit arm tightened. It is estimated that the mechanical error in setting the slit in this manner did not exceed 0.05 degrees in \(\theta\). To this must be added \(1/4\) the error in the position of the zero of the sample arm scale, which probably does not exceed 0.025 degrees. An additional error of perhaps 0.05 degrees in the measured \(\theta\) might be produced by errors in positioning the line focus of the source (see Section B-4 of this chapter). The maximum error from these three sources is \(\pm 0.125\) degrees, and the probable error is \(\pm 0.075\) degrees.

After the adjustment of the \(\theta\)-scale had been made in this manner, the observed positions of the diffraction lines of sodium chloride were compared with the theoretical positions. The average deviation, \(\overline{\Delta \theta}\), for 14 lines was found to be 0.016 degrees, and the maximum deviation 0.03 degrees in \(\theta\), as shown in Table 16. However, at the time this comparison was made the small displacements, \(\overline{e}\), of peak position produced by absorption and vertical divergence (see Section B of Chapter III, especially Table 1) had not been calculated. When these displacements are taken into account, it appears that the \(\theta\)-scale as set gives readings that are about 0.066 degrees too high (for a detailed discussion see Section F of Chapter VI). This value is within the probable error estimated above. As it is a constant error in \(\theta\), allowance for it is easily made in the identification of diffraction maxima, and it was not considered worthwhile to reset the
In the present investigation quantitative intensities are required, but the Bragg angle $\theta$ is used only for the identification of the lines.

2. Alignment of Sample Holder

As discussed in Section A-3 of Chapter III, the optics of the present spectrometer require that the sample lie on the focal circle, or in practice (since the sample is of finite height) on a vertical cylinder through the focal circle. The face of the sample holder, K, in which the powder sample is placed, is cut to form a section of this cylinder, and the sample holder is firmly and reproducibly positioned on the sample table, T, by a pin and slot arrangement. The provisions for precise mechanical translation and rotation of this table relative to the sample arm, C, are described in Section A-4 of the present chapter.

The sample table is first translated vertically until the mid-line of the sample holder is at the same level as the midpoint of the exit slit, S. The flat top of the main spectrometer casting forms a convenient reference plane. Vertical distances above this plane are transferred by means of a Browne and Sharp height gauge purchased for this purpose. This vertical adjustment is not critical, provided the height of the sample exceeds that of the slit, and no scale is provided for this translation.

The sample holders have narrow brass rims at their top and bottom edges which are machined to the radius of curvature of the focal circle and are flush with the sample surface when the holder is
filled. These rims are clearly visible in Fig. 7. The upper rim is brought to the focal circle by small alternate radial translations and rotations of the sample table about a vertical axis, while testing with a radius gauge constructed for this purpose. The body of this gauge is an aluminum cylinder 1.5 inches in diameter and 2.5 inches in height, which is bored axially with a hole of nominal 3/4 inch diameter so as to fit tightly over the section of the main drive shaft which extends 1.5 inches above the main slit arm as shown in Fig. 7. An arm of 1/4 inch aluminum tubing extends radially from the cylinder. The arm is threaded into the cylinder and provided with a lock nut so that its length is adjustable over the range 7.1-7.2 inches. Mounted within the tube at the end of the arm is a 3/16 inch diameter hardened, ground, and polished, stainless steel ball bearing, which rolls freely but with negligible play.

The length of the arm was adjusted with the aid of a magnifying glass until the outermost surface of the ball extended to the center of the auxiliary shaft bearing the detector platform within a tolerance of about 0.001 inch. This adjustment is facilitated by a small (0.01 inch diameter) centering hole on the upper end of the shaft, the trueness of which is easily verified by rotating the shaft. The center of this shaft is 7.162 inches from the center of the main shaft of the spectrometer, this distance defining the radius of the focal circle. After this adjustment was completed, the lock nut was tightened and sealed with a hard wax.
When the sample table and holder have been properly positioned as described above, the ball on the radius gauge rolls with a light contact along the entire length of the rim of the sample holder as the arm on the gauge is rotated. The adjustment is made easier and more quantitative by a scale on the radial translation of the sample table reading to 0.001 inch, and a scale for the rotation of the table about a vertical axis graduated to 1/6 degree (a rotation of 1/2 division or 1/12 degree moves the ends of the sample holder radially about 0.001 inch). With these refinements it is a simple matter to position the rim of the sample holder on the focal circle with a precision of about 0.001 inch.

3. Alignment of Detector Platform and Exit Slits

The principle on which the pulley alignment system for the detector platform operates is discussed in Section A-3 of Chapter III, and the mechanical details of its construction in Section A-6 of the present chapter. The alignment involves simply rotation of the inner pulley, $P_1$, by means of the associated worm and gear until the normal to the face of the exit slit, $S$, is directed at the center of the face of the sample (or sample holder). This adjustment may, in principle, be made for arbitrary positions of the sample arm, $C$, and slit arm, $A$, but is most readily and accurately accomplished when these arms are diametrically opposite on the focal circle. The adjustment was easily made by optical sighting so as to bring the pin at the center of the sample table (see Section A-4 of this chapter), the exit slit, and the vertical collector wire of the counter tube in line with one another.
This was permissible because the counter wire was positioned with sufficient accuracy on the normal to the exit slit face. It should be noted that the procedure of sighting on the pin at the center of the sample table would not be correct if the sample and main slit arms were not diametrically opposed, unless the center of the pin had been brought to the focal circle. In normal operation the face of the sample holder is on the focal circle, and the pin which engages the holder is outside the circle.

The precision of this adjustment, about 0.2 degree in the rotation of the detector platform, is entirely adequate. The adjustment should be checked occasionally as there could conceivably be slight slippage of the steel tape on the pulleys after many starts and stops of the drive mechanism (however, no evidence of such slippage was observed).

4. Alignment of Line-Focus of Source

In the present instrument the x-ray tube mount is provided with three mutually-perpendicular translations, as described in Section A-1 of this chapter. The midpoint of the x-ray tube window is first brought to the same height as the midpoint of the exit slit, S, by means of the vertical translation, using the height gauge and procedure discussed in connection with the similar adjustment of the sample holder in Section B-2 of this chapter. The two precision horizontal translations, with scales reading to 0.001 inch, are then used to bring the vertical line-focus on the target face of the x-ray tube to the primary fiducial point, F, on the focal circle (see Section A-3 of Chapter III and Fig. 4). This positioning of the line-focus
must be made by an indirect method, because the line-focus is not accessible to direct observation. The procedure adopted was that of making small alternate translations in the two mutually perpendicular directions in the horizontal plane, until maximum intensity and minimum line width were obtained for several strong reflections of a suitable sample (sodium chloride was used). It was found that a displacement of the line-focus by 0.005 inch produced an observable decrease in the peak intensities and broadening of the contours of the diffraction maxima, so it may be assumed that the focus of the tube was brought to within this distance of the fiducial point.

As further verification of this, the observed Bragg angles agreed within a few hundredths of a degree with the calculated values, as already noted in Section 3-1 of this chapter. It is clear from the optics of the spectrometer, as illustrated in Fig. 4, that the apparent values of the Bragg angle at the peak of the contour as read on the $\theta$-scale will be affected primarily by displacements of the line-focus from the point F on the focal circle in the direction of the tube axis (or more precisely, in a direction normal to the center line of the incident beam, which differs by 6 degrees from the former direction). In these measurements the distance from the line-focus to the center of the sample was 5.48 inches, as calculated from Eq. (3.2) with $\alpha = 22.5$ degrees (see also Fig. 1). Thus, a displacement of 0.005 inches in this direction would change the apparent value of $\theta$ by about 0.05 degrees. The sensitivity of the peak intensities to this displacement is enhanced by the screening effect of the divergent entrance slits,
$H_1$ and $H_2$ in Fig. 4, which were carefully aligned to converge on the fiducial point, $F$, as described in Section A-2 of the present chapter.

The line contours will be broadened by displacements from the focal circle in either of two mutually perpendicular directions in the horizontal plane, because of failure to satisfy the condition for exact focusing, which requires that the source, sample, and exit slit all lie on the same circle. It has not seemed worthwhile to develop the theory of the effect of such displacements on the line contours, although this could be accomplished by methods similar to those used to discuss the effect of other factors on the line contours in Section B of Chapter III. However, it is obvious from qualitative considerations that the widths of the lines will be broadened most by displacements perpendicular to the tube axis (more accurately, in the direction of the incident beam which is taken off at 6 degrees from the former direction). Such displacements will cause the diffracted beam to come to an approximate focus in front of, or behind, the exit slit, $S$. On the other hand, displacements in the direction of the tube axis (or normal to the beam direction) will not change the focal distance in a first approximation, but will produce an asymmetry in the line contours (in addition to shifting the position of the peak or the apparent Bragg angle as discussed in the preceding paragraph).
C. Supply and Detector Circuits

1. High-Voltage Power Supply

A power supply, constructed at an earlier time under the supervision of P. M. Harris, and capable of supplying at least 20 milliamperes at 40 kilovolts, was available for this investigation. It was used to operate a Philips Norelco, Type 32113 short-anode molybdenum-target x-ray diffraction tube. The power supply was of the conventional design, containing a variable power transformer to supply the primary voltage of an oil-immersed high-voltage transformer, two rectifier filament transformers, and an oil-immersed x-ray filament transformer powered by a second variable transformer. Full wave rectification of the output of the high-voltage transformer was provided by two oil-immersed diode rectifiers, with the positive end grounded.

Stabilization of the input line voltage was obtained by the use of a 2 KW Sorensen voltage regulator. The x-ray filament voltage was further stabilized through the use of a 1/2 KW Sorensen voltage regulator which was powered by the output of the first regulator. With this arrangement no difficulty was encountered in maintaining an x-ray tube current of 15 milliamperes constant to 0.3 percent for indefinite periods after an initial warm-up period.

2. Proportional Counter and X-ray Detector Circuits

The radiation detector employed with the present spectrometer is a Philips Norelco Type 62031 proportional counter. A description of
this counter and its performance characteristics has been given by Dowling, Hendee, Kohler, and Parrish (30). The counter is mounted at the rear of the detection platform as shown in Fig. 6. This counter is filled with xenon at a pressure of 32 cm Hg, with a small quantity of methane added as a quenching agent. Unabsorbed radiation leaves the counter through a second window diametrically opposite the entrance window. Both windows are covered with thin mica, made conducting by evaporation onto their surfaces of a thin layer of beryllium. The counter was operated at 1600 volts when measuring MoKα radiation, since at this voltage well-shaped pulses were produced with a mean amplitude of approximately five millivolts. The dead-time of the counter (minimum time by which two absorbed quanta of radiation must be separated if two separate pulses are to be resolved) is reported by the manufacturer to be about 0.2 microseconds.

The probability distribution function for the time interval between two successive counts random in time is given by the Poisson distribution,

\[ W(\tau) = \nu \exp(-\nu \tau). \]  

(4.1)

This is normalized,

\[ \int_0^\infty W(\tau)d\tau = 1 \]  

(4.2)

and yields for the mean time interval between successive counts

\[ \overline{\tau} = \int_0^\infty W(\tau)d\tau = (1/\nu). \]  

(4.3)

Thus \( \nu \) is the mean counting rate. The fraction of pairs of successive
counts falling within the dead-time, \( \tau_c \), and, therefore, being registered as a single count is

\[
\int_0^{\tau_c} \rho(\tau) \, d\tau = \nu \int_0^{\tau_c} \exp(-\nu \tau) \, d\tau = 1 - \exp(-\nu \tau) = -\frac{1}{2} (\nu \tau_c)^2 + \ldots \quad (4.4)
\]

The second term in the series expansion is entirely negligible for the counting rates occurring in the present investigation, and on setting \( \tau_c = 2 \times 10^{-7} \) seconds, the percentage error arising from coincidences of pairs of counts is predicted to be

\[-100 \nu \tau_c^2 = -2 \times 10^{-5} \nu \text{ (percent)}. \quad (4.5)\]

Therefore, the error from this cause should not exceed 0.1 percent at the highest counting rates, not exceeding 5000 counts per second, occurring in this investigation (this figure refers to the rate at which photons enter the counter).

An Atomic Instrument Company Model 205B linear preamplifier is mounted directly above and connected to the proportional counter tube, as shown in Fig. 5. This preamplifier has a fixed pulse-amplification factor of twenty, and in addition serves to match the high output impedance of the counter with the low input impedance of the linear amplifier. Pulses from the counter enter the preamplifier through a short noise-free connector which is completely shielded and insulated with Teflon. The high voltage required to operate the counter is supplied through the same connector by means of a high-voltage inlet mounted on the side of the preamplifier.

The negative output-pulses from the preamplifier are further amplified by an Atomic Instrument Company Model 204B linear
amplifier having an adjustable gain. Throughout the present investigation the gain was adjusted to give output pulses with a mean amplitude of 15 volts, corresponding to the five-millivolt pulses produced in the proportional counter by the Mo\textsubscript{K\alpha} radiation. A rise time of 0.8 microseconds was allowed for the output pulse from the amplifier, since the shorter input pulses are not so suitable for triggering the pulse-height analyzer circuit.

The shaped output-pulses from the linear amplifier are fed into an Atomic Instrument Company Model 510 single-channel pulse-height analyzer. This instrument allows only those input pulses falling between two set amplitude levels to pass through to the output to be counted. Pulses of all other amplitudes are rejected in the unit and do not appear at the output. However, the output pulses from this instrument have a fixed (but adjustable) amplitude which is independent of the amplitudes of those input pulses which it passes.

The output pulses from the pulse-height analyzer are counted with an Atomic Instrument Company Model 1030 A scaler unit, in combination with a Model 1227 timer unit. The scaler unit contains a high-voltage power supply which is sufficiently stable so that it could be satisfactorily used to operate the proportional counter when the primary voltage input to the scaler unit was stabilized by means of a 1/2 kW Sorensen voltage regulator. The combined scaler unit and timer unit made possible automatic operation in counting to a pre-set time or to a pre-determined number of counts.
D. **Performance of the X-ray Detector Circuits**

1. **Pulse-Height Distribution Curves**

   The heights or amplitudes of the pulses produced in the proportional counter are proportional to the energy of the x-ray quanta that produce the pulses. This energy to pulse-height relationship is preserved in the preamplifier and linear amplifier, but each pulse receives an overall amplification by a factor of several thousand. The distribution of the pulse amplitudes may be measured by means of the pulse-height analyzer previously described. In using the pulse-height analyzer a base line and channel width are selected to bracket the desired range of pulse heights. Only those pulses which exceed the voltage of the base-line setting, but not the sum of the voltages of the base-line and the channel width, are passed by the analyzer. In measurements of the amplitude distribution of the pulses, the base-line voltage is varied while maintaining a constant and narrow channel width.

   Figure 9 shows the pulse-height distribution curves which represent the energy distribution of MoKα radiation after diffraction from pure NaCl and NaBr. These measurements were made with the proportional counter set to receive the peak intensity of the (422) reflection of each substance. The counting rate was determined as a function of the base-line voltage at 0.5 volt intervals, with a fixed channel width of 0.25 volts. The amplification of the linear amplifier was adjusted for these measurements so that the pulses produced by the characteristic MoKα quanta would have a mean amplitude of 15 volts. Thus the peaks in both curves of Fig. 9 which
Fig. 9 Pulse Height Distribution
occur at 15 volts are due to the characteristic radiation. The peaks which occur at about 6 volts in both curves are known as escape peaks and are believed to be caused by the fluorescent emission of x-ray quanta by the xenon gas in the counter (30). The apparent magnitudes of these escape peaks are exaggerated in the figure because of the logarithmic scale employed. The maximum in the NaCl curve which occurs at about 11 volts is probably a second escape peak. The enormous peak which occurs in the NaBr curve at 10 volts is caused by bromine fluorescence. It may be seen that the fluorescent radiation is about twenty times more intense than the characteristic radiation (integrated values).

Unlike the characteristic radiation, the intensity of the fluorescent radiation is independent of the Bragg angle \( \Theta \), and thus it contributes only to the background intensity. However, because of its high intensity, the fluorescent radiation will almost completely mask the diffracted radiation if they are both measured together. It was found that this fluorescent radiation could be nearly all eliminated by the use of the pulse-height analyzer as an electronic filter. This is accomplished by selecting the base-line and channel width so as to bracket the voltage range which contains the maximum ratio of pulses produced by the characteristic radiation to pulses produced by fluorescent radiation, consistent with an adequate counting rate. Any variation in pulse amplification resulting from instability of the preamplifier or the linear amplifier or from a variation in voltage applied to the proportional counter will produce an approximately
proportional change in the base-line voltages in Fig. 9. The preceding criterion will also tend to minimize the variations in counting rate which results from fluctuations in pulse amplification. For the case shown in Fig. 9, it was found that the most stable operating conditions were obtained with the base-line set at 12.5 volts with a channel width of 5.0 volts.

2. Counting Accuracy

Since the x-ray photons generated in an x-ray tube are emitted in a random manner with respect to time, the number of counts registered in any relatively short interval of time will in general vary somewhat from the number to be expected on the basis of the mean intensity of the beam as measured over a longer time interval. These random fluctuations in counting rate are to be distinguished from secular or fluctuating variations in mean beam intensity produced by other factors than the statistics of photon emission. The most important factor of the latter type is variation in the x-ray tube filament current, which in turn produces variations in the tube current or the rate at which electrons impinge on the target. It was found that the mean x-ray intensity emitted by the present tube varied nearly linearly with the x-ray tube current in the experimental range. Since a tube current of 15 milliamperes could be maintained constant to within 0.05 milliamperes, the mean x-ray intensity may be expected to be constant to within 0.3 percent over extended periods of time. Variations in the high-voltage on the tube vary the amount by which the energy of the electrons exceeds the critical excitation energy
for production of the characteristic x-radiation (which is about 20
electron-kilovolts for MoKα radiation). However, the evidence
indicated that stabilization of the tube voltage was sufficiently
good so that this factor produced negligible variation in x-ray beam
intensity relative to that produced by variation in filament current.

Two methods of counting are commonly used, counting for a fixed
time interval, and measuring the time necessary to record a pre-selected
number of counts. The present equipment is adaptable to the use of
either method. The second method was used in the present investigation
because measurements at both high and low intensities then have the
same statistical percentage error of the type discussed below.

Consider an experiment in which the diffracted radiation from a
given line is measured until a total of N quanta has been counted in
a time interval $t_1$. If the measurement is repeated, it will be found
that the time required to record the same number, N, of quanta will
generally be somewhat different, even under identical operating
conditions, as a result of the random or stochastic nature of the
photon emission process. Let a total of n such measurements be made
under identical operating conditions, where in each measurement the
time $t_1$ required to count a fixed number, N, of quanta is recorded.
The average time required to record the N counts will be

$$\overline{t} = \frac{1}{n} \sum_{i=1}^{n} t_i , \quad (4.6)$$

and the average absolute deviation of $t_1$ from $\overline{t}$ is given by,

$$|\Delta t| = \frac{1}{n} \sum_{i=1}^{n} |(t_1 - \overline{t})| . \quad (4.7)$$
It can be shown by means of the theory of random processes or time sequences that in the limit of large \( N \) and large \( n \), the average absolute relative deviation, \( \langle |\Delta t|/\bar{t} \rangle \) approaches asymptotically the value:

\[
\langle |\Delta t|/\bar{t} \rangle \rightarrow \sqrt{2/\pi N}.
\]

This equation is strictly valid only if the observed counting rate fluctuates about a constant mean value. If the mean counting rate varies with time, then the observed value of \( \langle |\Delta t|/\bar{t} \rangle \) calculated from Eqs. (4.6) and (4.7) will be larger than the theoretical value calculated from Eq. (4.8).

In addition to the factors previously discussed which may produce variations in the mean beam intensity, changes in the mean counting rate or apparent beam intensity may also arise as a result of variations in the operating characteristics of the counter or counting circuits. When a pulse-height analyzer is used as in the present investigation, the counting rate will be affected by variations in the gain of the preamplifier and amplifier, and in the base-line and channel width voltages of the analyzer. The stability of these circuits is undoubtedly adequate when the analyzer is used simply to separate ordinary background or continuous radiation from the characteristic radiation. However, the stability requirements are considerably more critical in the present measurements on sodium bromide and its solid solutions, because of the intense bromine fluorescent radiation described in Section D-1 of this chapter.
As indicated there, a small percentage variation in the pulse amplification factor can produce a much larger percentage variation in the counting rate.

In Table 6 are listed values of the average absolute percentage deviation, \(100\left(\frac{\bar{\Delta t}}{t}\right)\), calculated from Eqs. (4.6) and (4.7), for the diffracted intensities from two reflections of NaCl and one reflection of NaBr. The number of runs made in each case is indicated by \(n\), and the values of \(\bar{t}\) indicate the average time per run taken to record a total of \(N=40,000\) counts. In the last column of Table 6 is given the value of \(100\left(\frac{\bar{\Delta t}}{\bar{t}}\right)\), calculated from Eq. (4.8). The pulse amplification factor was adjusted for these runs so that the pulses produced by the characteristic radiation had a mean amplitude of 15.0 volts. The pulse-height analyzer was set with the base-line at 12.5 volts and a channel width of 5.0 volts.

It is seen from Table 6 that the observed fluctuations in the counting rate for radiation diffracted from NaCl may be attributed almost entirely to statistical fluctuations. Thus it may be assumed that in these measurements, at least, the average fluctuation in the x-ray intensity was much less than the maximum value of 0.3 percent previously given. Although the counting rate fluctuation for NaBr is larger, undoubtedly due to the presence of bromine fluorescence, the precision is still quite satisfactory.
TABLE 6

Mean Deviation in Counting Time for a Total of $N = 40,000$ Counts

| Substance  | $n$ | $\bar{t}$ (min) | $|\Delta t|$ (min) | $\frac{100}{\bar{t}} |\Delta t|$ | $100 \sqrt{\frac{2}{\pi n}}$ |
|------------|-----|-----------------|-----------------|------------------|------------------|
| NaCl (600) | 36  | 4.032           | 0.017           | 0.42             | 0.40             |
| NaCl (422) | 50  | 1.560           | 0.0066          | 0.42             | 0.40             |
| NaBr (420) | 50  | 2.178           | 0.019           | 0.87             | 0.40             |

Under the operating conditions specified previously in this section, a counting rate of about 5 counts per minute was obtained with the receiving slit of the spectrometer closed (but with the x-ray unit on). This background rate, which is caused by noise pickup in the detector circuit and by stray quanta which enter the counter, is sufficiently low so that it may be neglected in this investigation.

E. Operating Procedure

The operating procedure described in this section was specifically developed to give as reproducible results as possible for those conditions imposed in the present investigation, and may not apply to other investigations. These conditions include the use of a molybdenum-target x-ray tube, the need to suppress the
radiation caused by bromine fluorescence, and the need for accurate intensity data.

1. Power Supply and X-Ray Tube

The molybdenum-target tube was operated at a voltage of 40.0 peak kilovolts and with a tube current of 15.0 milliamperes. The tube voltage was indicated by a microammeter on the panel of the instrument rack which was shunted to read one-half the current flowing through a 470 megohm resistor connected from the high voltage to ground. Therefore, the mean voltage in kilovolts was obtained by multiplying the reading in microamperes by a factor 0.94. To obtain the peak voltage it is necessary to multiply by an additional factor \( \pi/2 \), or an overall factor of 1.48. The tube current (cathode to anode current) was measured by a milliammeter on the same panel. The meter was shunted to read one-fifth of the true tube current in milliamperes. There is little danger that the x-ray tube will be harmed if the filament current is increased slowly so as not to allow the tube current to surge above twenty milliamperes. It was found that the x-ray tube should remain on for two hours at full operating voltage and tube current before use in order to stabilize the x-ray tube beam intensity.

The radiation emitted by the molybdenum-target tube is passed through a zirconium filter having a thickness of 0.038 mm (filter number 1 on filter wheel of spectrometer). This filter absorbs about 95 percent of the MoKa\(\beta\) radiation, while absorbing less than 50 percent of the MoK\(\alpha\) radiation.
2. Detector Circuits and Counting Procedure

The x-ray detector circuits are adjusted while they are transmitting pulses produced by the characteristic radiation. Diffraeted radiation from the (422) reflection of NaCl ($\theta_0 = 17.95^\circ$) was found to be suitable for this purpose. The voltage applied to the proportional counter should be in the range of 1550 to 1650 volts. Throughout the present investigation the counter was operated at about 1600 volts. It should be noted that with the procedure outlined in this section it is not necessary to reproduce the same counter voltage exactly each time the instrument is operated in order to obtain reproducible x-ray intensity data. It is only important that the counter voltage remain constant during a given run. The high-voltage supply provided by the scaler unit was found to satisfactorily fulfill this requirement if the primary input voltage to the scaler unit was stabilized through the use of a 1/2 KW Sorensen voltage regulator, and if the high-voltage unit was allowed to remain on at the desired operating voltage for at least 24 hours prior to use.

The amplification factor was adjusted so that the pulses produced by the MoKα quanta had a mean amplitude of 15 volts. This was accomplished by setting the pulse-height analyzer to a base-line voltage of 15.0 volts with a channel width of 0.1 volt, and then adjusting the fine-gain control of the linear amplifier until the maximum counting rate was attained. Finally, the pulse-height analyzer was reset to a base-line of 12.5 volts with a channel width.
of 5.0 volts. The linear amplifier is always to be set to receive negative input pulses, and to have a pulse response of 0.8 microseconds, when used with the present counter and preamplifier.

All pulses passed by the pulse height analyzer are counted by means of the scaler unit which has been previously described. A detailed description of the operation and circuitry of this instrument is given in the scaler instruction manual provided by the manufacturer. Throughout this investigation the counting was carried to a pre-determined number of counts, rather than to a pre-determined time. In this counting method the scaler automatically records the time required for the instrument to count to the pre-determined number. The advantage of this method is that the statistical percentage error will be independent of the observed counting rate. The stop clock provided with the timer unit was found to be accurate under automatic operation to within 0.005 minutes. Therefore, the number of pre-determined counts should be chosen to insure a counting time of at least one minute in order to reduce the timing error to 0.5 percent. In the present investigation most counting times were in the range of two to five minutes.

The intensity contours of the diffraction lines from the materials studied in this investigation were all obtained by direct point-by-point counting. The diffraction spectrum for each sample was obtained by manually rotating the exit slit arm through small angular increments, and measuring the counting rates at various fixed values of $\theta$. The increments of $\theta$ were 0.05 degree over the most
important part of the contour of all diffraction peaks, and 0.10 degree over most of the background intensity regions. At each point a minimum of 10,000 pre-determined counts were recorded. For those points near the peaks of the intensity contours 40,000 pre-determined counts were generally recorded. Figure 10 shows a typical intensity contour of the (422) reflection of NaCl obtained by this procedure with the sample arm at a fixed angle, $\alpha_0$, of 22.5 degrees. In this figure the experimental points between 17.70 and 18.15 degrees were obtained with a pre-determined count of 40,000, and the remaining points with a pre-determined count of 10,000. The counts were made at increments of 0.05 degrees in $\Phi$ between 17.70 and 18.20 degrees. The data for this intensity contour were obtained in about 45 minutes. The line under the curve in Fig. 10 indicates the estimated background intensity, and the enclosed area is proportional to the integrated intensity of the reflection.

It was shown in Section D-2 of the present chapter that the intensity of the incident x-ray beam deviated from its mean value by considerably less than 0.3 percent over extended periods of time if the x-ray tube was continuously operated. However, if the x-ray unit was shut off for several hours or more and then reactivated, it was found that the beam intensity might differ by as much as five percent from its previous value. Thus, it was necessary to determine the relative intensity of the x-ray beam during each period of operation, for the comparison of the diffraction data. In the present investigation this was accomplished by running the intensity contour
Fig. 10 The (422) Reflection for NaCl
of the (422) reflection of NaCl during the course of each operating period in the manner described above. The calculated area of this diffraction line was then proportional to the intensity of the x-ray beam for that particular series of measurements. Thus, the area of the (422) reflection of NaCl was used as a standard by means of which the integrated intensities of all reflections studied could be compared on the basis of equal x-ray beam intensity.
CHAPTER V
PREPARATION OF SAMPLES

A. Solid Solutions of Sodium Bromide and Sodium Chloride

In the present investigation the integrated intensities were obtained for a series of reflections from pure sodium chloride, pure sodium bromide, and three solid solutions containing 25, 50, and 75 percent of sodium chloride in sodium bromide. The reasons for choosing solid solutions of these particular salts were discussed in Section D of Chapter II.

An x-ray diffraction investigation of NaCl-NaBr solid solutions has been carried out by Nickels, Fineman, and Wallace (18, 19) using photographic powder techniques. By means of the well-known extrapolation method applied to the back-reflection lines, these investigators determined accurate lattice spacings of nine solid solutions of these components over the complete range of composition as well as the lattice spacings of the pure components. They found that this system follows Vegard's rule quite closely over the complete range of composition with a maximum deviation of the observed lattice spacings from those computed assuming a linear variation with composition of only 0.14 percent.

No experimental solid solubility data pertaining to the NaCl-NaBr system could be found in the published literature. However, the heats of formation of these solid solutions were obtained by Fineman and Wallace (17), and from these data they derived a provisional
phase diagram for the system. Their calculations indicate that the system will have a critical solution temperature at about 340°K at a composition of 45 mole percent sodium bromide. Their derived phase diagram further indicates that the stable form of the system below 300°K should consist of two phases over a major portion of the composition range. However, they report that none of the solid solutions which were studied gave any indication of a phase transformation into the stable two-phase system over a period of five weeks.

This predicted phase separation was observed in the present investigation in solid solutions containing 50 and 75 percent sodium chloride when the powdered samples were exposed to air containing appreciable water vapor. It was noted that spontaneous phase separation occurred (on the surface of the sample, at least) when the vapor pressure of the water exceeded about 15 mm. The evidence for this phase separation was a decrease in intensity of the diffraction lines of the solid solution together with the formation of new lines. An example of this effect is shown in Fig. 11. The intensity contours of the (422) reflection in this figure were obtained from the same sample which contained 50 percent sodium chloride, before and after phase separation, and in the manner described in Section E-2 of Chapter IV. A similar effect was observed with other reflections which were studied. The positions of the new lines which appear indicate that this solid solution decomposes at room temperature into two phases containing about 25 and 75 mole percent sodium chloride, respectively. A similar decomposition, but occurring at a much slower rate, was
Fig. 11 Example of Phase Separation in 50% NaCl - 50% NaBr.
observed in solid solutions containing 75 percent sodium chloride and 25 percent sodium bromide, as discussed in detail in Section C of Chapter VI. The solid solution of this composition decomposed into two phases which contained pure sodium chloride and 25 percent sodium chloride, respectively. In view of this it is concluded that the phase containing 75 percent sodium chloride into which the solid solution containing 50 percent sodium chloride initially decomposed is metastable, and that a further decomposition of this phase might be expected after a longer period of time. However, this was not observed. These results also suggest that at room temperature any solid solution of sodium chloride and sodium bromide containing more than 25 mole percent of sodium chloride will be metastable and will tend to decompose into two phases, one of which is pure sodium chloride and the other of which is a solid solution containing 25 mole percent sodium chloride.

B. Preparation of the Solid Solutions

The three solid solutions used in this investigation were prepared from reagent grade sodium chloride and sodium bromide having reported purities of 99.99 and 99.83 percent, respectively. The salts were dried by fusing in a platinum dish, then cooled, thoroughly ground, and stored in a desiccator. The purity of these salts was determined by analyzing volumetrically for total halogen content with standardized
silver nitrate solution using potassium chromate as an indicator:

<table>
<thead>
<tr>
<th>Salt</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>100.00 ± 0.1%</td>
</tr>
<tr>
<td>NaBr</td>
<td>99.91 ± 0.1%</td>
</tr>
</tbody>
</table>

The purified salts were weighed out with a precision of 0.05 percent and thoroughly combined to form mixtures containing 25.00, 50.00, and 75.00 percent sodium chloride, respectively. Each mixture was melted in a platinum dish at about 825°C, thoroughly stirred, and poured into another cold platinum dish and allowed to solidify. The salt cake was then thoroughly ground and remixed, and the powdered solid solution was annealed in a platinum dish at 650°C for 12 hours. Each solid solution was then reground and stored in a desiccator over anhydrous magnesium perchlorate for future use.

Samples of each of these solid solutions were volumetrically analyzed for halogen content in the manner described above:

<table>
<thead>
<tr>
<th>Solid solution</th>
<th>Mole percent chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 % NaCl</td>
<td>25.00 ± 0.1 %</td>
</tr>
<tr>
<td>50 % NaCl</td>
<td>49.90 ± 0.1 %</td>
</tr>
<tr>
<td>75 % NaCl</td>
<td>75.11 ± 0.1 %</td>
</tr>
</tbody>
</table>

A further check on the composition of these solid solutions was obtained by comparing the lattice spacings calculated from the diffraction data with the precise lattice spacings for this system reported by Nickels, Fineman, and Wallace (18, 19). This comparison showed the deviation of the composition of each solid solution from its nominal value of 25, 50, or 75 percent to be less than 0.15 percent in agreement with the analytical results. For further details see Section F of Chapter VI.
C. Preparation of Powder Samples for Diffraction

In order to obtain reliable and reproducible intensities of the diffraction peaks, certain precautions must be observed in the preparation and mounting of the powder. The crystallite size of the powder must be sufficiently small to ensure that there will be enough crystallites contributing to each reflection to generate signals of reproducible intensity. Also it is well-known that the reduction of the particle size by prolonged grinding of the powder reduces primary and secondary extinction and the effect of preferred orientation. The experimental procedure for the preparation of the sample which is described in this section was developed to minimize the error in the intensities from these effects as much as possible. In the next section these sources of error will be individually considered.

The following procedure was applied to the pure sodium chloride, pure sodium bromide, and the three solid solutions which were all prepared as described in Section B of this chapter. The powder was ground in an agate mortar, and that fraction of the ground powder which passed a 400-mesh sieve was collected. The 400-mesh sieve used had openings of dimension 38 microns. Examination of representative samples of the sieved powder with a micrometer comparator having a 30-power microscope and a precision of 1 micron revealed no particles with dimensions larger than 38 microns. The average particle size was estimated to be about 35 microns. The 35 micron powder was then thoroughly reground to further reduce the particle size. In order to obtain a fairly uniform particle size in this
final grinding process only small batches of powder were ground at one time (about 5 mg of powder per batch), and each batch was ground for approximately five minutes. Since the sample holders used in this investigation contained a sample volume of $\frac{1}{16} \times \frac{5}{8} \times \frac{3}{2}$ cubic inches or about one cubic centimeter, two to three grams of sample were required to fill them. Therefore, thirty to forty hours of total grinding time were required to prepare each sample. Examination of samples of the powder obtained by this grinding procedure with a micrometer comparator revealed the powder size to be quite uniform. The particle size of at least ninety percent of the crystallites was in the range of one to ten microns, and the average particle size was estimated to be about 8 microns. The largest crystallites observed had a particle size of 15 microns.

Although the grinding technique described above is very time consuming and tedious it was believed to be necessary for this investigation due to the accuracy required in the x-ray intensity data. It was found that if the powder was ground in larger quantities or for significantly shorter periods of time, the resulting particle sizes were much less uniform.

The sample holders employed in this investigation formed powder layers having a thickness of 1/16 inch. The horizontal rims of each holder are machine cut to the 7.162 inch radius of curvature of the focal circle of the spectrometer, and the surface of the sample must be brought to this same curvature. Thus each sample was mounted by placing the holder face up and gently filling all regions of the
cavity with the aid of a spatula. An excess of the powder was then added until the layer protruded about 1/8 inch above the rims of the holder. The sample was then packed into the holder by applying downward pressure by means of a convex die of the same curvature as the holder. Care was taken to use as little sliding motion as possible, in order not to produce preferred orientations of the crystallites at the surface of the sample. This simple mounting procedure was found to be quite satisfactory and capable of yielding reproducible intensity data with samples of 8 micron particle size, as is shown in the next section. All mounted samples were kept in a desiccator over anhydrous magnesium perchlorate when not in use.

It was shown in Section C-3 of Chapter III that the total radiation diffracted from an infinitely thick sample is independent of the packing fraction of the powder. Thus for an infinitely thick sample, local variations in powder density within a given sample or variations in powder density between different samples of the same substance will not affect the integrated intensity of the diffracted beam. The powder thicknesses of 1/16 inch which were used throughout this investigation may be considered infinite for the experimental conditions of this research. Thus with sodium chloride, which has the smallest absorption coefficient for MoKα radiation of the substances measured (μ = 18.2 cm⁻¹), the innermost powder layer contributes only about 0.01 percent of the intensity contributed by the surface layer of equal thickness for a spectrometer setting of α = 22.5° and θ = 30.0°, assuming a packing fraction of 0.75 for the powder. For samples
containing sodium bromide or for smaller values of $\Theta$, the innermost powder layer will contribute even less to the intensity.

In Section A of this chapter mention was made of the thermo-dynamic instability of NaCl-NaBr solid solutions noted in the presence of water vapor. Moreover, the sodium bromide proved to be quite hygroscopic. Both of these factors make it imperative that the powder samples be exposed to as little water vapor as possible during the course of the intensity measurements. If the samples are exposed to moist air during the intensity measurements, the intensity contour of a given line may radically change its appearance in a short time interval, as was demonstrated in Fig. 11. It was found that this difficulty could be eliminated satisfactorily by keeping a stream of dry nitrogen flowing over the surface of the samples during the time of the measurements.

D. **Effect of Crystallite Size on Line Intensities**

A crystalline powder must meet certain requirements in order to be suitable for precise x-ray intensity measurements. The sample examined should be representative of the particular lot of material being investigated, the method of preparing the powder for analysis must not distort the lattice and thereby impair the quality of the diffraction lines, and the size of the crystallites composing the powder must fall within acceptable limits. The last requirement is of particular importance since the effects of primary and secondary extinction, preferred orientation of the crystallites, and statistical
fluctuations in line intensities due to an insufficient number of crystallites irradiated, all are dependent upon the size of the crystallites. Each of these potential sources of error will be considered separately in this section.

As is well-known, the effect of primary extinction is caused by the screening of the lower layers of a perfect crystal from the incident x-ray beam during total diffraction because of the diversion of the energy of the beam into the diffracted beam from the upper layers of the same crystal. It will be recalled that one of the underlying assumptions in the derivation of the expression for the integrated intensity diffracted by a small crystallite given by Eq. (3.44) was that the crystallite be small enough so that the incident beam is not affected by the process of diffraction. When primary extinction occurs, the intensity of the incident beam rapidly diminishes as it passes through the crystal, and the integrated intensity of the diffracted beam may be much less than that given by Eq. (3.44). However, most real crystals are not perfect and may be treated as though they were each composed of a number of small perfect blocks slightly different in orientation so as to be optically independent. If each block or fragment within the crystallite is sufficiently small so that the effect of primary extinction is negligible, then Eq. (3.44) will apply, and the crystal or crystallite is said to have a mosaic structure. Real crystals which exhibit a mosaic structure probably do not consist of sharply defined small fragments but rather contain dislocations due to warping of the planes,
or to other causes, so that exact regularity does not extend over more than a few thousand atomic planes.

It is well-known that the intensity data obtained by powder diffraction methods in which the samples have been thoroughly ground are not significantly affected by primary extinction for most substances, in contrast to the data obtained by single crystal methods. Probably the stresses applied to the crystallites during the grinding process produce dislocations which cause each crystallite to exhibit a mosaic structure. It was found by Bragg, James, and Bosanquest (31) that even single crystals of sodium chloride usually very closely approach the ideal mosaic structure and show very little primary extinction. Since the five materials studied in the present investigation were all thoroughly ground and similar in structure to sodium chloride, it is virtually certain, from what has been said above, that the intensity data obtained are free from significant primary extinction.

Crystals which have been found to approach an ideal mosaic structure, and which as a result show little or no primary extinction may still show an effect known as secondary extinction. Secondary extinction is caused by reflecting blocks near the surface of a mosaic crystal which reduce the beam intensity for deeper blocks similarly oriented for reflection at a given setting of the crystal. Thus the intensity of the radiation reaching any block is reduced not only by the ordinary processes of absorption, but also by reflection from the nearly parallel blocks through which the incident
beam has passed. Formally this may be allowed for by using an effective absorption coefficient which is in excess of the ordinary coefficient of the material by an amount proportional to the intensity of the spectrum concerned. When intensity measurements are made from crystal powders, secondary extinction, which depends on an approximately parallel orientation of optically independent crystal fragments, is greatly reduced if the crystal particles are small enough and if they are arranged entirely at random. Havighurst (16) made a thorough study of the effect of particle size on the degree of secondary extinction from powder samples of sodium chloride and concluded that secondary extinction is negligible if the particle size is no larger than about ten microns. In the present investigation the mean particle size of each of the five substances studied was about eight microns and only a small fraction (about 10 percent) exceeded 10 microns. In addition, the most intense reflections, which would be most affected by secondary extinction, were not measured (the 420 reflection was the most intense spectrum measured for each substance in this investigation), because the reflections of low order are less useful as indicators of lattice distortion. Therefore, the error in the intensity data due to secondary extinction is probably not significant.

The effect of preferred orientation will be considered next. The discussion in Chapter III, Section C, of the intensities of the diffraction lines obtained from a powder sample assumed a specimen whose crystallites were randomly oriented. However, this condition is often difficult to attain when preparing a flat powder specimen
for spectrometer analysis. The pressure applied when mounting the
sample may tend to align the focus of the crystallites at the surface
of the specimen so as to falsify the intensity data for certain
reflections. For instance, the reflections from planes approximately
parallel to the faces of the crystallites will be abnormally strong
under these conditions because an unduly large proportion of the
crystallites tend to lie with their flat surfaces approximately
parallel to the surface of the mounted specimen. It has been found
by many investigators that reduction of the size of the crystallites
in the powder by prolonged grinding aids greatly in reducing preferred
orientation. This was also found to be true in the present research.
The intensity data obtained from powder specimens of sodium chloride
having a mean particle size of 35 microns were apparently affected by
preferred orientation to a serious extent using the mounting technique
described in Section C of the present chapter, as was evidenced by
abnormally high intensities and lack of reproducibility of the (400)
reflection as shown in Table 7. However, the relative intensities of
the reflections measured with the more finely ground sodium chloride
were in fair agreement with the data obtained by other investigators
(see Table 16), and it may, therefore, be assumed that the previously
described method of grinding and mounting the samples was adequate to
prevent the occurrence of this effect to any serious extent.

Aside from the errors which may result from secondary extinction
and preferred orientation of the crystallites in powder specimens,
there are two statistical factors that limit the precision obtainable
TABLE 7

Effect of Particle Size on Intensity Fluctuations

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Area of Diffraction Lines of NaCl</th>
<th>35 Micron Particle Fraction</th>
<th>8 Micron Particle Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(400) (420), (331) (422)</td>
<td>(400) (420), (331) (422)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>106.56 192.93 96.99</td>
<td>85.99 176.24 90.60</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>106.98 186.18 93.54</td>
<td>82.95 175.91 91.46</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>113.01 192.44 96.37</td>
<td>83.45 176.30 92.43</td>
<td></td>
</tr>
<tr>
<td>Mean Area</td>
<td>101.01 180.60 95.91</td>
<td>83.84 176.32 91.50</td>
<td></td>
</tr>
<tr>
<td>Mean Deviation</td>
<td>±3.29 ±2.21 ±1.67</td>
<td>±0.83 ±0.32 ±0.62</td>
<td></td>
</tr>
<tr>
<td>% Uobs</td>
<td>±3.0 ±1.1 ±1.3</td>
<td>±0.99 ±0.18 ±0.62</td>
<td></td>
</tr>
<tr>
<td>% Ucalc</td>
<td>±5.6 ±2.6 ±2.6</td>
<td>±0.61 ±0.29 ±0.28</td>
<td></td>
</tr>
</tbody>
</table>
in intensity measurements. One of these factors is related to the limitations of counting accuracy and has been discussed in Section D-2 of Chapter IV. The other factor, which will be discussed here, relates to the finite size of the crystallites. Thus, for samples with a relatively large mean crystallite size, the number of crystallites which through their orientation contribute to the intensity of a given diffraction profile may be much too small to yield a true and reproducible average intensity of that line. The intensity variations may extend over a surprisingly large limit as has been shown by Alexander, Klug, and Kummer (32). These investigators derive the following general equation, based upon Laplacian probability theory, which can be used to predict the reproducibility of the intensities of x-rays diffracted by crystalline powders:

\[ U = \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{1-m}{Nm} \right)^{1/2} \] (5.1)

In this equation \( U \) is the mean relative deviation predicted for the integral intensity of a given line for a finite number of particles irradiated, \( N \) is the total effective number of particles irradiated, and \( m \) is the ideal fraction oriented so as to give rise to a diffracted ray from the planes (hkl). However, the expressions which they derive for \( N \) and \( m \) are applicable only for the geometry of a conventional flat sample spectrometer. For the present focusing spectrometer \( m \) and \( N \) are instead given by

\[ m = \left( \frac{p}{8\pi} \right) \cos \theta \left[ A(\alpha) + B(\beta) \right] \Delta \theta, \] (5.2)

where

\[ \Delta \theta = \omega_o + \left( \frac{\omega_e}{4\pi} \sin \alpha \right). \] (5.3)
and 

\[ N = \left( \frac{AC}{\mu_0} \right) \left( \frac{\sin \phi}{\sin \alpha + \sin \phi} \right). \]  

Eq. (5.2) follows directly from Eq. (3.46) and Eq. (3.101) where \( p \), \( A(\alpha) \), and \( B(\beta) \) are defined, and where \( \Delta \theta \) is the increment in Bragg angle through which a crystallite may be rotated and still give rise to diffraction for the given set of planes. \( \Delta \theta \) is given by the sum of the natural half-width of the line, \( w_0 \), plus the apparent angular width of the line source as viewed by a crystallite (see Section B-1 of Chapter III), both expressed in radians. An appropriate value for \( w_0 \) in Eq. (5.3) can be estimated by means of Eq. (3.41), using the calculated value of \( \sigma_0 \) from Table 2. If an average value of 0.09 degrees is chosen for \( \sigma_0 \) for the lower order reflections of NaCl, then \( w_0 = 0.0037 \) radians and \( \Delta \theta = 0.0041 \) radians. In Eq. (5.4) \( \alpha \) is the mean volume of each crystallite, \( \mu \) is the linear absorption coefficient of the sample, \( A = 3.50 \) cm\(^2\) is the area of sample irradiated, and \( C \) is the absorption factor correction for sample curvature as given by Eq. (3.61), which is ignored in the present investigation. The expression for \( N \) in Eq. (5.4) is obtained by considering the ratio of the total radiation actually diffracted from the entire sample to the radiation which would be diffracted if not attenuated by sample absorption within a small volume element, \( dv \), containing \( (\rho'/\rho)(dv/\mu) \) crystallites, and follows from Eqs. (3.60) and (3.5).

Table 7 gives the results of intensity measurements on two NaCl powder fractions having mean crystallite sizes of 35 and 8
microns, respectively. The intensities of three lines of four
different samples of the 35 micron fraction and of three samples of
the 8 micron fraction were measured under as nearly identical conditions
as possible. The three tabulated line profiles for a given sample
were measured consecutively while maintaining a constant x-ray
intensity. The intensities of the lines were obtained by point-by-
point counting over the diffraction profiles, plotting the counts,
and measuring the area above background as described in Section E-2
of Chapter IV and Sections A and B of Chapter VI. The total probable
error in the reported intensities due to the uncertainties arising
from counting statistics, area measurement, and x-ray beam fluctuation
or drifting is 0.4 percent.

Although too few measurements of each line intensity were made
during this study to yield a reliable mean intensity or a reliable
value for the mean deviation, the data and results given in Table 7,
nevertheless, show a significant trend and are in quite good agreement
with the theoretical expectations. It will be noticed that the mean
deviation, \( U_{\text{obs}} \), in the intensities of the lines of the 35 micron
particle fraction is about three times greater than the deviation
for the 8 micron fraction. It will also be noticed that for both
the 8 and 35 micron fractions, the mean deviation of the intensity
of the (400) line is appreciably greater than the deviation of the
other lines, as would be predicted because of its smaller multiplicity
factor. Also given in Table 7 for each of the lines of both fractions
are the theoretical mean deviations, \( U_{\text{calc}} \), as calculated from
Eq. (5.1) through (5.4). For the 35 micron fraction the calculated mean deviation is about twice as large as the observed deviation for the three lines, but this is considered to be quite satisfactory agreement in view of two rather large sources of indeterminacy affecting the theoretical calculations. Three sources of error are (1) uncertainty in the value for the natural line widths, and (2) lack of consideration of a distribution of particle sizes. Both of these errors would be expected to cause about the same relative error in the calculated mean deviation for all of the lines, as is observed. For the 8 micron fraction the observed mean deviation of the intensities is larger than the calculated deviation. These results can be understood by noticing that the calculated deviations for this fraction are of the same magnitude as the 0.4 percent deviation attributed to counting statistics, etc.

The results given in Table 7 and the preceding discussion indicate that Eq. (5.1) can be employed with reasonable assurance to predict the probable error in line intensities measured in this investigation which arises from particle orientation. These calculated deviations will, therefore, be included when significant in the total probable error estimated for the experimental diffraction intensities reported in the following chapter. The largest calculated probable error due to orientation for the intensity data obtained in this investigation occurs for the (400) line of NaBr for which $U_{\text{calc}} = 12.0$ percent.
A. Experimental Diffraction Data

The experimental diffraction patterns obtained in this research for three solid solutions containing 25, 50, and 75 mole percent of sodium bromide in sodium chloride, and for the pure components, are shown in Figures 12 through 26. Each point in the figures represents an experimental determination of counting rate at a fixed value of $\theta$, using the experimental techniques and operating procedures as described in Section E of Chapter IV. The counting rate was determined at increments of 0.05 degrees in $\theta$ over the range of all diffraction peaks, and at increments of 0.1 degrees over the background regions, by counting to the pre-determined number of 10,000 counts, except that at each of the three points nearest the peak of a given contour, 40,000 pre-determined counts were recorded. Thus, as shown by Eq. (4.8), the average error due to statistical fluctuations in counting rates is expected to be 0.8 percent for each of the experimental points, except for the three points near the peaks of the diffraction lines, for which it should be 0.4 percent.

The diffraction data shown in Figures 12 through 26 were obtained over a period of about four months, using about 800 hours of x-ray tube time. For the higher order reflections of sodium chloride and sodium bromide the $k\alpha$ doublet of the characteristic radiation is nearly completely resolved, as can be seen in the figures. It will be noted that the diffraction pattern of the solid solution containing
Plate I, Fig 12. Diffraction Pattern of 100% NaCl.
Plate I, Fig. 13   Diffraction Pattern of 100% NaCl
Plate I, Fig 14  Diffraction Pattern of 100% NaCl
Plate I, Fig. 15  Diffraction Pattern of 100% NaCl
Plate II, Fig 16  Diffraction Pattern of 75\% NaCl - 25\% NaBr
Plate II, Fig. 17  Diffraction Pattern of 75% NaCl - 25% NaBr
Plate II, Fig.13  Diffraction Pattern of 75% NaCl - 25% NaBr
Plate III, Fig. 19  Diffraction Pattern of 50% NaCl – 50% NaBr
Plate III, Fig. 20  Diffraction Pattern of 50% NaCl - 50% NaBr
Plate IV, Fig 21  Diffraction Pattern of 25% NaCl - 75% NaBr
Plate IV, Fig. 21  Diffraction Pattern of 25% NaCl - 75% NaBr
Plate IV, Fig. 23  Diffraction Pattern of 25% NaCl - 75% NaBr
Plate IV, Fig 24 Diffraction Pattern of 100% NaBr
Plate V, Fig. 25  Diffraction Pattern of 100% NaBr
Plate V, Fig. 26 Diffraction Pattern of 100% NaBr
75 percent sodium chloride contains unindexed, though well defined, diffraction maxima at Bragg angles of 17.2 and 21.2 degrees, as well as other unindexed maxima and shoulders that are less well defined. These additional diffraction peaks are due to a relatively small amount of a solid solution phase containing 25 percent sodium chloride into which some of the original solid solution decomposed during the period of the measurements. The method of correction of the integrated intensities for this decomposition is described in Section C of this chapter. It will also be noted in these diffraction patterns that the background radiation is not always continuous. This is a result of the lack of precise reproducibility of the x-ray intensity and detector characteristics on different days. However, since the x-ray intensity was accurately determined for each series of measurements by a procedure to be later described and the background radiation did not appreciably vary during a single series of measurements, this background variation will cause no significant error in the measured integrated intensities.

The strong bromine fluorescence radiation presented a special problem, as discussed in Chapter IV, Section D. It will be recalled that the fluorescence radiation contributes to only a moderate extent to the counts passing the pulse-height analyzer, and does not affect significantly the measured integrated intensities of the lines after the correction of the latter for background radiation, provided the linear amplifier, the preamplifier, and proportional counter (including its high-voltage supply) are stable during the time required to obtain
the intensity data for a given line contour. However, the time required to obtain this data often exceeded several hours, and observable drifting of the background rate occasionally occurred during this period. The policy adopted to check for possible drifting was to remeasure the counting rate at some angle in the background region where the intensity had been accurately determined previously near the beginning of the particular series of measurements. If these values differed by more than two percent, then all the data collected during these measurements were discarded, and the measurements were repeated. It was found by comparison of the integrated intensities of various contours obtained with and without the occurrence of background drifting that this procedure was adequate to insure the reliability of the intensity of the line to within one percent (excluding statistical uncertainties).

B. Calculation of Integrated Intensities

The integrated intensity of a given diffraction line is proportional to the area of its contour above background, which was calculated by the following procedure. The experimental intensity data were plotted on a scale sufficiently large so that their deviation from a smooth curve was apparent by inspection. The total range of the intensity scale on these graphs was 500 millimeters, subdivided to 1 millimeter; the scale on the abscissa for the Bragg angle, \( \Theta \), was 500 millimeters per degree. The total length of the graph for each of the five systems was thus more than 7 meters, giving a high degree
of enlargement. What was judged to be the best smooth curve on the basis of the relative errors and spacings of the points was then drawn with a spline, and a smooth background curve was drawn by the same procedure. The background curve was extended when possible over at least several diffraction profiles so as to minimize the error. The area of the line contour plus background and the area of the background alone was then calculated by Simpson's rule, and the difference taken to obtain the observed area of the contour.

This procedure in drawing the line contours was of necessity modified for those lines whose contours overlap appreciably, such as the (331) and (420) lines of sodium chloride. These complex contours were resolved graphically into contours of their components by making use of the following criteria: (1) the sum of the intensities of the overlapping components at any angle must be equal to the total observed intensity, or stated otherwise, the principle of superposition must apply; (2) the peaks of both of the overlapping contours must lie at their calculated Bragg angles; (3) the width of each of the resolved contours at half-maximum intensity must be the same as that of the closest neighboring line whose half-width could be accurately measured; and (4) the shape of the resolved contours on the side of decreasing Bragg angle (the other side being generally asymmetric due to the \( \alpha_2 \) component) must be in reasonable agreement with that of a neighboring isolated contour. These four criteria are mutually compatible, and it is believed that a majority of the overlapping contours could be graphically resolved quite accurately.
through their application. For instance, the estimated uncertainty due to this overlap in the integrated intensity of the weak (331) reflection of sodium chloride is only about 9 percent, and this represents an extreme case where the contour is almost entirely obscured by the much more intense contour of the (420) reflection.

The decision to use Simpson's rule for the determination of the areas of the contours was arrived at after consideration of several forms of the general Newton-Cotes formula for numerical integration. This study was carried out by numerical evaluation of the area under a constructed curve whose exact area could be precisely calculated (such as a Lorenzian curve), using the various approximational methods. It was concluded that the error due to neglect of higher-order terms in Simpson's rule was entirely negligible relative to the experimental errors for the intervals on the abscissa which were used. In evaluating the areas of the contours ordinates were read from the smoothed curves at increments of 0.02 degrees, and the number of points used for the calculation of the area of each contour varied between about thirty and fifty, depending upon its intensity and breadth.

C. Correction of Intensities for Phase Separation

The evidence that a partial phase separation occurred in the solid solution containing 75 percent sodium chloride has been presented in Section A of this chapter. The method of treatment of
the intensity data to correct for the phase separation is given in
the present section. Such a correction is essential, as prior to the
recognition of the separation the calculated distortion factors for
the positive ion in this solid solution were inconsistent both with
the other two solid solutions and with theory. During the first four
days that intensity measurements were being carried out for this
particular composition, the intensity of certain reflections whose
contours were redetermined on subsequent days was observed to be
decreasing. In fact, upon many occasions during this period the
intensity of various reflections was observed to be decreasing even
during the time required to measure their contours. Unfortunately,
these effects were not associated with sample decomposition until
after the experimental program had been completed, but were instead
attributed to some physical effect such as absorption of water vapor
by the sample. At this time the procedure of having dry nitrogen
(oil-pumped and passed over phosphorus pentoxide) flow over the sample
during the periods of intensity measurement was adopted and was
employed during the remainder of the measurements. (This procedure
was also used while obtaining all of the intensity data for the other
two solid solutions). All of the intensity data reported in Table 11
were obtained with the sample in a dry atmosphere and were obtained in
two periods of measurements separated by thirty days. Although a
small amount of decomposition did occur in the interval between these
two periods of measurements, as will be evident from the intensity
analysis that is given below, no decomposition was detected during
the time of either set of measurements. Therefore, the corrected intensity data reported in Table II should be reasonably accurate.

The following analytical procedure is based on the fact that in a mixture of components the intensity of the diffraction pattern of each component, after correction for the effects of absorption, is proportional to the amount of that component present. An application of this principle to the case of diffraction from a flat powder sample has been developed by Alexander and Klug (33), and the results of their findings can be applied in a precise manner to the present problem since the intensity correction for sample curvature is negligibly small for the composition of interest. The basic relationship derived by these investigators (33), which underlies all quantitative analyses with an x-ray powder spectrometer, is

\[ I_n = \frac{K_n x_n}{\rho_n \left[ x_n \left( \mu_n^* - \mu_n^* \right) + \mu_n^* \right]} \]  

This expression, which is rigorously correct, relates the integrated intensity of a selected diffraction line of component \( n \) to its weight fraction \( x \), its density \( \rho \), its mass absorption coefficient, \( \mu_n^* = \mu_n / \rho \), and the mass absorption coefficient of the remaining components, \( \mu_n^{*M} \) defined by

\[ \mu_n^{*M} = \sum_{i=1}^{N} \frac{\mu_i^* x_i}{x_n} \]  

\( K_n \), in Eq. (6.1) depends upon the nature of component \( n \) and the geometry of the apparatus. Since Eq. (6.1) is valid for all
concentrations of components \( n \), it can be transformed to the following expression, which is the one employed in the present investigation of sample decomposition.

\[
\frac{I_n}{(I_n)_0} = \frac{x_n \mu_n^*}{x_n \mu_n + (1-x_n) \mu_M^*} \quad (6.3)
\]

In Eq. (6.3), \( (I_n)_0 \) is the measured intensity of a given diffraction line of pure component \( n \), and \( I_n \) is the measured intensity of the same line of this component in the material \( M \).

In order to employ Eq. (6.3) it is necessary to know the composition of the new phases formed upon the decomposition of the solid solution. The composition of one of the phases formed, the phase containing 25 mole percent of sodium chloride, is known quite accurately from the positions of the new diffraction maxima that appear in the diffraction pattern of the decomposed solid solution. The other phase formed must contain more than 75 mole percent sodium chloride, and is believed to be composed of pure NaCl. Although no diffraction lines due to this phase were observed, this conclusion may be justified by the following argument. If the second phase that is formed also contains an appreciable quantity of sodium bromide, then a relatively large amount of it must be formed, due to the stoichiometry required by the decomposition. The presence of such a phase would almost surely be detected by a broadening or distortion of the diffraction contours of the remaining undecomposed solid solution. However, no such broadening was experimentally observed, even though the course of the decomposition was followed over an
appreciable change in overall composition of the undecomposed phase. Therefore, it is concluded that the second phase is composed of pure sodium chloride, the diffraction lines of which would probably not be detected in the diffraction pattern of the solid solution because of the low intensities with which they would appear (see Table 8).

Therefore, the equation for the decomposition is assumed to be

\[ 3 \text{NaClBr} \rightarrow \text{NaClBr}_3 + 2 \text{NaCl} \]

and the stoichiometry of the decomposition requires that the weight fractions of \( \text{NaClBr}_4 \), \( \text{NaClBr}_3 \), and \( \text{NaCl}_4 \) in coexistence be

\[(1 - 2.275x), x, \text{and } 1.275x, \text{respectively. With this information together with the measured intensity of one of the lines diffracted by the phase containing 25 percent sodium chloride, the weight fraction of each phase present in the system, as well as the ratio, } (I/I_o), \text{of the intensity of its lines relative to their intensities in the corresponding pure phase, may be calculated by successive applications of Eq. (6.3). The results of these calculations are given in Table 8.}

In Table 8 the values given for period A are based on an observed intensity of 1.325 for the (600) line of the component containing 25 percent sodium chloride which occurs at \( \theta = 21.17 \) degrees. The values given for period B, the data for which were obtained thirty days later, are based on an observed intensity of 4.391 for the (422) line of the component containing 25 percent sodium chloride which occurs at \( \theta = 17.20 \) degrees. This table gives the weight fraction present
### TABLE 8

Weight Fractions and Relative Line Intensities for Phases Present after Partial Decomposition of Solid Solution Containing 75% NaCl - 25% NaBr

<table>
<thead>
<tr>
<th>Period</th>
<th>75% NaCl</th>
<th>100% NaCl</th>
<th>25% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Weight Fraction ... 0.636 0.0920 0.0720</td>
<td>(I/I₀) ... 0.837 0.0263 0.138</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Weight Fraction ... 0.780 0.118 0.0923</td>
<td>(I/I₀) ... 0.789 0.0342 0.176</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 9

Correction of Integrated Intensities of 75% NaCl - 25% NaBr Solid Solution for Decomposition

<table>
<thead>
<tr>
<th>hkl</th>
<th>I&lt;sub&gt;obs&lt;/sub&gt;</th>
<th>I&lt;sub&gt;NaCl&lt;/sub&gt;</th>
<th>I&lt;sub&gt;25% NaCl&lt;/sub&gt;</th>
<th>I&lt;sub&gt;Dif&lt;/sub&gt;</th>
<th>I&lt;sup&gt;0&lt;/sup&gt; int</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>26.03</td>
<td>3.20</td>
<td>---</td>
<td>22.83</td>
<td>28.95</td>
</tr>
<tr>
<td>331</td>
<td>15.44</td>
<td>0.425</td>
<td>8.05</td>
<td>6.97</td>
<td>8.84</td>
</tr>
<tr>
<td>420</td>
<td>50.42</td>
<td>6.13</td>
<td>---</td>
<td>44.29</td>
<td>56.10</td>
</tr>
<tr>
<td>422</td>
<td>29.41</td>
<td>3.44</td>
<td>---</td>
<td>25.97</td>
<td>32.88</td>
</tr>
<tr>
<td>333,511</td>
<td>3.83</td>
<td>0.273</td>
<td>---</td>
<td>3.56</td>
<td>4.51</td>
</tr>
<tr>
<td>440</td>
<td>5.77</td>
<td>0.354</td>
<td>---</td>
<td>5.24</td>
<td>6.26</td>
</tr>
<tr>
<td>531</td>
<td>3.04</td>
<td>0.162</td>
<td>---</td>
<td>2.88</td>
<td>3.44</td>
</tr>
<tr>
<td>600,442</td>
<td>9.57</td>
<td>0.908</td>
<td>---</td>
<td>8.66</td>
<td>10.35</td>
</tr>
<tr>
<td>620</td>
<td>5.38</td>
<td>0.465</td>
<td>0.636</td>
<td>4.28</td>
<td>5.12</td>
</tr>
<tr>
<td>533</td>
<td>0.416</td>
<td>0.037</td>
<td>---</td>
<td>0.379</td>
<td>0.453</td>
</tr>
<tr>
<td>622</td>
<td>3.85</td>
<td>0.345</td>
<td>0.081</td>
<td>3.41</td>
<td>4.07</td>
</tr>
<tr>
<td>444</td>
<td>1.011</td>
<td>0.055</td>
<td>0.513</td>
<td>0.443</td>
<td>0.530</td>
</tr>
<tr>
<td>711,551</td>
<td>0.494</td>
<td>---</td>
<td>---</td>
<td>0.484</td>
<td>0.578</td>
</tr>
<tr>
<td>640</td>
<td>2.30</td>
<td>0.242</td>
<td>0.340</td>
<td>1.72</td>
<td>2.055</td>
</tr>
<tr>
<td>642</td>
<td>2.91</td>
<td>0.267</td>
<td>0.143</td>
<td>2.50</td>
<td>2.99</td>
</tr>
<tr>
<td>731,553</td>
<td>0.324</td>
<td>---</td>
<td>---</td>
<td>0.324</td>
<td>0.410</td>
</tr>
</tbody>
</table>
of the phase indicated, and the intensity $I/I_0$, with which the lines of this phase appear relative to their intensity in the pure material. It will be noted in Table 8 that only a small amount of additional decomposition occurred between the two periods of measurements.

In the second column of Table 9 are tabulated the integrated line intensities of the solid solution containing 75 percent sodium chloride as they were experimentally measured. In the third and fourth columns are given the intensities calculated from the data of Table 8 arising from the phases containing pure sodium chloride and 25 percent sodium chloride, respectively, which overlap the line indicated to such an extent that they could not be graphically resolved. In the fifth column are given the integrated intensities which are contributed by the reflections of the 75 percent sodium chloride phase only, obtained by subtracting the intensities of the overlapping lines from the measured intensities. In the last column are tabulated the theoretical integrated intensities which would have been obtained if decomposition had not occurred, obtained by division of the intensities in the fifth column by the ratio $(I/I_0)$ for this phase and the appropriate period as given in Table 8. The corrected intensities of reflections (400) through (333) in Table 9 are calculated from the ratio given for period B, and the intensities of the remaining reflections are calculated from the ratio given for period A. It is these corrected intensities for this phase that are given in the third column of Table 11.
D. Experimental Structure Factors

In Tables 10 through 14 are given the values of the integrated intensities obtained from this research for the x-ray reflections from three solid solutions of sodium chloride and sodium bromide and the pure components, as well as the experimental structure factors derived from these data.

At the top of each table is given the period over which the data was obtained. The values of $\mu$, the linear absorption coefficient in units of $\text{cm}^{-1}$, and $v^2$, the square of the mean unit cell volume in units of $\text{Å}^2$, for the particular composition involved are given in the footnote. The unit cell volume for each composition is computed from the accurately known cell constants (13,19) of sodium chloride $^0$ ($a = 5.6288 \text{ Å}$) and sodium bromide ($a = 5.9617 \text{ Å}$), assuming a linear variation of the cell constant of the solid solution with composition (Vegard's law). It should be pointed out that this assumption was found to be valid by Fineman, Wallace, and Nickels (18,19) to within 0.14 percent deviation over the entire range of composition. A study of Bragg angles obtained in the present research verified this linear relation to about the same precision, as discussed in Section F of this chapter. The linear absorption coefficients for these materials are calculated from the well-known expression

$$\mu = \rho \sum x_i \mu_i' ,$$

where $\rho$ is the density of the material and $\mu_i'$ is the mass absorption coefficient of element $i$ occurring with the weight fraction, $x_i$. In
### TABLE 10

**Experimental Intensities and Calculated Structure Factors for 100% NaCl**

(Data of 5-10 to 5-17-58)

| hkl   | $\theta_0$ | $I_{\text{int}}$ | p  | $\sigma(\theta_0)$ | $H(\alpha, \beta)$ | $|F|$ | % Error in $|F|$ |
|-------|-------------|-------------------|----|---------------------|---------------------|------|-----------------|
| 400   | 14.54       | 93.45             | 6  | 28.91               | 0.08160            | 12.99| 0.5             |
| 331   | (15.89)     | 12.43             | 24 | 27.48               | 0.07407            | 2.545| 4.7             |
| 420   | 16.335      | 179.33            | 24 | 22.51               | 0.07188            | 10.37| 0.4             |
| 422   | 17.945      | (100.85)          | 24 | 19.34               | 0.06492            | (9.50)| -               |
| 333,511 | 19.07      | 8.00              | 32 | 16.04               | 0.06084            | 2.56 | 1.5             |
| 440   | 20.85       | 20.02             | 12 | 13.16               | 0.05528            | 7.66 | 0.6             |
| 531   | (21.845)    | 6.16              | 48 | 11.86               | 0.05264            | 2.29 | 4.2             |
| 600,442 | 22.18      | 34.44             | 30 | 11.45               | 0.05176            | 7.04 | 1.1             |
| 620   | 23.455      | 17.61             | 24 | 10.10               | 0.04883            | 6.17 | 0.5             |
| 533   | (24.35)     | 1.410             | 24 | 9.287               | 0.04701            | 1.86 | 6.6             |
| 622   | 24.67       | 13.43             | 24 | 8.998               | 0.04635            | 5.96 | 0.8             |
| 444   | 25.35       | 2.09              | 8  | 8.090               | 0.04418            | 4.32 | 1.2             |
| 711,551 | (26.70)   | 1.728             | 48 | 7.515               | 0.04278            | 1.69 | 5.4             |
| 640   | 26.298      | 7.43              | 24 | 7.339               | 0.04232            | 5.05 | 1.3             |
| 642   | 28.09       | 10.14             | 48 | 6.964               | 0.04065            | 4.46 | 0.5             |
| 731,555 | 28.90      | 1.829             | 72 | 6.279               | 0.03953            | 1.62 | 2.0             |
| 800   | 30.205      | 0.796             | 6  | 5.686               | 0.03788            | 3.97 | 4.8             |
| 733   | (30.99)     | -                 | 24 | 5.371               | 0.03698            | -    | -               |
| 820,644 | 31.255     | 4.74              | 48 | 5.271               | 0.03669            | 3.61 | 1.6             |
| 822,660 | 32.265     | 2.582             | 36 | 4.918               | 0.03562            | 3.24 | 1.2             |
| 751,555 | 32.995     | 0.554             | 56 | 4.687               | 0.03490            | 1.24 | 4.8             |
| 562   | 33.235      | 1.471             | 24 | 4.614               | 0.03468            | 3.15 | 2.1             |
| 840   | 34.245      | 0.945             | 24 | 4.334               | 0.03377            | 2.62 | 2.5             |

* $\mu = 18.21; \quad v^2 = 3.1805 \times 10^4$
#TABLE 11

Experimental Intensities and Calculated Structure Factors  
for 75% NaCl - 25% NaBr  
Solid Solution*  
(Data of 6-1 to 7-21-58)

| hkl   | $\theta_0$ | $I_{int}$ | p  | $g(\theta_0)$ | $|F|$  | % Error in $|F|$ |
|-------|-------------|------------|----|----------------|-------|--------------|
| 400   | 14.365      | 28.95      | 6  | 29.67          | .08268| 14.75        | 0.9 |
| 331   | 15.67       | 8.84       | 24 | 24.62          | .07519| 4.69         | 2.4 |
| 420   | 16.13       | 56.10      | 24 | 23.14          | .07279| 12.41        | 0.7 |
| 422   | 17.725      | 32.88      | 24 | 18.84          | .06578| 11.06        | 0.6 |
| 333,511 | 18.815    | 4.51       | 32 | 16.53          | .06170| 3.91         | 1.8 |
| 440   | 20.57       | 6.26       | 12 | 13.56          | .05608| 8.70         | 1.4 |
| 531   | 21.54       | 3.44       | 48 | 12.23          | .05341| 3.48         | 2.9 |
| 600,442 | 21.865   | 10.35      | 30 | 11.53          | .05257| 7.635        | 1.5 |
| 620   | 23.14       | 5.12       | 24 | 10.41          | .04953| 6.73         | 1.1 |
| 533   | (24.00)     | 0.453      | 24 | 9.579          | .04768| 2.14         | 7.5 |
| 622   | 24.325      | 4.07       | 24 | 9.291          | .04702| 6.55         | 2.5 |
| 444   | 25.47       | 0.530      | 8  | 8.364          | .04480| 4.43         | 11. |
| 711,551 | 26.27     | 0.578      | 48 | 7.798          | .04346| 1.99         | 7.0 |
| 640   | 26.58       | 2.055      | 24 | 7.593          | .04296| 5.38         | 2.7 |
| 642   | 27.67       | 2.99       | 48 | 6.929          | .04128| 4.96         | 1.4 |
| 731,553 | 28.45     | 0.410      | 72 | 6.509          | .04014| 1.55         | 8.3 |

* $\mu = 72.2$; $\nu^2 = 3.4732 \times 10^4$
| hkl   | θ₀     | I<sub>int</sub> | p | G(θ₀) | H(x,θ) | |F| | % Error in |F|
|-------|--------|----------------|---|--------|--------|-------|-----|----------------|
| 400   | 14.12  | 23.23          | 6 | 30.78  | 0.08431| 17.38 | 1.1 |
| 331   | (15.415)| 14.39          | 24| 25.50  | 0.07656| 7.91  | 3.2 |
| 420   | 15.84  | 51.01          | 24| 24.06  | 0.07432| 15.55 | 1.1 |
| 422   | 17.435 | 24.77          | 24| 17.28  | 0.06705| 13.46 | 0.6 |
| 333,511| 18.515 | 6.74           | 32| 17.12  | 0.06282| 6.32  | 1.2 |
| 440   | 20.23  | 4.80           | 12| 14.075 | 0.05710| 10.36 | 1.5 |
| 531   | 21.20  | 5.25           | 48| 12.58  | 0.05432| 5.68  | 2.3 |
| 600,442| 21.53  | 7.85           | 30| 12.24  | 0.05344| 9.02  | 1.8 |
| 620   | 22.74  | 3.73           | 24| 10.825 | 0.05045| 7.61  | 1.6 |
| 533   | (23.62)| 0.912          | 24| 9.951  | 0.04852| 4.00  | 11  |
| 622   | 23.915 | 3.05           | 24| 9.657  | 0.04755| 7.48  | 3.9 |
| 444   | (25.04)| <0.6           | 8 | 8.657  | 0.04564| <6.2  | -   |
| 711,511| (25.86)| 1.517          | 48| 8.083  | 0.04416| 4.24  | 4.6 |
| 640   | 26.135 | 1.706          | 24| 7.331  | 0.04370| 6.43  | 5.5 |
| 642   | 27.165 | 1.158          | 48| 7.226  | 0.04203| 4.92  | 3.6 |

*μ = 121.71; \(\nu^2 = 3.7981 \times 10^4\)
### TABLE 13

**Experimental Intensities and Calculated Structure Factors**

for 25% NaCl - 75% NaBr

**Solid Solution**

(Data of 8-7 to 8-16-58)

| hkl | $\theta_0$ | $I_{\text{int}}$ | p | $G(\theta_0)$ | $H(\alpha, \beta)$ | $|F|$ | % Error in $|F|$ |
|-----|------------|-----------------|---|--------------|-------------------|------|----------------|
| 400 | 13.96      | 24.02           | 6 | 31.51        | .08531            | 21.27| 1.3            |
| 331 | 15.255     | 16.06           | 24| 26.09        | .07743            | 10.03| 1.1            |
| 420 | 15.855     | 45.67           | 24| 24.67        | .07526            | 17.69| 0.7            |
| 422 | 17.185     | 24.91           | 24| 20.16        | .06803            | 15.17| 0.7            |
| 333,511 | 18.25 | 7.53            | 32| 17.67        | .06379            | 7.97 | 1.3            |
| 440 | 19.945     | 5.23            | 12| 14.53        | .05797            | 12.54| 1.5            |
| 531 | 20.87      | 5.33            | 48| 13.13        | .05522            | 6.82 | 2.8            |
| 600,442 | 21.19 | 9.61           | 30| 12.69        | .05435            | 11.77| 2.7            |
| 620 | 22.40      | 4.74            | 24| 11.20        | .05124            | 10.11| 1.3            |
| 533 | (23.265)   | 1.214           | 24| 10.28        | .04925            | 5.51 | 5.4            |
| 622 | 23.54      | 3.40            | 24| 10.01        | .04865            | 9.40 | 2.5            |
| 444 | 24.64      | 0.588           | 8 | 9.023        | .04641            | 7.31 | 7.5            |
| 711,511 | (25.45) | 1.495           | 48| 8.392        | .04489            | 5.01 | 4.6            |
| 640 | (25.71)    | 2.22            | 24| 8.191        | .04443            | 8.79 | 4.5            |
| 642 | 26.78      | 2.46            | 48| 7.465        | .04275            | 6.99 | 1.6            |
| 731,553 | 27.54 | 1.035           | 72| 7.004        | .04120            | 3.88 | 3.5            |

* $\mu = 166.91; \quad \nu^2 = 4.1266 \times 10^4$
TABLE 14

Experimental Intensities and Calculated Structure Factors for 100% NaBr

(Data of 5-23 to 5-28-58)

<table>
<thead>
<tr>
<th>hkl</th>
<th>θ&lt;sub&gt;0&lt;/sub&gt;</th>
<th>I&lt;sup&gt;0&lt;/sup&gt;&lt;sub&gt;int&lt;/sub&gt;</th>
<th>p</th>
<th>G(θ&lt;sub&gt;0&lt;/sub&gt;)</th>
<th>Η()</th>
<th>F</th>
<th>% Error in F</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>13.74</td>
<td>33.31</td>
<td>6</td>
<td>32.61</td>
<td>.08683</td>
<td>23.02</td>
<td>2.0</td>
</tr>
<tr>
<td>331</td>
<td>15.045</td>
<td>19.30</td>
<td>24</td>
<td>26.57</td>
<td>.07365</td>
<td>12.52</td>
<td>1.1</td>
</tr>
<tr>
<td>420</td>
<td>15.44</td>
<td>47.60</td>
<td>24</td>
<td>25.42</td>
<td>.07641</td>
<td>20.22</td>
<td>0.7</td>
</tr>
<tr>
<td>422</td>
<td>16.96</td>
<td>27.30</td>
<td>24</td>
<td>20.69</td>
<td>.06901</td>
<td>13.35</td>
<td>0.7</td>
</tr>
<tr>
<td>333, 511</td>
<td>18.02</td>
<td>10.40</td>
<td>32</td>
<td>18.18</td>
<td>.06846</td>
<td>10.54</td>
<td>1.0</td>
</tr>
<tr>
<td>620</td>
<td>19.68</td>
<td>5.12</td>
<td>12</td>
<td>14.96</td>
<td>.05881</td>
<td>14.15</td>
<td>1.6</td>
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<tr>
<td>531</td>
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<td>48</td>
<td>13.50</td>
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<td>8.96</td>
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<td>.05511</td>
<td>13.97</td>
<td>1.0</td>
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<td>5.46</td>
<td>24</td>
<td>11.535</td>
<td>.05387</td>
<td>12.28</td>
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<td>1.62</td>
<td>24</td>
<td>10.595</td>
<td>.04995</td>
<td>7.25</td>
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<tr>
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<td>23.25</td>
<td>4.10</td>
<td>24</td>
<td>10.295</td>
<td>.04927</td>
<td>11.78</td>
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<td>0.790</td>
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<td>9.278</td>
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<td>9.67</td>
<td>4.3</td>
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<td>711, 551</td>
<td>25.135</td>
<td>1.49</td>
<td>48</td>
<td>8.624</td>
<td>.04546</td>
<td>5.67</td>
<td>2.8</td>
</tr>
<tr>
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<td>2.01</td>
<td>24</td>
<td>8.428</td>
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<td>9.55</td>
<td>1.9</td>
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<td>8.61</td>
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<td>72</td>
<td>7.217</td>
<td>.04177</td>
<td>5.59</td>
<td>1.7</td>
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</tbody>
</table>

\* v = 208.24; \ v^2 = 4.4897 \times 10^4

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applying this equation \( \Phi \) was determined from the accurately known
cell constants, and the values of \( \mathcal{M}_1 \) used (3.36 for Na, 11.62 for
Cl, and 82.2 for Br) were taken from the "International Tables for
the Determination of Crystal Structure" (34). These values for the
mass absorption coefficient are experimental quantities which are
subject to rather large uncertainties. Any error in these values will,
of course, be reflected in the values of the experimental structure
factors derived for the materials studied in this investigation.
However, this research is primarily concerned with the investigation
of the lattice distortion occurring in these solid solutions, and
from the manner in which these structure factors are employed to
obtain this information, an error in the values of the absorption
coefficients will not appreciably effect the values for the calculated
distortion factors, as will be evident from the treatment given in
the following chapter.

The first column in Tables 10 through 14 give the Miller indices
for the particular reflection. In the second column of these tables
is given the experimental Brass angle in degrees at which the peak of
the reflection (for the \( \mathcal{M}_1 \) component of the radiation) occurs. The
values of the angles given in parentheses, for those reflections whose
contours are obscured by close-lying neighboring reflections, are
calculated values from Table 18 adjusted for the observed deviations
given there.

In the third column of the tables is given the integrated
intensity of the reflection, \( I^0_{\text{int}} \), in dimensionless units. These
Intensities are calculated from Eq. (3.126), letting \( \text{int}_{\text{stand}} = 100.85 \), where \( \text{int} \) is the area of the contour of the given reflection and \( \text{int}_{\text{stand}} \) is the area of the (422) reflection of sodium chloride for which intensity data were obtained in the same time period in order to calibrate the x-ray beam intensity incident on the sample. Both of these areas are measured in the manner described in Section B of the present chapter. It should be mentioned that the intensity of the standard (422) line of sodium chloride, \( \text{int}_{\text{stand}} \), is assigned a value of 100.85 instead of the more natural value of 100.00 to compensate for the difference in the area calculated when a linear background curve was drawn for the individual reference contour, and that calculated when the best non-linear background curve was drawn over the range of the reference contour and several adjacent contours. The simpler linear background curve was used for convenience for the frequent calibrations of beam intensity based on the reference contour, and the area calculated by this procedure was assigned the value of 100.00 (see Section 2-2 of Chapter IV). Thus the integrated intensities given in these tables are all relative values on a scale on which the standard intensity of the (422) reflection of sodium chloride as accurately computed with a non-linear background curve has a value of 100.85. The reported intensities in Tables 10, 12, 13, and 14 are obtained directly from the experimental data, while those in Table 11 for the solid solution containing 75 percent sodium chloride are the values corrected for decomposition in the preceding section and given also in the final column of Table 9.
The modulus of the structure factor, $|F|$, given in the seventh column of Tables 10 through 14 is calculated from the intensity data through the use of Eq. (3.127). In this equation $p$ is the multiplicity factor for the particular reflection given in the fourth column of these tables. $G(0^0)$ and $H(\alpha^0, \rho^0)$ in Eq. (3.127) are defined by Eqs. (3.110) and (3.111), respectively, and their values for each of the reflections are tabulated in columns five and six of the tables. The constant $K$ that appears in Eq. (3.127) is defined by Eq. (3.128), and has the value $K = 2.2650 \times 10^{-4}$ for the standard reference reflection chosen.

It should be pointed out that the tabulated values of $H(\alpha^0, \rho^0)$ in the tables are not corrected for the sample curvature factor, $C(\mu', \alpha^0, \rho^0)$, defined by Eq. (3.61), as its possible importance was not appreciated at the time the experimental intensity data were treated. Because of the manner of dependence on $C(\mu', \alpha^0, \rho^0)$ of $\mu$ and $\rho^0$, it is evident that this correction will be most important for reflections occurring at small Bragg angles and for materials having small absorption coefficients. For example, for the (400), (422), and (800) reflections of NaCl, the calculated values of this factor are 0.9728, 0.9841, and 0.9950, respectively, and for the (400) reflections of the solid solutions containing 75 and 50 percent sodium chloride, the values of this factor are 0.9926 and 0.9954, respectively, assuming a packing fraction of 0.75 throughout. Since the calculated structure factors are inversely proportional to the square root of $C(\mu', \alpha^0, \rho^0)$, the omission of this factor causes the
values of the structure factors for the first five reflections of
sodium chloride reported in Table 10 to be low as follows: (400),
1.36 percent; (331), 0.88 percent; (420), 0.79 percent; (422), 0.080
percent; and (333, 511), 0.67 percent. The reported factors of the
other reflections of sodium chloride and all the reflections for the
other materials studied are in error by less than 0.5 percent due to
this omission. With regard to the present study of lattice distortion
this error in structure factors for the first several reflections
of sodium chloride is of essentially no consequence and causes little
error in the calculated distortion factors, which depend principally
on the intensities of reflections of higher order. However, it must
be emphasized that for accurate structure factor determinations of
materials having low absorption coefficients, this correction may be
of considerable significance and should be included in the
calculations.

The estimated accidental (non-systematic) errors in the measured
structure factors are given in the final column of the tables, and
discussed in the next section.

The values of the experimental structure factors obtained in
this research, and given in the seventh column of Tables 10 to 14,
are plotted as functions of \((\sin \theta/\lambda)(\sqrt{h^2+k^2+l^2}/2a_0)\) in
Figures 27 to 31. It will be noted that separate smooth curves can
be drawn quite accurately through the experimental structure factors
corresponding to \(h k l\) an even and an odd integer, respectively. This
is a well-known result for the NaCl type lattice, the even and odd
Fig. 27 Structure Factor Curves for 100% NaCl
Fig. 28 Structure Factor Curves for 75% NaCl - 25% NaBr.
Fig. 29  Structure Factor Curves for 50\% NaCl — 50\% NaBr.
Fig. 30 Structure Factor Curve for 25% NaCl - 75% NaBr.
Fig. 31 Structure Factor Curves for 100% NaBr
structure factors being proportional to the sum and difference, respectively, of the scattering powers of the cation and anion (see the discussion in Section A of Chapter VII).

E. Accuracy of Experimental Intensities and Structure Factors

1. Estimated Accidental Errors of Intensities and Structure Factors

The mean absolute percentage error to be expected in the integrated intensity and structure factor for each reflection as a result of accidental (non-systematic) errors of measurement is estimated in the present section. The detailed discussion will be restricted to the percentage error in the integrated intensity, since the structure factor is proportional to the square root of the intensity and has a percentage error just half that of the intensity. The principal errors considered and procedures used are as follows:

a) Particle size error. Intensity measurements with powder samples are subject to error because only a finite number of crystallites contribute to any one reflection. The observed intensity is influenced by variations of the number of properly oriented crystallites from the number calculated on the basis of completely random orientation of crystallites in the theory of integrated intensities given in Section C of Chapter III. The relative variations in intensity from this cause decrease as the crystallite size decreases and the volume irradiated increases, with a resulting increase in total number of particles irradiated. The effective
volume irradiated increases as the absorption coefficient decreases, or in the present investigation as the ratio of chloride to bromide ion increases. The particle size error also decreases as the multiplicity factor for the reflection increases. The necessary equations for calculating the expected mean relative deviations of integrated intensity, U, are given in Section D of Chapter V, Eqs. (5.1) through (5.4). The error was computed individually for each powder reflection of each of the two pure components and three solid solutions. When two or more crystal reflections for which $h^2 + k^2 + l^2$ has the same value superimpose in diffraction from the powder samples, $p$ in Eq. (5.2) is to be taken as the sum of the multiplicities of the separate reflections, and the calculated value of $U$ is the error in the total integrated intensity of the superimposed reflections.

As an example, consider the (422) reflection of NaCl used as the intensity standard in the present investigation. The values of the multiplicity, Bragg angle, and absorption coefficient are given in Table 10. The value of $\phi$ may be calculated from the Bragg angle and Eq. (3.1), with $\alpha = 22.5$ degrees. The value of $m$ calculated from Eq. (5.2) with $\Delta \theta = 0.0041$ radians is $5.2 \times 10^{-4}$. The mean crystallite size for the samples used in the main part of the present investigation has been estimated as 8 microns in Section of Chapter V, yielding a mean crystallite volume of $u = 5.1 \times 10^{-10}$ cm$^3$ in Eq. (5.4), and a calculated value of $N = 1.56 \times 10^8$ for the total number of particles irradiated. Insertion of the values of $m$ and $N$
in Eq. (5.1) yields for the mean relative deviation of the integrated intensity the value $U = 0.0028$, or 0.28 percent. The values calculated for the various reflections in this way varied from 0.17 to 2.0 percent.

b) Counting rate error. The integrated intensities are obtained by numerical evaluation of the area enclosed by the experimental diffraction contours of Figs. 12 through 25 and an appropriate base-line for each contour as discussed in Section B of this chapter. The contour for each reflection is determined by a number of separate experimental determinations of counting rate, each of which is indicated by a point in the figures. The mean error to be expected in a single determination of counting rate has been discussed in Section D-2 of Chapter IV. Equation (4.6) gives the mean relative deviation in the time required to count a pre-determined number, $N$, of counts, and, therefore, also the mean relative error in the individual counting rate determinations plotted in Figures 12 through 25. However, it is clear that a correct evaluation of the errors in the integrated intensities must take account of the number, $n$, of separate counting rate measurements that enter into the determination of a given contour, since the mean error will certainly decrease as this number increases, other factors being equal. On the other hand it is sufficient for the estimation of the errors to use an approximate model. Thus, it may be assumed that the area under the contour is calculated from the trapezoidal rule, rather than the more accurate Simpson's rule actually used, and
simplifying assumptions may also be introduced regarding the form of the contour and base-line. In fact, it is obvious that the latter simplifications are essential if a simple generally applicable formula is to be obtained, as the form of the individual contours varies considerably.

Let $I_i$, where $i = 1, 2, \ldots, n$, be the individual counting rate values entering into the determination of a given contour. These values are assumed to be measured at equal intervals, $\Delta \theta$, in the Bragg angle as in the present investigation. Let $I_{0,i}$ be the base-line counting rate at the value of the Bragg angle corresponding to the measured value $I_i$. Then the trapezoidal rule yields for the integrated intensity,

$$I_{\text{int}} = \Delta \theta \sum_{i=1}^{n} (I_i - I_{0,i}). \quad (6.5)$$

The errors in the separate determinations of counting rate, $I_i$, are clearly independent. The errors in the base-line values, $I_{0,i}$, are independent of those in the $I_i$'s, since they depend upon counting rate determinations to either side of the interval of $\theta$ covered by the contour. On the other hand the errors in the base-line values, $I_{0,i}$, are not independent of one another, as they are interpolated rather than individually measured values. However, any quantitative attempt to take account of the interdependency of the base-line errors greatly complicates the discussion, and they will, therefore, be treated as independent errors. A qualitative analysis indicates that this does not greatly affect the calculated error. Then, from
the theory of independent random errors the mean deviation of the
function \( I_{\text{int}} \) of the quantities \( I_i \) and \( I_{o,i} \) defined by Eq. (6.5)
is given by

\[
\Delta I_{\text{int}} = \left[ \sum_{i} (\partial I_{\text{int}} / \partial I_i)^2 (\Delta I_i)^2 + \sum_{i} (\partial I_{\text{int}} / \partial I_{o,i})^2 (\Delta I_{o,i})^2 \right]^{1/2} 
\]

where \( I_i \) and \( I_{o,i} \) are the mean absolute deviations of \( I_i \) and
\( I_{o,i} \), respectively. As shown by Eq. (4.8) the mean relative error
in \( I_i \) is

\[
(\Delta I_i / I_i) = \left( \frac{2}{\pi N_i} \right)^{1/2}, \quad (6.7)
\]

where \( N_i \) is the number of counts in the \( i \)th measurement. As dis-
cussed in Section A of this chapter, \( N_i = 10^4 \), except for three
measurements nearest the peak of the contour for which \( N_i = 4 \times 10^4 \).
However, it will be assumed for simplicity that \( N_i \) has the constant
value \( N \), and in the calculations the latter will be assigned the
lower value \( 10^4 \); the error will thus be overestimated which will tend
to compensate for the other approximations introduced in the present
calculation. The mean deviations are, therefore, assumed to be given
by

\[
\Delta I_i = \left( \frac{2}{\pi N} \right)^{1/2} I_i. \quad (6.8)
\]

It may reasonably be assumed that the mean deviation in the inter-
polated base-line values is given by the similar expression

\[
\Delta I_{o,i} = \left( \frac{2}{\pi N} \right)^{1/2} I_{o,i}. \quad (6.9)
\]
Substitution of $\Delta I_1$ and $\Delta I_{0,i}$ from Eqs. (6.8) and (6.9) in Eq. (6.6) yields for the mean deviation of the integrated intensity,

$$I_{\text{int}} = \Delta \theta (2/\pi N)^{1/2} \left[ \sum_{i} (I_1^2 + I_{0,i}^2) \right]^{1/2}.$$  (6.10)

Division of $\Delta I_{\text{int}}$ as given by Eq. (6.10) by $I_{\text{int}}$ as given by Eq. (6.5) now yields for the mean relative deviation of the integrated intensity,

$$\frac{\Delta I_{\text{int}}}{I_{\text{int}}} = (2/\pi N)^{1/2} \left[ \sum_{i} (I_1^2 + I_{0,i}^2) \right]^{1/2} \left[ \sum_{i} (I_1 - I_{0,i}) \right]^{1/2}$$

$$= (2/\pi N) \left( I_1^2 + I_{0,i}^2 \right)^{1/2} \left( I_1 - I_{0,i} \right)^{1/2},$$  (6.11)

where the mean and mean square values of $I_1$ are defined by

$$\bar{I}_1 = \frac{1}{n} \sum_{i} \tilde{I}_1,$$  (6.12)

$$\bar{I}_1^2 = \frac{1}{n} \sum_{i} \tilde{I}_1^2,$$  (6.13)

and similarly for $I_{0,i}$ and $I_{0,i}^2$.

In order to obtain a reasonably simple evaluation of the right-hand size of Eq. (6.11) it will be assumed that the line contour may be approximated as a triangle, with $I_1$ increasing linearly (with $\theta$) from the value $I_o - \Delta I_o$ at one edge of the line to a maximum or peak value, $I_p$, at the center of the line, and then decreasing linearly to the value $I_o + \Delta I_o$ at the opposite edge of the line. Furthermore, the (less radical) assumption will be made that the background curve
increases linearly from $I_o - \Delta I_o$ to $I_o + \Delta I_o$ in crossing the contour in the same direction, with a value $I_o$ at the center or peak position. The ratio of background to peak height at the center of the contour is then

$$f = \frac{I_o}{I_p},$$

(6.14)

while the relative slope of the background is characterized by the ratio

$$f = \frac{\Delta I_o}{I_p}.$$  

(6.15)

These ratios are easily measured on the original large scale plots which are reproduced in Figures 12 through 26. With these assumptions, and the approximation of the sums in Eqs. (6.12) and (6.13) by integrals, elementary calculation yields the following mean values,

$$I_{o, i} = I_o,$$  

(6.16)

$$\bar{I}_{o, i}^2 = I_o^2 + (1/3)(\Delta I_o)^2,$$  

(6.17)

$$I_i = \frac{1}{2}(I_p + I_o),$$  

(6.18)

$$\bar{I}_i^2 = \frac{1}{3} I_p^2 + I_I^2 + I_o^2 + (\Delta I_o)^2.$$  

(6.19)

Substitution of these mean values in Eq. (6.11), and use of Eqs. (6.14) and (6.15), then yields

$$\frac{\Delta I_{int}}{I_{int}} = 2(2/3 \pi nN)^{1/2} \left[1 + f + 4f^2 + 2(\Delta f)^2 \right]^{1/2} \sqrt{1 - f}.$$  

(6.20)

The relative error in the integrated intensity is thus predicted to
be inversely proportional to the square root of the total number of counts, \( nN \), as expected from the theory of the counting process as given in Section D-2 of Chapter 4, but is also dependent on the ratio of background to peak height, \( f \). The correction for background slope, \( \Delta f \), is negligible for the contours in Figures 12 through 26, and was ignored in the estimation of the errors.

As an example, for the (422) reflection of sodium chloride in Fig. 12, \( I_0 \) and \( I_p \) have values of 110 and 415 counts per second, yielding a ratio of \( f = 0.26 \). Insertion of \( N = 10,000 \) counts, \( n = 12 \), and the calculated value of \( f \) in Eq. (6.20) yields \( \left( \frac{\Delta I_{\text{int}}}{I_{\text{int}}} \right) = 0.0043 \), or 0.43 percent.

\( \text{e}) \) Resolution error. As discussed in Section B of this chapter it was necessary in the case of overlapping reflections to resolve the integrated area into two parts to be assigned to the individual reflections. The error in this process is not susceptible to a simple analysis, but was estimated in each case from the large scale plots by considering the greatest variation that could be made in the shapes of the two resolved contours subject to the criteria stated in Section B. For overlapping reflections this was usually the largest single estimated error, and was assigned the following values for the reflections and compositions indicated: (331) 9, (420) 0.6, (531) 8, (600,442) 2, (533) 10, (622) 1, (711,551) 6, (640) 2, (820,644) 3, (751,555) 2 and (622) 2 percent, for pure NaCl; (331) 3, (420) 1, (531) 4, (600,442) 2, (533) 5, (622) 3, (711,551) 5, and (640) 2 percent, for 75 percent NaCl-25 percent NaBr; (331) 6,
(420) 2, (531) 4, (600, 442) 3, (533) 20, (622) 7, (711, 551) 8, and (640) 10 percent, for 50 percent NaCl-50 percent NaBr; (331) 1, (420) 0.5, (531) 5, (600, 442) 5, (533) 7, (622) 4, (711, 551) 8, and (640) 8 percent, for 25 percent NaCl-75 percent NaBr; and (400) 3, (531) 1, (600, 442) 1, (533) 5, (622) 2, (711, 551) 2, and (640) 2 percent, for pure NaBr.

d) **Intensity calibration error.** As discussed in Section E-2 of Chapter IV and Section D of the present chapter, it was necessary to calibrate the intensity of the x-ray beam by measuring the integrated intensity of the (422) reflection of NaCl at the beginning and end of each day's measurements. The calibration measurements were made with the same sample of NaCl powder as was used in the main series of measurements on NaCl, the sample being kept in a desiccator when not in use. The particle size or orientation error of 0.28 percent and the counting error of 0.43 percent calculated in parts (a) and (b) of this section, respectively, for the (422) reflection of NaCl, have been assigned as beam intensity calibration errors for the measurements of all other reflections. As these two errors are independent, the total calibration error is taken as \[
\left[(0.28)^2 + (0.43)^2\right]^{1/2} = 0.51\text{ percent.}
\]

e) **Decomposition error.** The solid solution containing 75 percent sodium chloride represents a special case, for in addition to the preceding errors there is also the error introduced by the necessity of correcting the integrated intensities for the effect of decomposition, as discussed in Section C of this chapter. While it
is believed that the theory of correction introduces no significant error in itself, the accuracy of the correction is limited by the accuracy with which the integrated intensity of the appropriate reflection of the decomposed phase can be experimentally measured.

The uncertainty in the intensity of the reflections used, either the (422) or the (600) lines of the phase containing 25 percent sodium chloride, are estimated to be about 4.0 and 20 percent, respectively. The large uncertainty in the intensity of the (600) reflection is a result of its low intensity and proximity to another reflection. The (422) reflection was used to correct the intensities of the (400) through (333,511) reflections, and the (600) reflection was used to correct the intensities of the (400) through (731,553) reflections. The corrections to the intensity for decomposition may be obtained by subtracting the observed from the corrected intensity of these reflections, as given in the second and sixth columns, respectively, of Table 9. The estimated uncertainty in these decompositions corrections is assumed to be 4 percent or 20 percent of the correction itself, depending upon whether the correction was based on the (422) or (600) reflection, respectively. This leads to the following estimated errors from this source in the integrated intensities for the indicated reflections of the 75 percent NaCl-25 percent NaBr solid solution: (400), 0.4; (331), 3.2; (420), 0.5; (422), 0.5; (333,511), 0.6; (440), 1.6; (531), 2.4; (600,442), 1.5; (620), 1.0; (533), 1.8; (622), 1.0; (444), 19; (711,551), 0.2; (640), 3.0; (642), 0.7; and (731,553), 4.4 percent.
f) **Total estimated error.** The particle size, counting rate, resolution, calibration and decomposition errors considered in the preceding parts of this section are independent, or essentially so. The total estimated mean percentage error in the integrated intensity of each reflection is, therefore, taken to be the square root of the sum of squares of those of the preceding errors that are applicable in each case. The structure factor for each reflection is proportional to the square root of the integrated intensity, and is, therefore, assigned half the total percentage error calculated for the intensity. These estimated percentage errors in the calculated structure factors are given in the final column of Tables 10 through 14. They are limited to errors of accidental type, and do not include systematic errors which are considered in Section 2-3 of this chapter.

2. Observed Deviations of Structure Factors of NaCl from Smoothed Values

As is well-known, the scattering power of an atom or ion having a spherical distribution of mean charge density depends on the Bragg angle, \( \theta \), and wave length of the x-radiation, \( \lambda \), only through the ratio \( (\sin \theta / \lambda) \). An equivalent statement is that the scattering power is in this case a function only of the distance from the origin of the reciprocal lattice of the crystal to the (hkl) reciprocal lattice point corresponding to the reflection having these indices. If, as is usually approximately true, the total charge density in a crystal corresponds to a simple superposition of atomic charge densities, the structure factor of the crystal is the sum of the scattering powers of the atoms within a unit cell, each multiplied by a phase factor.
which depends on its position and is complex in general. However, in the NaCl type lattice these phase factors are ±1, and it is readily shown that the structure factor per ion pair for the (hkl) reflection has the form

$$F_{hkl} = f_+ \pm f_-,$$

where $f_+$ and $f_-$ are the scattering powers of the cation and anion, respectively, and the plus or minus sign is to be used for $h+k+l$ an even or odd integer, respectively. It follows that if the atoms retain their spherical symmetry in the lattice, and the superposition approximation is valid, the structure factors for even $h+k+l$ will be a function only of $(\sin \theta / \lambda)$, or of the distance from the origin in reciprocal space, and similarly for odd $h+k+l$. The functions will, of course, be different for the even and odd structure factors, the latter being everywhere smaller in magnitude than the former, and vanishing for the special case $f_+ = f_- \ (\text{which is approximately fulfilled in the KCl or } K'^+Cl^- \text{ crystal}).$

The experimental structure factors given in Tables 10 through 14 have been plotted versus $(\sin \theta / \lambda)$ in Figures 27 through 31. It is clear that the even and odd structure factors are to a good approximation continuous functions of $(\sin \theta / \lambda)$. (For the solid solutions the structure factors obtained from the intensities of the Laue-Bragg reflections are mean values averaged over all unit cells of the lattice). Examination of the relatively small deviations of the observed structure factors from the smooth curves in these figures has failed to reveal any systematic dependence of these deviations on the indices (hkl) of the reflections. It, therefore, seems probable that these deviations are a result of accidental experimental errors of the type considered...
in the preceding section, rather than a consequence of failure of the superposition approximation or non-sphericity of the ions. Of course, departures of the latter type must occur as a result of overlap of atomic orbitals, polarization, etc., but evidently the deviations produced by these effects are smaller than the accidental experimental errors of the present investigation.

The preceding conclusion is supported by the detailed analysis of the observed deviations for NaCl presented in Table 15. This is the most favorable case for consideration as the data covers the greatest range of the Bragg angle, $\Theta$, and the errors are smallest due to the absence of bromine fluorescence. In Table 15 the second column lists the observed structure factors, as given in the seventh column of Table 10. These values were plotted on an enlarged version of Fig. 27 in which the scale for $F$ was 0.02 per millimeter, and the scale for $(\sin \Theta/\lambda)$ was 0.001 reciprocal Angstroms per millimeter, and the best smooth curves drawn with a spline through the even and odd structure factors. The smoothed values of $F$ read from these curves at the experimental values of $(\sin \Theta/\lambda)$ are given in the third column of Table 15, and the deviation of each observed value of $F$ from the corresponding smoothed value is given in the fourth column, as $\Delta F$. These are converted to observed percentage deviations in the fifth column, while the final column of Table 15 lists the estimated values of the total mean accidental error as given in the final column of Table 10. The observed mean absolute deviations are $\pm 0.065$ and $\pm 0.051$, and the observed mean relative deviations are $\pm 1.56$ and $\pm 2.92$
TABLE 15

Deviations of Structure Factors for NaCl from Smoothed Values

<table>
<thead>
<tr>
<th>hkl</th>
<th>Structure Factor, $F$</th>
<th>$\Delta F$</th>
<th>$100(\Delta F/F)$</th>
<th>Est. Error (percent)</th>
</tr>
</thead>
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<td>9.50</td>
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<td>0.0</td>
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<td>7.665</td>
<td>0.005</td>
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</tr>
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<tr>
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<tr>
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</tr>
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<tr>
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Mean Absolute Deviation ± 0.065 ± 1.56 ± 1.31

<table>
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<tr>
<th>hkl</th>
<th>Structure Factor, $F$</th>
<th>$\Delta F$</th>
<th>$100(\Delta F/F)$</th>
<th>Est. Error (percent)</th>
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</thead>
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<td>531</td>
<td>2.29</td>
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<tr>
<td>533</td>
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</table>

Mean Absolute Deviation ± 0.051 ± 2.92 ± 4.17
percent, for the even and odd reflections, respectively. The estimated mean accidental errors are 1.31 and 4.17 percent for the even and odd reflections, respectively. The ratio of the observed to the estimated mean percentage deviation is 1.2 for the even reflections (0.9 if the abnormally large percentage deviation for the weak (840) reflection is omitted from the average), and is 0.7 for the odd reflections. Thus, the observed deviations are in qualitative agreement with the estimated accidental errors, within the uncertainty of the latter.

3. Comparison of Structure Factors of NaCl with Other Experimental and Theoretical Values

a) Experimental values. In the present section the relative structure factors for NaCl obtained in this investigation are compared with the results of other investigators. Several investigations of the absolute intensities of the reflections from single crystals of NaCl have been reported. The very early measurements of Compton and Wasastjerna on the (200) reflection were made before the role of secondary extinction was elucidated and are only of historical interest now. The first extensive series of measurements on single crystals of NaCl was that of Bragg, James, and Bosanquet (31). These authors carried out the first systematic investigation of secondary extinction in a single crystal, and developed a procedure for correcting the measured intensities for extinction which has been used by subsequent investigators. A critical discussion of this aspect of the single crystal measurements of these and other investigators is given.
in Section E-3b of the present chapter. Bragg, James, and Bosanquet were also the first to establish that the structure factors of even and odd order for NaCl lie on separate smooth curves within the accuracy of the experimental data. Apparently for this reason, and also because their primary objective was the investigation of the electron distribution in the ions, they followed the unusual procedure of listing smoothed and interpolated values of the even and odd structure factors at even intervals of \( \Theta \) (other than the one absolute value, \( F_{200} = 20.10 \), to which their other values are referred). In view of this, no detailed comparison will be made with their work, but it merits mention because of their study of secondary extinction. However, sometime after the work of these authors additional measurements with the same radiation, Rh \( \alpha \), and improved experimental conditions were carried out by Bosanquet. He obtained somewhat higher values for the higher-order structure factors than were obtained by Bragg, James, and Bosanquet. Although Bosanquet apparently never published his results, some of his structure factors are given by James and Firth (35), and it is these values that are listed in the second column of Table 16.

James and Firth (35) carried out measurements of the intensity of reflection from single crystals of NaCl at 86, 290, and 900°K, using Mo Ka radiation, with a view to studying the effect of thermal vibration on the intensities. All their values are relative to the value for the (200) reflection, which they determined on an absolute basis. The values of the structure factors given in the third column of Table 16 are those obtained at 290°K, which is also the approximate
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*The structure factors obtained in this research, and those of Havighurst, are relative values measured with a powder sample, while the values of the remaining investigators are reported as absolute values obtained using single crystals. See the test for the procedure used in adjustment of the absolute values for the two former investigations, and for references. Values in parentheses have been interpolated graphically.
temperature at which all other data in Table 16 were obtained. A theoretical analysis of the temperature dependence found by James and Firth was given by Waller and James (36), and the temperature factors they report for the Na\textsuperscript{+} and Cl\textsuperscript{−} ions are discussed subsequently.

Brill, Grimm, Herman and Peters (37) were the first investigators to carry out intensity measurements from single crystals of NaCl using incident Mo K\textsubscript{α} radiation made monochromatic by preliminary reflection. These measurements, which were made by the reflection method, were carried out on an absolute basis, using both photographic and counting methods to determine the power of the incident radiation. For the values of the integrated intensities of the reflections of high and medium intensity measured with monochromatic radiation an estimated total error of 1 to 2 percent is given, while for the weak reflections where monochromatic radiation was not used the error in the intensities is estimated to be from 5 to 10 percent. The values of the structure factors for NaCl reported by these workers are given in the fourth column of Table 16.

Renninger (38) has measured the absolute intensity of x-ray reflections from single crystals of NaCl at room temperature and at 20°C using Mo K\textsubscript{α} (as well as Cu K\textsubscript{α} and Ag K\textsubscript{α}) radiation from a crystal monochromator in order to re-determine with greater accuracy the values of the temperature factors and the scattering powers of the ions in NaCl. The experimental values of the structure factors of NaCl reported by Renninger are given in the fifth column of Table 16.
The most recent absolute reflection intensity measurements from NaCl have been made by Witte and Wölfel (39), and the experimental structure factors obtained by these workers are given in the sixth column of Table 16. The intensities of the reflections were measured from single crystals by the transmission method using Mo Kα radiation. The total probable error in each structure factor, which includes the uncertainty in the measurement of the incident radiation, the error in the determination of the integrated intensity of the reflection, and the error in the determination of the baseline of the background radiation, is estimated by the authors to be about 2.4 percent. A detailed redetermination of the effect of secondary extinction on the intensity of the most intense reflections is also given by these workers, and this will be discussed further in the following section.

The structure factor data given in Table 16 as reported in the investigations discussed above (35, 37, 38, 39) were all determined by absolute intensity measurements on single crystals of NaCl. However, the experimental structure factors given in the last two columns of Table 16 as determined by Havighurst (16) and in the present research are relative values determined by measuring the relative intensities of the reflections from briquets of NaCl powder. In both investigations Mo Kα radiation was employed. Havighurst estimates that the error in his measured intensities of the reflections is about 5 percent, except in the case of very weak reflections for which it is greater. The relative structure factors of NaCl reported by Havighurst and given in the seventh column of Table 16 are based on an
assigned value of $F=15.75$ for the (220) reflection, which is according to Havighurst the value of $F$ for this reflection as determined on an absolute basis by Bragg, James, and Bosanquet (31). The structure factor values reported in this research for the five systems studied (including those given in the last column of Table 16 for NaCl) are all relative to a value of 9.50 which was arbitrarily selected for the structure factor of the (422) reflection of NaCl. This particular value was chosen simply as an average of the other values of $F$ for this reflection given in Table 16, and in view of the considerable range of values obtained by these workers cannot be considered to be particularly reliable. In fact, the comparison of the values of the relative experimental scattering factors of the ions in NaCl with the most recent quantum theoretical values which is given in Section E-3c of this chapter (and which was made at a later date than the selection of the average value 9.50 for the (422) reflection) indicates that the values of the structure factors as reported for this research may all be low by from 2 to 5 percent. However, this error in absolute value is of little importance in the present study of lattice distortion, since for the calculation of distortion factors in the following chapter, use is made only of relative intensities.

Because of the large range in the values of the structure factor for each reflection obtained in the various investigations, it is difficult to see from inspection of Table 16 the relative trends in their variation with the order of the reflection. For this reason a tabulation of the deviations, $\Delta F$, of the experimental structure
factors given in Table 16, $F_i$, from the values of a set of smoothed mean structure factors, $\overline{F}_i$, have been given in Table 17. The values of $\overline{F}_i$ were obtained by computing the mean of the values of the structure factors given by James and Firth, Brill and Grimm, Witte and Wolfel, Havighurst, and this research, for each reflection, plotting these mean structure factors as a function of $(\sin \theta / \lambda)$ on a large-scale graph, drawing the best curves through the points for even and odd indices, and interpolating smoothed values of $\overline{F}_i$ from these curves at the appropriate values of $(\sin \theta / \lambda)$. The deviations are given separately in Table 17 for even and odd reflections, since their structure factors lie on different curves. Also given in the table are the mean deviations, $\Delta_i$, occurring in each investigation for the even and odd reflections, as well as the mean absolute deviations of the $\Delta_i$ from $\overline{\Delta}$. The latter is a measure of the precision of each investigation, if it is assumed that the true structure factors lie on smooth curves as they will if the ions are spherical.

An inspection of Table 17 discloses that the more recent values of the structure factors obtained by single crystal measurements tend to be higher than those obtained at an earlier date. It is reasonable to presume that the most recent values are more reliable, because of the advances in technique made in this field during the past several decades. Indeed, the essential correctness of these higher values is supported by their close agreement with the theoretical values after correction for the temperature factor, as will be discussed later. However, it should again be emphasized that no significance
TABLE 17

Deviations, $\Delta_i = F_i - F'_i$, from Smoothed Mean Structure Factors of NaCl

<table>
<thead>
<tr>
<th>hkl</th>
<th>Bosanquet</th>
<th>James &amp; Firth</th>
<th>Brill &amp; Grimm</th>
<th>Renninger</th>
<th>Witte &amp; Wolfel</th>
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<tbody>
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<td>-0.93</td>
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<td>0.40</td>
<td>0.33</td>
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<td>-0.34</td>
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<td>0.66</td>
<td>-0.40</td>
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<td>422</td>
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<td>0.77</td>
<td>-0.44</td>
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<td>622</td>
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<td>0.05</td>
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<td>642</td>
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<td>0.61</td>
<td>0.25</td>
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<td>0.14</td>
<td>0.03</td>
<td>0.735</td>
<td>0.68</td>
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<td>-0.17</td>
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<td>0.79</td>
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<td>-0.24</td>
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<td>---</td>
<td>0.40</td>
<td>---</td>
<td>0.73</td>
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<td>---</td>
<td>0.42</td>
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</tr>
</tbody>
</table>

$\bar{\Delta} = \frac{1}{\Sigma} \Delta_i = -0.156 -0.213 0.112 0.601 0.708 -0.449 -0.036$

$\frac{1}{\Sigma} |\Delta_i| - \bar{\Delta} = 0.310 \pm 0.101 \pm 0.191 \pm 0.136 \pm 0.108 \pm 0.053 \pm 0.196$

<table>
<thead>
<tr>
<th>hkl</th>
<th>Bosanquet</th>
<th>James &amp; Firth</th>
<th>Brill &amp; Grimm</th>
<th>Renninger</th>
<th>Witte &amp; Wolfel</th>
<th>Havighurst</th>
<th>This Research</th>
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<tr>
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<td>333,511</td>
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<td>0.175</td>
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<td>533</td>
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<td>-0.335</td>
<td>-0.275</td>
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<td>733</td>
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<td>---</td>
<td>-0.13</td>
<td>---</td>
<td>0.14</td>
<td>---</td>
<td>---</td>
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<tr>
<td>751,555</td>
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<td>-0.07</td>
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<td>0.11</td>
<td>0.17</td>
<td>---</td>
<td>-0.36</td>
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</table>

$\bar{\Delta} = \frac{1}{\Sigma} \Delta_i = 0.00 -0.043 0.009 0.173 0.172 -0.258 -0.134$

$\frac{1}{\Sigma} |\Delta_i| - \bar{\Delta} = 0.02 \pm 0.029 \pm 0.155 \pm 0.061 \pm 0.038 \pm 0.075 \pm 0.210$
is to be attached to the lower values of the structure factors given in Table 16 for this research, as their absolute values have been arbitrarily chosen. On the other hand, it is significant that the rate of decrease of the values of the structure factors with increasing order of the reflections is somewhat greater for this research than for the most recent single crystal investigations, as can be seen from Table 17. Since the trend in the variation of the structure factors found in this research is in good agreement with that found by Havighurst, it seems probable that this difference in trend is an effect connected with the use of powder rather than single crystals. This effect may be simply due to systematic error in the powder measurements, resulting for example from the greater background intensity, or it may conceivably represent a real but not yet understood difference between powder and single crystal reflectivity. A possible explanation along the latter lines will be considered in Section E-3(c).

Aside from this difference in trend, the values of the structure factors for sodium chloride obtained in this research do appear to be anomalously high for the (400) and perhaps also the (420) reflection. This may be due to some systematic error such as particle orientation or unknown optical aberration of the spectrometer. The occurrence of the former source of error to the extent required to account for these results seems unlikely, however, in view of the internal consistency of the structure factor data obtained in this study (see Section E-2 of this chapter). Since the contours of the (400) reflections of the materials studied are somewhat broader than those of the other
reflections, it is possible that these most forward reflections are affected by some aberration due to misalignment of the instrument or some other cause. Furthermore, it should be mentioned that there are still unsettled questions regarding the correction for secondary extinction in single crystal measurements as will be discussed in the following section. Since this correction is of greatest magnitude for the most intense (and, therefore, the extreme forward) reflections, it is uncertain to what extent the values of the structure factors obtained for these forward reflections in this investigation are in error.

b) Secondary extinction. A discussion of primary and secondary extinction with particular emphasis on their importance in intensity measurements from crystals of sodium chloride has been given in Section D of Chapter V. It was pointed out there that primary extinction has been shown experimentally to be essentially absent even in large single crystals of NaCl, through the quantitative agreement of the intensity data with the theoretical formula for mosaic crystals (31). However, for mosaic-type single crystals of sufficient thickness so that an appreciable fraction of the intensity of the incident x-ray beam is absorbed in passing through them, correction must be made for secondary extinction (16). The effect of secondary extinction is to increase the effective absorption coefficient, \( \mu \), of a crystal by an increment, \( \delta \), relative to the ordinary absorption coefficient, \( \mu_0 \), when the crystal is oriented so that the incident radiation is
undergoing Bragg reflection. This result was predicted theoretically by Darwin (40), who was the first to elucidate the distinction between primary and secondary extinction. It is also confirmed experimentally by the technique described subsequently in which an x-ray beam traversing a plate-like crystal, and thus subject to absorption, undergoes Bragg reflection within the plate. Thus,

\[ \mu = \mu_0 + \epsilon, \]

where the increment, \( \epsilon \), in the normal absorption coefficient is called the extinction coefficient.

The intensity of the Bragg reflections of unpolarized radiation from a small crystal is proportional to the conventional quantity \( \omega \) defined by Eq. (3.45), which is in turn proportional to the square of the modulus of the structure factor for the given reflection. The theoretical analysis of Darwin indicated that \( \epsilon \) should be of the form,

\[ \epsilon = g_2 \omega - \left( \frac{5}{4} g_3 - g_2^2 \right) (\omega^2/\mu_0), \]

where \( g_2 \) and \( g_3 \) are constants for a given single crystal which are dependent on the degree of perfection or the mosaic structure of the particular specimen, but are independent of wave length. It is usually assumed that the quadratic term in \( \omega \) is sufficiently small so that Eq. (6.21) reduces to the simple linear form \( \epsilon = g_2 \omega \), and this is often referred to as Darwin's theoretical relation for the extinction coefficient. However, the available data on secondary extinction in sodium chloride indicates that there are significant departures from
this linear relation for the reflections of higher intensity. It seems of some importance to demonstrate this, as in no less than three of the investigations of the absolute intensities reflected from single crystals of sodium chloride the corrections for secondary extinction have been based on an assumed linear relation, $\varepsilon = g_2 Q$. Furthermore, as will be shown, there is good reason to believe that the value of $g_2$ assumed in these investigations is less than half the true value.

Only two experimental studies of secondary extinction in crystals of sodium chloride have been reported in the literature. The first of these was carried out by Bragg, James, and Bosanquet (31) and the second by Witte and Wolfe (39). In both investigations the effective absorption coefficients, $\mu$, were determined by studying the intensities of the Bragg reflections of an x-ray beam traversing a single crystal ground to a plate of uniform thickness, $t_0$, and so oriented that reflection occurred internally at a set of crystal planes. We will consider here only the simplest case in which the reflecting planes are perpendicular to the faces of the plate. The distance travelled by the incident beam within the plate, and, therefore, also the volume of the crystal contributing to the scattering per unit cross-section of the incident beam, is $t = t_0 \sec \Theta$, where $\Theta$ is the Bragg angle for the reflection. It follows from Eq. (3.44) that in the absence of absorption the integrated intensity, $J$, of the Bragg reflection would be given by $IQT$, where $I$ is the power in the incident beam. However, the incident and diffracted rays travel a combined distance of $t$ within the plate, so that

$$J = I Q t \exp (-\mu t),$$

(6.22)
where $\mu$ is the effective absorption coefficient, and $t-t_0 \sec \theta$.

Witte and Wölfel have generalized this relation for the case in which the reflecting planes are not normal to the surfaces of the plate. In both investigations measurements were carried out for several reflections, with plates of several thicknesses $t_0$, and the logarithm of either $(J/It_0)$ or $(J/It)$ plotted versus $t_0$ for each reflection. These plots were found to be linear as predicted by Eq. (6.2a), although Witte and Wölfel's data show considerable scatter for the two strongest reflections, (200) and (220). It is apparent that the values of $\mu$ and $Q$ can be calculated from the slope and intercept, respectively, of such a plot, after allowance for the factor $\sec \theta$. In general $\mu$ would be expected to approach the ordinary absorption coefficient, $\mu_0$, as $t_0$ approaches zero, and the extinction coefficient is calculated from Eq. (6.20) or as $\epsilon = \mu - \mu_0$ (however see the discussion of Witte and Wölfel's work below). Since such measurements are capable of yielding both $\epsilon$ and $Q$, it is possible to test the validity of the linear relation, $\epsilon = \epsilon_0 Q$, or conversely, the importance of the quadratic term in $Q$ in Eq. (6.21).

The more recent and thorough investigation of Witte and Wölfel will be discussed first as their data are more reliable and useful than those of Bragg, James, and Bosanquet. Table 18 shows the results obtained by Witte and Wölfel by the method described in the preceding paragraph for the five reflections for which the logarithmic plot yielded good straight lines.
### TABLE 18

Secondary Extinction in NaCl

(Data of Witte and Wölfel;
Mo Kα radiation;
\( \mu_0 = 17.38 \))

<table>
<thead>
<tr>
<th>hkl</th>
<th>( \mu )</th>
<th>( \epsilon = \mu - \mu_0 )</th>
<th>( Q \times 10^3 )</th>
<th>( \epsilon / Q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>222</td>
<td>21.96</td>
<td>4.58</td>
<td>6.39 ± 0.32</td>
<td>717. ± 36</td>
</tr>
<tr>
<td>400</td>
<td>20.63</td>
<td>3.25</td>
<td>4.00 ± 0.22</td>
<td>815. ± 45</td>
</tr>
<tr>
<td>422</td>
<td>19.50</td>
<td>2.12</td>
<td>2.08 ± 0.06</td>
<td>1020. ± 30</td>
</tr>
<tr>
<td>111</td>
<td>19.39</td>
<td>2.01</td>
<td>1.46 ± 0.06</td>
<td>1380. ± 57</td>
</tr>
<tr>
<td>440</td>
<td>18.97</td>
<td>1.59</td>
<td>1.23 ± 0.04</td>
<td>1290. ± 43</td>
</tr>
</tbody>
</table>

The values \( \epsilon = \mu - \mu_0 \) in Table 18 are those calculated by Witte and Wölfel using a value of \( \mu_0 = 17.38 \). The latter value was calculated by Wagner, Witte and Wölfel (41) from the measured transmission of a rock-salt plate of sufficient thickness so that the latter could be accurately measured mechanically. It will be noted from Table 18 that these values of \( \epsilon \) yield ratios (\( \epsilon / Q \)) showing a very marked dependence on \( Q \), so that the values of \( \epsilon \) as calculated by Witte and Wölfel are not even approximately linear. These authors show a plot of \( \epsilon / Q \) versus \( Q \) in their Figure 3, and from the limiting slope of this curve at \( Q = 0 \) they derive a value \( g_2 = 1220 \). However, a more sensitive test of the data may be obtained by plotting the values of \( \epsilon / Q \) in final column.
of Table 18 versus $Q$. If the theoretical relation for $\mu$, Eq. (6.21), is applicable this plot should be linear, with the value of the slope given by the expression

$$m = \frac{d(\epsilon / Q)}{dQ} = \left(\frac{5}{4}\epsilon_3 - \epsilon_2^2\right)/\epsilon_0$$

(6.23)

and an intercept

$$\epsilon_2 = \left(\frac{\epsilon}{Q}\right)_{Q=0} = (d\mu/dQ)_{Q=0}.$$  

(6.24)

Unfortunately, a plot of this type using Witte and Wölfel's values of $\epsilon/Q$ in the final column of Table 18 is far from linear, and $\epsilon/Q$ appears to be approaching an indefinitely large value as $Q \to 0$. In fact, the observed values of $\epsilon/Q$ for the two lowest values of $Q$ in Table 18 are already significantly greater than the extrapolated value $\epsilon_2 = 1220$ assumed by Witte and Wölfel. Any reasonable extrapolation of their values of $\epsilon/Q$ which took account of the data for the (111) and (400) reflections would yield a value of $\epsilon_2$ as defined by Eq. (6.24) of at least 1700. As a result of this apparent inconsistency W. J. Taylor was led to the following critical reexamination and recalculation of the data of Witte and Wölfel which appears to yield remarkable agreement with the theoretical expression for the extinction coefficient, Eq. (6.21), as well as physically reasonable values for the constants $\epsilon_2$ and $\epsilon_3$, and probably represents the correct treatment of secondary extinction in sodium chloride.

A large scale plot of the values of $\mu$ in Table 18 versus the values of $Q$ shows that the data lies on an apparently smooth curve of slight negative curvature, except for the value of $\mu$ for the (111)
reflection, which is clearly high by about 1.3 per cent. Extrapolation of a smooth curve through the other four points yields 
\[ \mu_0 = 18.18 \pm 0.04. \] No reasonable weighting of the data in Table 18 could possibly yield a value of \( \mu_0 \) less than 18.10, to say nothing of a value as low as 17.38, which was the value obtained in a separate investigation on the same rock salt plates by Wagner, Witte, and Wölfel, and used by Witt and Wölfel for the calculation of \( \epsilon \). The basis for this inconsistency is not understood, but may be related to the fact that the value 17.38 is the measured absorption coefficient when Bragg reflection is absent, while the extrapolated value \( \mu_0 = 18.18 \) refers to radiation which has undergone Bragg reflection within the salt plate. The former radiation was reflected from a crystal monochromator (pentaerythritol), but the latter is in effect further monochromatized by the additional Bragg reflection within the plate. The accurate determination of \( \mu_0 \) is difficult, and a considerable range of values has been reported. Havighurst (16) gives the value 17.45, and James and Firth (35) report the measured values 16.53, both of which are lower than the value of Wagner, Witte, and Wölfel. However, Jönsson (42) subsequently reported in his Upsala dissertation a value of \( \mu_0 = 18.13 \) for NaCl, as the result of a specialized investigation of absorption coefficients. Jönsson's results were accepted as the best available by the 1935 edition of the International Tabellen (34), and is in excellent agreement with the value 18.18 obtained by extrapolation of the data in Table 13. In any case it seems essential to use the extrapolated value in correlating the extinction data of Witte and Wölfel, rather than the lower value of Wagner, Witte and Wölfel,
because the principal objective of the correlation is the calculation of \( g_2 \) which, by Eq. (6.24), is the limiting slope at \( Q=0 \) of the smooth curve through the data. It is impossible to calculate a meaningful derivative with the use of a value of \( \mu_o \) which departs grossly from the intercept of the extrapolated smooth curve. On the other hand the use of the extrapolated value of \( \mu_o \) will give values of \( \varepsilon \) and \( g_2 \) which are strictly correct if the \( \mu \)'s are subject to a constant error, and which are essentially correct if the \( \mu \)'s are subject to a small constant percentage error.

The extinction data of Witte and Wolfel in Table 18 has been recomputed in Table 19 using the smoothly extrapolated absorption coefficient at zero intensity \( \mu_o = 13.18 \) for the computation of \( \varepsilon = \mu - \mu_o \).

### TABLE 19

Recomputation of Secondary Extinction in NaCl

(Data of Witte and Wolfel; K\(\alpha\) radiation; \( \mu_o = 18.18 \))

<table>
<thead>
<tr>
<th>hkl</th>
<th>( \mu )</th>
<th>( \varepsilon = \mu - \mu_o )</th>
<th>( Q \times 10^3 )</th>
<th>( (\varepsilon/Q)_{obs} )</th>
<th>( (\varepsilon/Q)_{calc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>222</td>
<td>21.96</td>
<td>3.78</td>
<td>6.39 ± 0.32</td>
<td>592. ± 30.</td>
<td>591.</td>
</tr>
<tr>
<td>400</td>
<td>20.63</td>
<td>2.45</td>
<td>4.00 ± 0.22</td>
<td>613. ± 34.</td>
<td>615.</td>
</tr>
<tr>
<td>422</td>
<td>19.50</td>
<td>1.32</td>
<td>2.08 ± 0.06</td>
<td>635. ± 18.</td>
<td>634.</td>
</tr>
<tr>
<td>111</td>
<td>19.39</td>
<td>1.21</td>
<td>1.46 ± 0.06</td>
<td>820. ± 34.</td>
<td>640</td>
</tr>
<tr>
<td>440</td>
<td>18.97</td>
<td>0.79</td>
<td>1.23 ± 0.04</td>
<td>642. ± 21.</td>
<td>643</td>
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</table>
Whereas the values of $\varepsilon /Q$ in Table 18 are not even approximately linear and do not approach any clear cut limit as $Q \to 0$, the values of $(\varepsilon /Q)_{\text{obs}}$ in Table 19 (exclusive of that for the (111) reflection which is grossly in error) lie on a straight line with an average deviation of only $\pm 1$ in $\varepsilon /Q$. Since the errors estimated by the authors are 20 to 30 times this magnitude, the accuracy with which the data satisfy the linear relation is no doubt partly fortuitous; on the other hand it is clear that the precision of the data is much greater than the error estimates of Wittte and Wölfel would indicate, except for the (111) reflection for which it is much worse. Extrapolation of the linear relation for $\varepsilon /Q$ to obtain the intercept at $Q=0$ yields, in accord with Eq. (6.24) and with a liberal estimate of the precision of the extrapolated value, $g_2 = 6.55 \pm 0.5$. This is scarcely more than half the value 1220. deduced by Wittte and Wölfel using a value of $\mu_0$ inconsistent with the extinction data. The slope of linear plot yields, in accord with Eq. (6.23), $g_2 = (1.00 \pm 0.05) \times 10^4$, where again the error represents an estimate of the precision rather than of the accuracy of the data. Substitution of these values of $g_2$ and $m$, and $\mu = 18.18$, in Eq. (6.23) yields $g_2 = 4.9 \times 10^5$, and $(g_3/g_2^2) = 1.14$. The values of $\varepsilon /Q$ calculated from Eq. (6.21) with these values of the parameters are given in the final column of Table 19.

The preceding values of the three parameters, $\mu_0$, $g_2$, and $g_3$, in Eq. (6.21) have been deduced from four experimental points and a further independent check is, therefore, desirable. This may be obtained by making use of the values $Q=22.6 \times 10^{-3}$ and $10.9 \times 10^{-3}$ obtained by
Witte and Wölfel for the (200) and (220) reflections, respectively, using fine sodium chloride powder. The latter was obtained by precipitation from solution, and had a crystallite size not greater than one micron, so that the powder data may be assumed to be free of extinction effects. Because of the scatter of their extinction data for these two reflections in the plot of $\log_{10}(J/It)$ versus $t_0$ discussed following Eq. (6.22), Witte and Wölfel relied on the powder data rather than attempting to correct the internal plate reflection data for these reflections for extinction. Substitution of the powder values of $Q$ into Eq. (6.21), as well as the values of $\mu_0$, $g_2$, and $g_3$ calculated above, yields values of $\zeta = 9.70$ and $5.95$, and, therefore, $\mu = 27.38 \text{ and } 24.13$, for the (200) and (220) reflections, respectively. From Eq. (7) of Witte and Wölfel (39), the plot of $\log_{10}(J/It)$ versus $t_0$ should have a slope of $(\mu \log_{10} e/\cos \theta)$, where $\theta$ is the Bragg angle for the reflection, and an intercept $\log_{10} Q$, at $t_0=0$. Using the preceding values of $\mu$ calculated from Eq. (6.21), and the Bragg angles $\theta = 7.25$ and $10.28$ degrees, yields calculated slopes for the logarithmic plot of $-12.2$ and $-10.65 \text{ cm}^{-1}$ for the (200) and (220) reflections, respectively. These are, of course, predicted slopes based on the plate reflection data for the reflections reported in Table 19, and the powder data (with extinction absent) for the (200) and (220) reflections, but without reference to the plate reflection data for the latter two reflections. In spite of this, they are in remarkably good agreement with the experimental slopes based on the plate reflection data for these two reflections, which are estimated as
\(-11.8 \pm 1.5\) and \(-10.6 \pm 1.0\), respectively, by careful measurement of the dashed lines in Fig. 1 of Witte and Wölfel. The relatively large estimated errors are a result of the scatter of the data for these two reflections. The dashed lines were drawn by Witte and Wölfel so as to have intercepts at \(t_0=0\) equal to \(\log_{10} Q\), where the value of \(Q\) was taken from the powder data. Thus, the experimental slopes are dependent to some degree on the powder data. The agreement of the calculated and experimental slopes for the logarithmic plots, well within the accuracy of the latter, is a particularly striking confirmation of Darwin's theoretical relation, Eq. (6.21), and the calculated values of the parameters in this equation, because the values of \(Q\) for the (200) and (220) reflections on which the predicted values are based are, respectively, 3.7 and 1.7 times as large as the greatest value of \(Q\) used in the determination of the parameters \((6.39 \times 10^{-3}\) for the (222) reflection).

The essential correctness of the preceding analysis of the extinction data of Witte and Wölfel for sodium chloride becomes still more convincing when the calculated values of \(g_2\) and \(g_3\) are inserted in the theoretical expressions for those parameters. Denote by \(\theta_0\) the mean angle at which a given Bragg reflection from a mosaic type crystal occurs, and let \(G(u)\) be the fraction of mosaic blocks so oriented that they give rise to the (same) reflection at a Bragg angle of \(\theta_0 + u\), where \(u\) is small.

Then

\[
\int_{-\infty}^{\infty} G(u) \, du = 1,
\]

(6.25)

where the limits of integration have been extended to \(u = \pm \infty\) for
convenience (James (28) normalizes the distribution function for $u$ to the value $Q$, but it is here normalized to unity for simplicity). Normally it is expected that $G(u) = G(-u)$, so that

$$\bar{u} = \int_{-\infty}^{\infty} u G(u) \, du = 0 ; \quad (6.26)$$

in this case $\Theta_0$ will be the calculated Bragg angle referred to the crystal planes or face. The root-mean-square angular deviation of the mosaic blocks from their mean orientation is

$$\sigma_u = \left( \overline{u^2} \right)^{\frac{1}{2}} , \quad (6.27)$$

where

$$\overline{u^2} = \int_{-\infty}^{\infty} u^2 G(u) \, du . \quad (6.28)$$

The relation of $g_2$ and $g_3$ to the distribution function is as follows:

$$g_2 = \int_{-\infty}^{\infty} G^2(u) \, du , \quad (6.29)$$

$$g_3 = \int_{-\infty}^{\infty} G^3(u) \, du . \quad (6.30)$$

It is not possible to proceed further without specifying the form of the function $G(u)$. However, as the number of mosaic blocks in a macroscopic crystal of this type is extremely large, and the orientation of the blocks is determined by essentially Markovian or stochastic processes, it may be anticipated on the basis of the central limit theorem of mathematical statistics that $G(u)$ will be very nearly a normal error or Gaussian function,

$$G(u) = \left( \frac{1}{\sqrt{2\pi} \sigma_u} \right) \exp \left( -\frac{u^2}{2 \sigma_u^2} \right) . \quad (6.31)$$

Here $\sigma_u$ is defined by Eqs. (6.27) and (6.28), and $G(u)$ is normalized
in accord with Eq. (6.25). Substitution of Eq. (6.31) in Eqs. (6.29) and (6.30), and evaluation of the integrals yields

\[ g_2 = \left( \frac{1}{2} \sqrt{\pi} \sigma_u \right), \quad (6.32) \]

\[ g_3 = \left( \frac{1}{2} \pi \sqrt{3} \sigma_u^2 \right). \quad (6.33) \]

Thus, for a Gaussian angular distribution of the mosaic blocks, the root-mean-square angular deviation, \( \sigma_u \), from the mean Bragg angle is related to the observed secondary extinction coefficient, \( g_2 \), of Eqs. (6.21) and (6.24) by the equation

\[ \sigma_u = \left( \frac{1}{2} \sqrt{\pi} g_2 \right). \quad (6.34) \]

In addition, the coefficients \( g_2 \) and \( g_3 \) in Eq. (6.21), or Eqs. (6.23) and (6.24), should satisfy the relation

\[ \left( g_3/g_2 \right)^2 = \left( 2/\sqrt{3} \right) = 1.155. \quad (6.35) \]

This is in excellent agreement with the observed value of 1.14 given following Table 19, which may be regarded as a striking experimental justification of the Gaussian distribution.

Substitution of the value \( g_2 = 655. \), calculated above on the basis of a reanalysis of Witte and "Hifel's secondary extinction data for polished natural rock salt plates, yields \( \sigma_u = 4.3 \times 10^{-4} \) radian, or 90 seconds of arc. Rocking angles for the (200) reflection of rock salt determined by the double crystal diffraction method have been reported by Renninger (43). For artificial crystals with a fresh cleavage face he finds a rocking angle of 3.5 seconds. This is in reasonable agreement with the theoretical natural line width of 5 seconds for a perfect crystal (7), indicating that the artificial
crystals used were essentially perfect without significant mosaic structure. Presumably artificial sodium chloride crystals of this type would show significant primary extinction, but little secondary extinction. On the other hand natural rock salt crystals with a fresh cleavage face showed rocking angles of 40 to 50 seconds, which increased to 900 seconds for a polished face. It is reasonable to attribute the rocking angles obtained with fresh cleavage faces to the natural mosaic structure of the crystal, and the increment observed on polishing to additional deformation of the surface layers. The surface layers would be of greatest importance for reflections from crystal faces, such as are used in the determination of rocking angles. On the other hand, even though Jitte and Gölfel's data was taken with sodium chloride plates having polished faces, the Bragg reflections of the transmitted beam occurred at internal crystal planes which were not parallel to the faces, and the secondary extinction would be expected to be determined by the natural mosaic structure of the crystal rather than the surface layers. Thus the value of $\sigma_u$ calculated above is of the right order of magnitude. Exact agreement is not to be expected because of the variation among different crystal specimens.

The only other reported study of secondary extinction in sodium chloride is the early work of Bragg, James, and Bosanquet (31) which was done with rhodium Kα radiation. The results of their investigation are given in Table 20 (because the present crystallographic conventions were not yet well established, these authors halved the
Miller indices for even reflections from sodium chloride).

TABLE 20

Secondary Extinction in NaCl

(Data of Bragg, James, and Bosanquet; Rh Kα radiation; $\beta_0=10.70$)

<table>
<thead>
<tr>
<th>hkl</th>
<th>$\mu$</th>
<th>$\varepsilon = \mu - \mu_0$</th>
<th>$(J/I) \times 10^3$</th>
<th>$\varepsilon' \times 10^3$</th>
<th>$(\varepsilon'/\lambda')_{\text{obs}}$</th>
<th>$(\varepsilon'/\lambda')_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>15.30</td>
<td>5.60</td>
<td>0.541</td>
<td>17.54</td>
<td>317.</td>
<td>355.</td>
</tr>
<tr>
<td>220</td>
<td>13.60</td>
<td>2.90</td>
<td>0.260</td>
<td>7.07</td>
<td>410.</td>
<td>535.</td>
</tr>
<tr>
<td>400</td>
<td>12.60</td>
<td>1.96</td>
<td>0.102</td>
<td>2.58</td>
<td>760.</td>
<td>610.</td>
</tr>
<tr>
<td>600</td>
<td>10.72</td>
<td>0.02</td>
<td>0.0250</td>
<td>0.536</td>
<td>49.</td>
<td>645.</td>
</tr>
</tbody>
</table>

The values of the absorption coefficient, $\mu$, in Table 20 were obtained by the method previously described in which the intensity of Bragg reflection of a beam transmitted through plates of varying thickness is studied; in fact the method was originated by these investigators. Plots of $\log_{10}(J/I_0)$ versus $t_0$ yielded straight lines from the slope of which $\mu$ was calculated. The extinction coefficient, $\varepsilon$, was calculated from these values of $\mu$ and $\mu_0$ as given in Table 20. Thus the values of $\mu$ and $\varepsilon$ are based on transmission measurements through plates. However, these authors did not calculate the values of $Q$ under the same conditions from the intercepts of the straight lines of the logarithmic plots at $t_0=0$ as
previously discussed, and it is not possible to recover these values from their published data as only relative intensities are given.

The reason these authors did not emphasize the $Q$ values for the transmission measurements was that their principal objective was to obtain extinction data for correcting independently obtained front-face reflection intensity data from (different) sodium chloride crystals.

These reflection intensities, $J/I$, as given in Table 20 have been calculated from the absolute value for the (200) reflection, $J/I = 0.541 \times 10^{-3}$, and the relative values for the other reflections as given in their paper. The values of $Q'$ in Table 20 have then been calculated from the intensities and the theoretical relation applicable to reflection from the face of an infinitely thick crystal,

$$ Q = 2\sqrt{J/I}, \quad (6.36) $$

a relation also assumed by Bragg, James, and Bosanquet. These are, therefore, composite values of $Q$ based on the intensities from crystal faces and absorption coefficients measured for separate crystalline plates.

As a justification for this procedure these authors also calculated the value of $Q$ for the (200) reflection applicable to the plate measurements by a variation of the preceding method also based on Eq. (6.22). In this method $(J/I)$ is plotted versus $t_0$, and it easily shown that

$$ Q = e \sqrt{J/I}_{\text{max}}, \quad (6.37) $$

where $(J/I)_{\text{max}}$ is the maximum ordinate of the resulting curve and $e$ is
the base of natural logarithms. This yielded $Q = 16.16 \times 10^{-3}$ for the (200) reflection, which is 8.4 percent lower than the composite value $Q' = 17.64$ given in Table 20. They regarded this as a satisfactory indication of the approximate equality of $\mu$ for the crystal plates and the crystals used in the front-face reflection measurements and did not consider the question further. However, the value $Q$ above is calculated using intensities and an absorption coefficient for the same crystal plates and must be presumed to be the more reliable value (assuming comparable accuracies for the intensities). As shown by Eq. (3.45), $Q$ should have the same value for the preceding two experiments, since the crystal, temperature, wave length, and value of $\theta_0$ were the same. The difference in the measurement of the intensities in Eqs. (6.36) or (6.37), or may possibly be due to a real difference between the values of $\mu$ in the crystals used resulting from a difference in their mosaic or surface structures. If the latter is assumed to be the case, insertion of $Q=16.16 \times 10^{-3}$ and $J/I = 0.541 \times 10^{-3}$ in Eq. (6.36) yields a value $\mu=14.9$ for the (200) reflection of the crystal used for the front-face reflection, as compared with the value 16.30 for the corresponding reflection of the crystal plates. The value of $\mu_0$ is unaffected by mosaic structure and was presumably 10.70 for both crystals. Thus, the value of $\varepsilon = \mu - \mu_0$ for the front-reflection crystal is reduced from 5.60 to 4.2, and the value of $\varepsilon/Q$ from 317. to 260. on the above supposition. On the other hand, the plate measurements yield, for the (200) reflection, $\varepsilon/Q = (5.6/16.16) \times 10^3 = 346$. Thus, there is considerable doubt concerning the
significance of the values of $\epsilon/Q$ computed from the data of Bragg, James and Bosanquet.

Although the theoretical treatment of Darwin represents $\epsilon$ as a function of $Q$, and this functional relationship has been emphasized by later workers, Bragg, James and Bosanquet preferred to make an empirical correlation of $\epsilon$ with $J/I$. They found on the basis of a limited amount of data the linear relationship

$$\epsilon = k(J/I), \quad (6.38)$$

where $k$ is a constant. They claimed that this linear relation supported the theoretical relation of Darwin, and this statement has been repeated by James (28). However, Darwin's theoretical expression, Eq. (6.21), represents as a quadratic function of $Q$, and from Eqs. (6.20) and (6.36),

$$Q = 2(\mu_0 + \epsilon)(J/I). \quad (6.39)$$

Thus, if the linear relation, Eq. (6.38), were to hold, $Q$ would be quadratic in $(J/I)$,

$$Q = 2\mu_0(J/I) + 2k(J/I)^2, \quad (6.40)$$

and on substitution of this result in Eq. (6.21) $\epsilon$ would be found to be quartic in $J/I$. Thus Eq. (6.38) of Bragg, James and Bosanquet is inconsistent with Darwin's Eq. (6.21). It would appear from the discussion of James that he had in mind in this connection the linear approximation to Darwin's relation in which the quadratic term in $Q$ in Eq. (6.21) is ignored. However, it is easily shown that even in this case Eqs. (6.21) and (6.38) are compatible only in the trivial and physically uninteresting case $k=g_2=0$, in which case $\epsilon=0$, and
secondary extinction is absent. Furthermore the preceding analysis of the data of Witte and Wölfel shows that the quadratic term in Eq. (6.21) makes a very significant (negative) contribution to the extinction coefficient for strong reflections. For these reasons no further attention will be given to Bragg, James, and Bosanquet's empirical correlation of $\epsilon$ with $J/I$.

In three subsequent investigations of absolute intensities for single crystals of sodium chloride which have been summarized in Table 16, those of James and Firth (35), Brill et al. (37), and Renninger (38), the corrections for secondary extinction have been based on an assumed linear form of Darwin's relation,

$$\epsilon = g \zeta,$$

(6.41) corresponding either to the neglect of the quadratic term in $\zeta$ in Eq. (6.21) (in which case $g=g_2$), or the use of a mean value of $g$. In all three investigations $g$ was assigned the value 320 on the basis of the single value of $\epsilon/\zeta'$ calculated for the (200) reflection from the data of Bragg, James, and Bosanquet in Table 20. It is difficult to see how these investigators could reconcile Eq. (6.41) with the data of Bragg et al., since the final column of Table 18 shows clearly that $\epsilon/\zeta'$ is not constant, but increases markedly as $\zeta'$ decreases. Furthermore, these investigators assumed that $g$ in Eq. (6.41) is independent of the wave length of the radiation, or that depends on wave length only through $\zeta$, since they applied the value of $g$ taken from the investigation of Bragg et al. with Rh K $\alpha$ radiation ($\lambda=0.6149 \, \AA$) to their own measurements using Mo K $\alpha$ radiation ($\lambda=0.7097 \, \AA$).
It will now be shown that a qualitatively satisfactory explanation of the ratios $\xi/Q'$ obtained by Bragg et al. with Rh Kα radiation, and given in the final column of Table 18, is provided by the theoretical equation of Darwin, Eq. (6.21), using the values of $g_2=655$ and $g_3=4.9 \times 10^5$ obtained by analysis of the precise data of Witte and Wölffel. An essential feature of this explanation is the inverse dependence on $\chi_0$ of the quadratic term in $Q$ in Eq. (6.21). For Rh Kα radiation $\chi_0=10.70$, as opposed to the value 18.18 for Lα Kα radiation, so that the ratio of the negative quadratic term is considerably greater in the former than the latter case (this is true even though the values of $Q$ decrease as the wavelength decreases). Substitution of the preceding values of the parameters into Eq. (6.21) yields, for Rh Kα radiation,

$$\xi/Q = 655 - 17.0(\xi x 10^3).$$

(6.42)

If $Q$ in Eq. (6.42) is replaced by the values $Q'$ calculated from the data of Bragg et al. in Table 20, the calculated values of $\xi/Q'$ in the final column of the table are obtained. Slightly different results are obtained if the values of $Q$ measured by Bragg et al., or by Witte and Wölffel with crystal plates are inserted into Eq. (6.42). The agreement with the observed values of $\xi/Q'$ is rather rough, especially for the weaker reflections for which the observed ratios may be greatly influenced by relatively small percentage errors in the absorption coefficient, $\chi$ (for example, the observed value of $\xi$ for the (600) reflection is clearly meaningless). However, the analysis is successful in explaining the principal feature of the
results of Bragg et al., namely the much smaller values of $\epsilon/Q$
observed for the strongest reflections of sodium chloride with Rh $K$ 
radiation than with Mo $K\alpha$ radiation. Thus, from calculations given
earlier, the corresponding calculated values for the (200) and (220)
reflections for Mo $K\alpha$ radiation, which are in good agreement with
the experimental observations of Witte and Hölfel, are $\epsilon/Q = 429$ and
546, respectively. At the same time, it is clear that there is no
justification for assuming a constant value of $g = \epsilon/Q = 320$ for
either Rh $K\alpha$ or Mo $K\alpha$ radiation, or for both, as was done in the
three investigations referred to. This is approximately the correct
value of $\epsilon/Q$ for the (200) reflection for Rh $K\alpha$ radiation, but the
correct value increases progressively as $\lambda$ decreases. On the other
hand, the value 320 is far smaller than the correct value even for
the (200) reflection of sodium chloride with Mo $K\alpha$ radiation. It is
clear that the corrections of the intensities for secondary extinction
in the three investigations of single crystals of sodium chloride
referred to have been made on a basis which is in conflict with both
Darwin's theory and the available experimental data. The value
$\epsilon/Q = 320$ (and, therefore, the extinction coefficient, $\epsilon$) used by
these authors is low by 25 percent for the strongest reflection, and
50 percent for the weak reflections. The resulting error in the
calculated absorption coefficient, $\mu$, is -8.8 percent for the (200)
reflection, corresponding to an error of -4.4 percent in the calculated
structure factor, $|F|$, for this reflection. For weaker reflections
the errors are smaller. This is in at least qualitative agreement with the fact that in the present investigation of sodium chloride powder, in which secondary extinction is absent, relatively higher structure factors are obtained for the stronger reflections. Higher values are also obtained by Witte and Wölfel who used experimental values of $Q$ for powders for the (200) and (220) reflections, and their experimentally measured absorption coefficients for the next five strongest reflections.

e) Comparison of experimental and theoretical scattering factors and calculation of temperature factors. In this section the values of the experimental scattering factors of the Na\(^+\) and Cl\(^-\) ions are compared with the theoretical $f$ values for their ions. Theoretical scattering factors are calculated by the Fourier transforms of the atomic charge densities which in turn are arrived at from theoretical atomic wave functions. A general discussion of these calculations is given by James (Chapter 3 of Reference 28). Calculations of theoretical $f$ values have been based almost entirely on wave functions computed by the three methods which are discussed in the following paragraphs.

The first wave functions employed for the scattering factor calculations were computed by means of the Hartree self-consistent field (SCF) method developed by Hartree and co-workers (44) in which exchange is not included. The electron distributions given by these Hartree wave functions were used by James and Brindley (45) to
calculate the values of the theoretical scattering factors of the lighter elements. These theoretical $f$ values, a compilation of which are given in the 1935 edition of the "Internationale Tabellen" (34), are the values that have been used by x-ray crystallographers until quite recently and are the values used in Section B of Chapter VII. Since one source of error in the James and Brindley $f$ values arises from an interpolation procedure which was employed to calculate the values for many of the elements necessitated by the limited number of Hartree wave function calculations which had been made at that time, it should be noted that the $f$ values for the Na, Na$^+$, and Cl$^-$ species were all based on Hartree wave functions then available.

As is well known, a major advance in the calculation of atomic wave functions was the development of the Hartree-Fock SCF procedure by Fock and Slater. This method takes into account the electron exchange of properly antisymmetrized wave functions of the entire atom in the form of a single Slater determinant. An extensive discussion of the calculation of atomic structures by atomic wave functions has been given by Hartree (46). The Hartree-Fock method yields greatly improved energies, but produces only relatively minor changes in the atomic scattering power which depends upon the results of electron charge density calculations. There is some reason to believe that these calculations produce a greater change in $f$ values for the negative ion than for the positive ion or neutral atoms as has been pointed out by Dawson (47). The $f$ values for Na$^+$ ion have been calculated by Freeman (48) from an electron distribution based
upon the Hartree-Fock wave function calculated by Hartree and Hartree (49). The \( f \) values for the \( \text{Cl}^- \) ion were calculated by Berghuis (50) from an electron distribution computed by Hartree and Hartree (51).

The principal advance in the calculation of atomic wave functions since the Hartree-Fock method is the so-called poly-detor method developed by Boys and co-workers (52). In this method greater flexibility is introduced into the wave function by the use of a large number of Slater determinants. The method is essentially one of variation of constants whereby the coefficients of the determinants are adjusted. These improvements may be regarded as due to the more detailed additional electron distribution correlation permitted by the poly-detor method as contrasted to the Hartree-Fock method which introduces only a limited amount of electron correlation. The energies for the light atoms as calculated by the poly-detor method show an improvement over the best Hartree-Fock methods. The \( f \) values for the \( \text{Na}^+ \) ion were computed by Dawson (47) using the poly-detor wave function calculated by Bernal and Boys (53). The \( f \) values for the \( \text{Cl}^- \) ion were also computed by Dawson (54) using the poly-detor wave functions calculated by Boys and Price (55).

The theoretical \( f \) values employed in Table 21 are taken from the recent edition of the "International Tables for Crystallography" (56). The \( f \) values for the \( \text{Cl}^- \) ion are those calculated by Berghuis (50). Although the \( f \) values given in these tables for the
Na\(^+\) ion are in very close agreement but not identical with those calculated by either the Hartree-Fock or poly-deter wave functions for this ion which are referred to above, they were nevertheless used for consistency in Table 21. The theoretical values of the scattering factors of these two ions taken from the above source (56), \(f^\text{ theor}\), which are given in Table 21 for the range of \((\sin \theta/\lambda)\) experimentally measured, have been corrected for anomalous dispersion of the MoK\(_\alpha\) radiation (see Section B of Chapter VII). This is a constant correction of \(0.04\) and \(0.14\) to each of the values of \(f^\text{ theor}\) for the Na\(^+\) and Cl\(^-\) ions, respectively.

**TABLE 21**

Comparison of Experimental and Theoretical Scattering Factors of Na\(^+\) and Cl\(^-\)

<table>
<thead>
<tr>
<th>(\sin \theta/\lambda)</th>
<th>(f_{\text{exp}})</th>
<th>(f^\text{ exp})</th>
<th>(f^\text{ theor})</th>
<th>(f_{\text{exp}})</th>
<th>(f^\text{ exp})</th>
<th>(f^\text{ theor})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>5.43</td>
<td>6.75</td>
<td>5.23</td>
<td>7.36</td>
<td>9.66</td>
<td>8.88</td>
</tr>
<tr>
<td>0.40</td>
<td>4.10</td>
<td>5.54</td>
<td>5.53</td>
<td>6.68</td>
<td>8.68</td>
<td>8.29</td>
</tr>
<tr>
<td>0.50</td>
<td>2.66</td>
<td>4.06</td>
<td>4.37</td>
<td>5.07</td>
<td>7.56</td>
<td>7.44</td>
</tr>
<tr>
<td>0.60</td>
<td>1.89</td>
<td>3.46</td>
<td>3.45</td>
<td>3.77</td>
<td>6.65</td>
<td>6.74</td>
</tr>
<tr>
<td>0.70</td>
<td>1.31</td>
<td>2.96</td>
<td>2.79</td>
<td>2.80</td>
<td>6.02</td>
<td>6.05</td>
</tr>
<tr>
<td>0.80</td>
<td>0.76</td>
<td>2.18</td>
<td>2.34</td>
<td>1.99</td>
<td>5.37</td>
<td>5.38</td>
</tr>
</tbody>
</table>

The values of \(f_{\text{exp}}\) given in Table 21 for the Na\(^+\) and Cl\(^-\) ions were determined by computing one half of the difference and the sum,
respectively, of $F_{\text{even}}$ and $F_{\text{odd}}$, whose values were read at the given values of $(\sin \theta/A)$ from an enlarged version of Fig. 27 as described in Section E-2 of this chapter. Also given in Table 21 are the values of $f_0^{\text{exp}}$, which is the experimental scattering factor corrected for thermal vibration and multiplied by a scale factor so as to obtain the best overall agreement with $f_0^{\text{theor}}$. In order to determine the most suitable values for the temperature factor, $B$, for each ion and the scale factor, $K$, the quantity $\log (f_{\text{exp}}/f_0^{\text{theor}})$ was plotted as a function of $(\sin \theta/A)^2$, and the two best straight lines (one line for the data of each ion) were drawn through these points to a common intercept. In accordance with the equation,

$$K f_x = f_0^{\text{exp}} \exp = B_x (\sin \theta/A)^2,$$  \hspace{1cm} (6.43)

the slopes of these lines are equal to $-B_x/\log e$ and the intercept to $-\log K$. In this manner were obtained the values $K = 1.02$, $B_{\text{Na}^+} = 1.62$, and $B_{\text{Cl}^-} = 1.52$. These values of $B_x$ and $K$ were then used in Eq. (6.43) to compute the values of $f_0^{\text{exp}}$ given in Table 21.

Of course, the assumption is tacitly made in the above treatment that $f_0^{\text{exp}}$ should be equivalent to $f_0^{\text{theor}}$ for all values of $(\sin \theta/A)$, where the deviations due to departure from spherical symmetry as assumed in the theoretical calculations would be largest. Therefore, the positive deviations in the values of $f_0^{\text{exp}}$ from $f_0^{\text{theor}}$ at the largest values of $(\sin \theta/A)$ in Table 21 may well be a real effect, particularly in view of the analysis given in the previous section which indicates that the values of
f° obtained from single crystal measurements may show a similar deviation when more accurate correction is made for the effect of secondary extinction.

In Table 22 are given the values of the temperature factors of the Na⁺ and Cl⁻ ions reported from the various investigations cited in Section B-3(a) of this chapter. The values for the data of James and Firth (35) and Renninger (38) were determined through a study of the variation of the intensity of various reflections with temperature, and the values by Witte and Wölfel (39) were determined by a similar method as employed in the present section for the data of this research. Brill and Grimm (37) employed the same values of $B_{Na^+}$ and $B_{Cl^-}$ as determined from the earlier investigation of James and Firth for comparison of the experimental structure factors with those calculated from the theoretical scattering factors.

<table>
<thead>
<tr>
<th></th>
<th>$B_{Na^+}$</th>
<th>$B_{Cl^-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>James &amp; Firth</td>
<td>1.55</td>
<td>1.25</td>
</tr>
<tr>
<td>Brill &amp; Grimm</td>
<td>1.55</td>
<td>1.25</td>
</tr>
<tr>
<td>Renninger</td>
<td>1.25</td>
<td>1.12</td>
</tr>
<tr>
<td>Witte &amp; Wölfel</td>
<td>1.25</td>
<td>1.10</td>
</tr>
<tr>
<td>This Research</td>
<td>1.62</td>
<td>1.52</td>
</tr>
</tbody>
</table>
It will be noted in Table 22 that the values of $B$ for sodium chloride powder obtained from the present investigation are significantly higher than those determined by the single crystal investigations. Since the trend in the variation of the experimental structure factors with $(\sin \theta/\lambda)$ found in the present research is very similar to that found by Havighurst (16) as can be seen from Table 16, consideration must be given to the possibility that the high values of $B$ are associated with the use of a powder. This conjecture would imply that the $B$ which is experimentally determined is not only a function of the thermal vibration of the ions but is also a function of the nature and degree of the mosaic structure of the crystal. This hypothesis could also explain the apparent discrepancy in values obtained in the various single crystal studies, as crystals having different histories very likely have quite different internal mosaic structures. It would appear that this hypothesis could be readily tested experimentally, and it seems worthy of further investigation.

F. Accuracy of Bragg Angles and Deviation of Lattice Constants of Solid Solutions from Vegard's Law

For the principal objective of the present research, which is the investigation of the displacement disorder within the lattices of the alkali halide solid solutions, accurate x-ray diffraction intensity data are required. However, it is not of primary
importance for this purpose that the lattice constants, and, therefore, the Bragg angles for the reflections, be measured with great accuracy. This may appear to be something of a paradox, as the mean lattice expansion which occurs in the solid solutions is certainly related to some degree to the displacements or distortion about the solute (bromide) ions. However, as discussed in Chapter II, the relation is somewhat indirect. The theory given there indicates, and the present research confirms (see Chapter VII), that it is the relatively large displacements of neighboring ions by the solute ions which are primarily responsible for the decrease in the intensities of the Laue-Bragg reflections. At larger distances from a solute ion the displacements are expected to decrease rapidly, and in fact to approach asymptotically proportionality to the inverse square of the radial distance, as predicted by elastic theory for a continuum. It is the superposition of these long-range inverse-square type displacements from the solute atoms which is responsible for the homogeneous expansion of the mean lattice, as shown by the theoretical analysis of Eshelby (13). Thus, a knowledge of the mean lattice expansion provides information only about the asymptotic form of the displacements at large distances, and tells nothing concerning the details of the short-range displacement disorder primarily affecting the Laue-Bragg intensities. It is true, however, that the small inverse-square displacements at relatively large distances are responsible for part of the decrease in the Laue-Bragg intensity. A theoretical analysis of this effect has been
given by Huang (3), and an improved formula by Taylor, as discussed in Chapter II. However, highly accurate lattice constants are not required for the purpose of calculating this correction to the intensities (see Chapter VII, Section C).

Although not of primary importance in connection with the Laue-Bragg intensities and the problem of lattice distortion, precise lattice parameters for the solid solutions are of interest as an indicator of the accuracy with which Vegard's law is obeyed. The precision and accuracy of the measured Bragg angles for the pure components is also of interest as a test of the performance of the spectrometer.

In Table 23 there are tabulated the values of the Bragg angle, \( \theta_c \) in degrees, calculated from Bragg's law for the lattice constants listed at the head of the corresponding column. The lattice constants for pure sodium chloride (\( a = 5.6288 \ \text{\AA} \)) and sodium bromide (\( a = 5.9617 \ \text{\AA} \)) given in the table are those reported by Fineman, Wallace, and Nickels (18,19). The lattice constants for the solid solutions are those calculated from the lattice constants of the pure components and Vegard's law, namely,

\[
\alpha_p = (1-p) \alpha_{\text{NaCl}} + p \alpha_{\text{NaBr}}
\]

(6.44)

where \( p \) is the mole fraction of sodium bromide contained in the particular solid solution.

Also tabulated in Table 23 are the values of the deviations, \( \Delta\theta = \theta_c - \theta_c \), of the observed positions of the diffraction maxima from the calculated positions, as well as the mean deviation, \( \overline{\Delta\theta} \),
**TABLE 23**

Calculated Bragg Angles and Observed Deviations

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>100% NaCl</th>
<th>75%NaCl-25%NaBr</th>
<th>50%NaCl-50%NaBr</th>
<th>25%NaCl-75%NaBr</th>
<th>100% NaBr</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$\theta_o$</td>
<td>$\theta_o - \Delta \theta$</td>
<td>$\theta_o$</td>
<td>$\theta_o - \Delta \theta$</td>
<td>$\theta_o$</td>
</tr>
<tr>
<td></td>
<td>(5.6288Å)</td>
<td>$\theta_o - \theta_0$</td>
<td>(5.7120Å)</td>
<td>$\theta_o - \theta_0$</td>
<td>(5.7953Å)</td>
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<td>14.345</td>
<td>0.020</td>
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<td>331</td>
<td>15.905</td>
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<td>15.664</td>
<td>0.006</td>
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<td>17.402</td>
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<td>0.003</td>
<td>18.774</td>
<td>0.041</td>
<td>18.495</td>
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<td>0.077</td>
<td>22.713</td>
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<td>23.964</td>
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<td>26.529</td>
<td>0.051</td>
<td>26.119</td>
</tr>
<tr>
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<td>28.070</td>
<td>0.020</td>
<td>27.614</td>
<td>0.064</td>
<td>27.184</td>
</tr>
<tr>
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<td>28.409</td>
<td>0.041</td>
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<td>800</td>
<td>30.193</td>
<td>0.017</td>
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<td>---</td>
</tr>
<tr>
<td>820,644</td>
<td>31.225</td>
<td>0.030</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Mean $\Delta \theta (\Delta \theta)$: 0.016  0.046  0.013  0.019  0.057
Mean of $\Delta \theta$: 0.010  0.015  0.020  0.014  0.008
Mean value: 0.048  0.039  0.029  0.020  0.011

\[ \bar{\theta} - \bar{\theta} \]
0.064  0.065  0.062  0.069
of the reflections for each composition. This mean deviation may be due to any of several factors, such as error in setting the θ scale, instrumental aberrations such as penetration of the sample or vertical divergence, or deviation of the solid solutions from Vegard's law. Below the value of \( \overline{\Delta \theta} \) is given the mean value of \( \Delta \theta - \overline{\Delta \theta} \), or the mean deviation of \( \Delta \theta \) from its mean. This is a measure of the average precision of measurement of the Bragg angles, which is seen to be better than 0.02 degree.

The average values of the displacement of the maxima of the diffraction contours due to the combined effects of x-ray beam penetration into the sample and vertical divergence of the beam, or \( \overline{\varepsilon} \), have been calculated in Chapter III, Section B, and the values given in Table 23 are taken from Table 1. The use of average values of \( \overline{\varepsilon} \) is permissible here since the variation of \( \varepsilon \) with \( \theta \) in the range of \( \theta \) covered in this research is less than the mean of \( (\Delta \theta - \overline{\Delta \theta}) \) for both sodium chloride and sodium bromide as shown in Table 1 and 23. The difference of the displacements, \( \overline{\Delta \theta} - \overline{\varepsilon} \), given in Table 23 for these pure components indicates the error in the setting of the \( \theta \)-scale of the spectrometer. It is seen in the table that \( \overline{\Delta \theta} - \overline{\varepsilon} \) for pure sodium chloride and sodium bromide are in good agreement and indicate that the \( \theta \) scale as set reads about 0.066 degree too high. The values of \( \varepsilon \) for the solid solutions are interpolated linearly between those for the pure components. The data reported by Nickels (19) indicate that the lattice parameters of the solid solutions containing 25, 50, and 75 mole percent sodium bromide in
sodium chloride exhibit a positive deviation, $\Delta a$, from those predicted by Vegard's law by 0.004, 0.008, and 0.008 Angstrom unit, respectively. Correction for these deviations lowers the calculated Bragg angles $\theta_0$, by 0.014, 0.028, and 0.028 degree, respectively, for the three solid solutions. With these corrections the values of $\Delta \theta - \overline{\Delta \theta}$ become 0.099, 0.070, and 0.067 degrees, respectively, for the solid solutions containing 25, 50, and 75 mole percent sodium bromide. It is seen that these corrected values of $\Delta \theta - \overline{\Delta \theta}$ are in good agreement with those of pure sodium chloride and sodium bromide for the 50 and 75 percent solid solutions, and about 0.03 degrees too high for the 25 percent solid solution. The discrepancy in the value of the latter may plausibly be ascribed to the effect of the closely overlapping diffraction contours of sodium chloride, which was formed by the decomposition of this particular solid solution (see Section C of this chapter).
A. Atomic Scattering Factors

In Chapter II it was shown in Eq. (2.14) that the effective scattering power of an atom in a distorted lattice is the product of the atomic scattering power, $f_1$, and the characteristic function of the displacement from the mean position, $\exp(iF \cdot \mathbf{u}_1^L)$, which may be regarded as the static distortion factor. It should be pointed out that in a lattice with both static displacement disorder and thermal vibration, as are present in the solid solution studied in this research, the necessary factor is the characteristic function of the total displacement from the mean. However, if these two displacements are independent of one another, then the characteristic function of the total displacement will equal the product of the characteristic functions for the two types of displacements taken separately. Although this assumption is not strictly true, it is probably the only practical approximation at present. Therefore, in the subsequent calculations it will be assumed that the temperature factor has been absorbed into $f_1$, whence only the static disorder need be considered explicitly for each type of ion. As was shown in Chapter II, the total characteristic function of static displacement
for each type of ion in the lattice may be represented as the product of two factors, given by Eq. (2.28) and by Eq. (2.23), and the method of calculation of each of these factors for the case of those solid solutions studied in this research will be individually presented in Sections C and D, respectively.

In this section the method of determination of the experimental atomic scattering factors of the ions in the materials investigated will be presented, and in Section B the method of calculation of the temperature factors for these ions will be given, and also a comparison of the temperature corrected atomic scattering factors of the pure sodium chloride and sodium bromide with the theoretical values will be made.

For convenience of calculation it will be useful to rewrite Eq. (2.14), which defines the structure factor of the unit cell, in the following form.

\[ \langle F_{\text{cell}} \rangle = \sum_i f_i' \exp(ik \cdot \vec{r}_{iL}), \]  

(7.1)

with

\[ f_i' = f_i \left\langle \exp \left( ik \cdot \vec{u}_{iL} \right) \right\rangle \]  

(7.2)

\[ = f_i^o \left\langle \exp \left( ik \cdot \vec{u}_{iL} \right) \left( \exp -M_i \right) \right\rangle \]  

(7.3)

\[ = f_i^o \left( \exp -M_i \right), \]  

(7.4)

where \( f_i^o \), as just defined, is the atomic scattering factor of the \( i \) th ion which does not contain thermal vibration but does contain static displacement disorder, and where \( f_i^o \) is the atomic scattering factor containing both thermal vibration and static displacement.

Of course, \( f_i' \) is the effective atomic scattering factor whose value
is derived directly from the experimental intensity data. The above equations are applicable to the distorted lattices of the solid solutions as well as to the undistorted lattices of the pure salts in which case \( f_i^* = f_i^\theta \). The defining of \( f_1', f_\theta, \) and \( f_1 \) in this manner introduces no approximations other than the assumption previously mentioned that the temperature factor, \( \exp(-\frac{1}{2}M) \), which arises from distortion due to thermal vibration can be factored from the distortion due to static displacement in the disordered lattice.

In the face-centered cubic lattice of the sodium chloride type there are four anions per unit cell located at \((000), (\frac{1}{4}0\frac{1}{4}), (0\frac{1}{4}0\frac{1}{4}), \) and \((0\frac{1}{4}0\frac{1}{4})\), and four cations located at \((\frac{1}{4}0\frac{1}{4}), (0\frac{1}{4}0\frac{1}{4}), (00\frac{1}{4})\), and \((\frac{1}{4}0\frac{1}{4})\). The structure factor for this lattice per ion pair, obtained by inserting these values for the positions of the ions into Eq. (7.1), reduces to

\[
F(hk1) = \left| f_x' - f_\text{Na}^+\right|, \text{ for } h, k, l \text{ all even, } (7.5)
\]

\[
F(hk1) = \left| f_x' - f_\text{Na}^+\right|, \text{ for } h, k, l \text{ all odd, } (7.6)
\]

and with all other reflection absent. It will be noted that \( F(hk1) \), when referred to an ion pair as given in Eqs. (7.5) and (7.6), is one fourth as large as would be calculated from Eq. (7.1) with the unit cell chosen as the basic scattering unit. The experimental \( F \) values tabulated in Tables 10 through 14 are all referred to the ion pair rather than to the unit cell in order to be consistent with and to allow comparison with the experimental structure factors of sodium chloride reported by the previous investigators cited (16,35,37,38,39).
In Eqs. (7.5) and (7.6) $|f'_{x^-}|$ is the effective mean atomic scattering factor of the anion. For pure sodium chloride and pure sodium bromide $|f'_{x^-}|$ will be equal to $f^o_{Cl^-} (\exp -M_{Cl^-})$ and $f^o_{Br^-} (\exp -M_{Br^-})$, respectively, since $\langle \exp(i\vec{r} \cdot \vec{u}'_{1L}) \rangle$ will be equal to unity for both of these materials. For the solid solutions investigated $|f'_{x^-}|$ will be given by

$$|f'_{x^-}|_p = |f^o_{x^-}|_p (\exp -M_{x^-})_p \langle \exp (i\vec{r} \cdot \vec{u}'_{x^-} L) \rangle_p \quad (7.7)$$

from Eq. (7.3), where $p$ is the mole fraction of sodium bromide present in the solid solution, and where $|f^o_{x^-}|_p$ is the mean scattering factor of the anion free of vibration and distortion and defined by

$$|f^o_{x^-}|_p = (1-p)(f^o_{Cl^-})_{NaCl} + p(f^o_{Br^-})_{NaBr} \quad (7.8)$$

In Eq. (7.7) $(\exp -M_{x^-})_p$ is the appropriate temperature factor for the mean anion in the particular solid solution, and its determination will be considered in the following section.

Since the experimental values of $f'_{Na^+}$ and also the derived values of $f^o_{Na^+}$ are somewhat different from the data obtained from sodium chloride and sodium bromide, equations similar to Eqs. (7.7) and (7.8) also will be used to define the scattering factor of the cation in the solid solutions.

$$(f'_{Na^+})_p = (f^o_{Na^+})_p (\exp -M_{Na^+})_p \langle \exp (i\vec{r} \cdot \vec{u}'_{Na^+} L) \rangle_p \quad (7.9)$$

with

$$(f^o_{Na^+})_p = (1-p)(f^o_{Na^+})_{NaCl^+} + p(f^o_{Na^+})_{NaBr^+} \quad (7.10)$$

It should be mentioned that the expression for the mean scattering factor of the anion as given by Eq. (7.8) involves only the assumption that the bromide and chloride ions are randomly substituted throughout the crystal, which is equivalent to the
assumption that there exists an a priori probability $p$ (the mole fraction of $\text{Br}^-$) of locating a bromide ion at any given anion site. Since $f^0_{x-}$ for the pure salts should be smooth functions of $(\sin \theta/\lambda)$ from theoretical considerations, it follows that $|f^0_{x-}|_p$ is also a smooth function of $(\sin \theta/\lambda)$, and its values can be calculated accordingly. Also the temperature factor for the anion of the disordered solid solution in Eq. (7.7) must theoretically be a smooth function of $(\sin \theta/\lambda)$ since it represents the superimposed effect of a quasi-continuous collection of normal modes and since it furthermore represents an average over many configurations of chloride and bromide ions in the solid solution.

On the other hand that part of the distortion factor which accounts for the effect of the largest distortion displacements by the substitution defects in the nearest shells surrounding the lattice sites are not theoretically expected to be smooth functions of $(\sin \theta/\lambda)$. In fact, the detailed formulas for these largest distortions, which will be given in Section D, show that they are defined only for discrete integral values of $h, k, l$ or for those specific values of $(\sin \theta/\lambda)$ corresponding to the observed reflections. It is, therefore, to be expected that the observed scattering factors, $f_i'$, given by Eq. (7.3), will also deviate from a smooth curve. However, it will be noted in Figures 27 through 31 that the experimental points of many of the structure factor values are appreciably off of the smooth curves drawn through the points
and yet may be considered to fall on the curves to within their experimental accuracy. Anticipating the results of the calculations to be made in Section D, it is asserted that the calculated deviations of the structure factors from the smooth curves due to the discrete distortion factors are always very much less than the deviation due to experimental error. Therefore, in the following calculations it will be assumed that the experimental scattering factors of the ions in the distorted solid solutions, \( f_i' \), can also be regarded as smooth functions of \( \sin \theta / \lambda \), and this assumption both greatly facilitates their determination and increases the reliability of the results obtained. The consequence of this simplifying assumption on the resultant loss of information that is thereby incurred will be discussed further in Section D.

In tables 25 through 32 the values of the effective scattering factor of the cation and anion, \( f_1' \), for the five materials studied, are tabulated for regular increments of \( \sin \theta / \lambda \).

These values of \( f_1' \) were determined from the smoothed curves through the experimental structure factors in Figures 27 through 31 by calculating at a given value of \( \sin \theta / \lambda \) one half of the sum and difference of \( F_{\text{even}} \) and \( F_{\text{odd}} \) for \( |f_{\text{Na}^+}'| \) and \( |f_{\text{X}^-}'| \), respectively as is dictated by Eqs. (7.5) and (7.6). The values of \( f_1^0 \) which are tabulated in these tables for the solid solutions, and the values of \( f_1^0 \) for the pure salts were determined by dividing the \( f_1' \) by an appropriate temperature factor as will be considered in the following section. The values of \( f_1^0 \) for the solid solutions in
the fourth columns of these tables were calculated from Eqs. (7.8) and (7.10), for the anion and cation, respectively.

B. **Thermal Vibration of the Ions**

As was shown in the previous section, the values of the effective scattering factors of the ions in each of the solid solutions are affected by both the disorder arising from thermal vibration and the disorder due to the static displacement of the ions. Therefore, in order to determine the magnitude of the static distortion factor for these ions, it is first necessary to correct the values of their scattering factors for thermal displacement. It will be shown in this section that the theoretical methods that have been developed to account for thermal vibration are not particularly quantitatively applicable for the materials studied in this research, and the need to adopt a somewhat more empirical approach to the problem will be considered.

A theoretical treatment relating the displacement of atoms from their ideal lattice positions because of thermal vibration to the intensities of the Laue-Bragg reflections has been given by Debye and by Waller. This theory is developed for a monatomic cubic lattice in terms of the distribution of frequencies of the normal modes of the lattice vibrations, and detailed accounts of it have been presented by many authors (see, for example, Chapter 4 of Reference 28). That result of the Debye-Waller theory which is of most importance for the present problem is the prediction that the effective
scattering factor of a vibrating atom, \( f \), is related to the theoretical scattering factor of the atom at rest, \( f^0 \), by

\[
f = f^0 \exp \left[-B\left(\frac{\sin \theta}{\lambda}\right)^2\right] = f^0 \exp [-B]
\]

(7.11)

where \( B \) is a function of temperature but is independent of the Bragg angle \( \theta \), and \( B \) is related to the mean of the square of the total thermal displacement of the atom, \( \overline{u^2} \), by

\[
B = \left(\frac{8}{3}\right) \pi^2 \overline{u^2}.
\]

(7.12)

For a monatomic cubic crystal \( B \) can also be related through the Debye-Waller theory to the Debye characteristic temperature for the crystal (28) and thus can be numerically determined if the characteristic temperature is known. The value of the characteristic temperature can be estimated either from low temperature heat capacity variation measurements or from measurements of the elastic constants of the crystal, by well known methods. Since the characteristic temperature of sodium bromide determined by heat capacity measurements could not be found reported in the literature, the characteristic temperatures of sodium chloride and sodium bromide were calculated to be 312°K and 214°K, respectively, from experimental elastic constant data reported for these materials (57), using the procedure described by Zachariasen (7). The values of \( B \) at 298°K for sodium chloride and sodium bromide were calculated to be 1.247 \( \AA^2 \) and 1.485 \( \AA^2 \), respectively, for these characteristic temperatures. However, these values of \( B \) when employed in Eq. (7.11) yield calculated values of the rest-mass scattering factors, \( f^0 \), of the
respective ions which are in poor agreement over the range of
\[(\sin \theta/\lambda)\] experimentally covered with the theoretical values of \(f_i^0\),
as determined from electron distribution calculated from the atomic
wave functions. It should be pointed out that this discrepancy is
not particularly surprising since the theoretical model upon which
these calculations were based in a lattice in which all atoms have
the same force constants, which is probably not a very accurate
approximation for the crystals under present scrutiny, particularly
for sodium bromide.

The preceding discussion suggests that for the materials
studied in this research it will be necessary to consider separately
the temperature factors for the cation and anion. For the pro-
cedure which is adopted in this research it is assumed that Eq.
(7.11) will be obeyed for the scattering factors of both the cation
and anion in each material although the values of \(B_i\) need not be
the same for the two types of ions. This appears to be the only
practical approximation which can be made at present. Furthermore,
in this procedure, \(B_i\) for each of the ions in sodium chloride and
sodium bromide is treated as an adjustable parameter in Eq. (7.11)
to obtain the best fit of the calculated values of \(f_i^0\) with the
theoretical values over the range of \((\sin \theta/\lambda)\) measured.

The values of \(B_i\) for the ions in sodium chloride and sodium
bromide, determined by a procedure similar to that presented in
Section E-3(c) of Chapter VI, are given in Table 24. Also given
in this table are the values of the root-mean-square total
displacement of each ion calculated from these values of $B_i$ by the use of Eq. (7.12). The values of the displacement of the ions in sodium chloride which were determined by Waller and James (36) through an analysis of the temperature dependence of the diffraction intensity data obtained by James and Firth (35) are also given in this table for comparison. It will be noted in the table that the value of $B_i$ for the sodium ion is greater than that of the corresponding anion, in agreement with the trend observed in other investigations (see Table 22). It will be noticed further that the values of $B$ for sodium bromide are larger than those for sodium chloride, which is in qualitative accord with the results obtained from the elastic constant calculations.

The value of $B_i$ given in Table 24 for each of the ions in NaCl is seen to be slightly different from the corresponding value reported in Table 22 of Chapter VI. This small discrepancy in values arises from the use of different sets of theoretical scattering factors. The values of $B_i$ for the ions in NaCl given in Table 24 were determined by the comparison of the experimental scattering factors with the theoretical values obtained from the 1935 edition of the "Internationale Tabellen" (34). Subsequent to the calculations reported here, which were made in 1958, new theoretical values for the scattering factors of the Na$^+$ and Cl$^-$ ions have been given in the recently issued "International Tables" (56). It is these more recent (and more accurate values that have been used in Section E-3(o) of Chapter VI for comparison with the experimental $f$ values for the
determination of the values of $B_i$ given in Table 22. The small error from this source in the values of $B_i$ given for the $Na^+$ and $Cl^-$ ions in Table 24 will introduce negligible error, however, in the values of the calculated distortion factors, as will be subsequently shown.

**TABLE 24**

**Temperature Factors and Mean Displacements for the Ions in NaCl and NaBr**

<table>
<thead>
<tr>
<th>Material</th>
<th>Ion</th>
<th>$B \ (\AA^2)$</th>
<th>$\sqrt{\bar{u}^2} \ (\AA)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>$Na^+$</td>
<td>1.63</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>$Cl^-$</td>
<td>1.56</td>
<td>0.24</td>
</tr>
<tr>
<td>NaBr</td>
<td>$Na^+$</td>
<td>1.83</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>$Br^-$</td>
<td>1.63</td>
<td>0.25</td>
</tr>
</tbody>
</table>

In Tables 25 and 26 are tabulated the values of $f^0$ for the ions in sodium chloride and sodium bromide as calculated from Eq. (7.11) using the experimentally determined effective scattering factors and the values of $B$ given in Table 24. Also given in these tables for comparison are the values of $f^0_{\text{theor}}$ for these ions determined by theoretical calculations, as will be presently discussed. It will be noted in these tables that for the values of $B$ chosen, fair agreement of $f^0$ and $f^0_{\text{theor}}$ is obtained over most of the range of $(\sin \theta / \lambda)$ measured. However, a comparison of the values of $f^0$ for the sodium ion in sodium chloride and sodium
<table>
<thead>
<tr>
<th>(\sin \theta /\lambda)</th>
<th>(f')</th>
<th>(f^0)</th>
<th>(f_{\text{theor}}^0)</th>
<th>(f')</th>
<th>(f^0)</th>
<th>(f_{\text{theor}}^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>5.78</td>
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<td>4.85</td>
<td>5.97</td>
<td>6.13</td>
</tr>
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<td>5.14</td>
<td>6.35</td>
<td>5.85</td>
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<td>5.85</td>
</tr>
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<td>5.29</td>
<td>3.61</td>
<td>4.83</td>
<td>5.29</td>
</tr>
<tr>
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<td>4.92</td>
<td>5.02</td>
<td>3.34</td>
<td>4.60</td>
<td>5.02</td>
</tr>
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<td>2.68</td>
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<td>4.10</td>
</tr>
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<td>2.34</td>
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### TABLE 26

Experimental, Temperature Corrected and Theoretical Scattering Factors for X' Ion

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<tr>
<th>( \sin \theta / \lambda )</th>
<th>( f' )</th>
<th>( f^0 )</th>
<th>( f^0_{\text{theor}} )</th>
<th>( f' )</th>
<th>( f^0 )</th>
<th>( f^0_{\text{theor}} )</th>
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<td>18.02</td>
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<td>18.79</td>
<td>17.58</td>
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<td>14.81</td>
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<td>7.88</td>
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<td>6.52</td>
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<td>14.12</td>
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<td>0.64</td>
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<td>6.37</td>
<td>6.74</td>
<td>13.11</td>
<td>13.80</td>
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<td>0.68</td>
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<td>6.07</td>
<td>6.04</td>
<td>5.93</td>
<td>12.51</td>
<td>13.13</td>
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</tbody>
</table>
bromide (Table 25) discloses an appreciable discrepancy for the lower values of \( \sin \theta / \lambda \). This discrepancy is not necessarily due to experimental error but may be a real effect, as it can be attributed to a departure from spherical symmetry of the outer shell electrons of the sodium ion due to the field of cubic symmetry exerted by the anions.

It will be assumed finally that the value of \( B \) appropriate for each of the ions in the solid solutions studied can be determined by the following equations.

\[
(\mathbf{B}_{\text{Na}^+})_{p} = (1-p) (\mathbf{B}_{\text{Na}^+})_{\text{NaCl}} + p(\mathbf{B}_{\text{Na}^+})_{\text{NaBr}},
\]

\[
(\mathbf{B}_{\text{X}^-}) = (1-p) (\mathbf{B}_{\text{Cl}^-})_{\text{NaCl}} + p(\mathbf{B}_{\text{Br}^-})_{\text{NaBr}},
\]

where \( p \) is the mole fraction of sodium bromide in the solid solution.

This approximation would seem to be quite reasonable as the temperature factors for the ions in the solid solutions represent the superimposed effect of a quasi-continuous collection of normal modes over many configurations of chloride and bromide ions. Furthermore, the procedure just described is self-consistent in the sense that it will minimize any error in the values of the distortion factors calculated in Section D arising from an error in the estimated temperature factors of the ions of the pure components.

The values of \( f^{\text{theor}}_{\text{Na}^+} \) in Tables 25 and 26 were obtained from the "Internationale Tabellen" (34). The values of \( f^{\text{theor}} \) for sodium and chloride are those for the \( \text{Na}^+ \) and \( \text{Cl}^- \) ions as calculated from Hartree self-consistent field wave functions (see Chapter VI, Section E-3(c)), and the values for bromide are those for the \( \text{Br} \) atom as calculated by the Thomas-Fermi method. It should be pointed
out that although atomic scattering factors calculated by the
Thomas-Fermi method are much less accurate than those calculated from
Hartree or Hartree-Fock atomic charge densities, the employment of
the scattering factor of the bromine atom rather than of the ion
introduces negligible error in itself, since it is well known that
the scattering power of the outer shell electron of the larger atoms
decreases very rapidly with increasing \((\sin \theta / \lambda)\), and even at the
smallest values of \((\sin \theta / \lambda)\) reported in this research the scattering
factors of the atom and the ion should be essentially the same.
The values of \(f^0\) for the three types of ions that are reported
in these tables are all corrected for the change in their absolute
values caused by the anomalous dispersion of the radiation due to
the proximity of the absorption edge of their K electrons to the
frequency of the molybdenum radiation used, employing the correction
procedure of Hönle as given by James (Appendix III of Reference 28).

Since the wave-length of the incident radiation \((0.7093 \AA)\) is
quite close to the wave-length of the K absorption edge of the
bromide ion \((0.9190 \AA)\), an appreciable change in phase of the
radiation scattered by these ions with respect to the radiation
scattered by the other ions in the crystal will occur, in addition
to the change in the absolute value of the scattering factor of
these ions caused by the anomalous dispersion. This effect may be
formally taken into account by considering the scattering factor
of the bromide ion to be complex and given by

\[
f = f' + if'' = |f| \exp i\delta, \quad (7.15)
\]
where the values of the real and the imaginary parts of the scattering factor, $f'$ and $f''$, and hence the phase factor, $\exp i\delta$, can be estimated from the tables tabulated by James, to which reference is made above. It is calculated that at $(\sin \theta/\lambda) = 0.70$ there is a phase shift of $\delta = 0.180$ radians of the radiation scattered by the bromide ions with respect to that scattered by the sodium or chloride ions. It is further calculated that for sodium bromide at $(\sin \theta/\lambda) = 0.70$, this phase shift will cause the experimentally determined value of $f^0_{\text{Na}^+}$ to be low by 1.7 percent and the value of $f^0_{\text{Br}^-}$ to be high by 0.07 percent. It should be noted that the values of the scattering factors reported in Tables 25 through 32 are not corrected for the effect of this phase shift. However, the omission of this correction will cause no appreciable error in the values of the distortion factors for the sodium ion reported in these tables since the correction will be less for the sodium ion in the solid solutions and will be of only second order importance for the ratio $f^\oplus /f^o$.

C. Elastic Theory Distortion Factor

In Tables 27 through 32 the tabulated values of $f^\oplus_i /f^o_i$ for each of the ions may be identified as the total distortion factor for that ion, $\exp ik\cdot\vec{u}^\oplus_{iL}$, as is evident from Eqs. (7.3) and (7.4). As has been previously discussed, this total distortion factor may be treated as the product of two factors, one of the factors being given by Eq. (2.23) for those defect sites near a
<table>
<thead>
<tr>
<th>sin θ/Å</th>
<th>f'</th>
<th>f^*</th>
<th>f^0</th>
<th>f^*/f^0</th>
<th>( \Pi )</th>
<th>( \Pi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>5.30</td>
<td>6.45</td>
<td>6.73</td>
<td>0.958</td>
<td>0.962</td>
<td>0.970</td>
</tr>
<tr>
<td>0.36</td>
<td>4.71</td>
<td>5.86</td>
<td>6.13</td>
<td>0.957</td>
<td>0.963</td>
<td>0.970</td>
</tr>
<tr>
<td>0.38</td>
<td>4.18</td>
<td>5.33</td>
<td>5.59</td>
<td>0.955</td>
<td>0.958</td>
<td>0.978</td>
</tr>
<tr>
<td>0.40</td>
<td>3.77</td>
<td>4.94</td>
<td>5.18</td>
<td>0.955</td>
<td>0.959</td>
<td>0.979</td>
</tr>
<tr>
<td>0.42</td>
<td>3.45</td>
<td>4.65</td>
<td>4.84</td>
<td>0.960</td>
<td>0.965</td>
<td>0.976</td>
</tr>
<tr>
<td>0.44</td>
<td>3.20</td>
<td>4.43</td>
<td>4.57</td>
<td>0.970</td>
<td>0.976</td>
<td>0.989</td>
</tr>
<tr>
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<td>2.96</td>
<td>4.23</td>
<td>4.34</td>
<td>0.975</td>
<td>0.982</td>
<td>0.994</td>
</tr>
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<td>0.48</td>
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<td>3.95</td>
<td>0.971</td>
<td>0.978</td>
<td>0.994</td>
</tr>
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<td>0.971</td>
<td>0.979</td>
<td>0.997</td>
</tr>
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<td>3.68</td>
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<td>0.962</td>
<td>0.980</td>
</tr>
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<td>3.58</td>
<td>0.945</td>
<td>0.954</td>
<td>0.975</td>
</tr>
<tr>
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<td>3.50</td>
<td>0.950</td>
<td>0.958</td>
<td>0.981</td>
</tr>
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<td>0.954</td>
<td>0.977</td>
</tr>
<tr>
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<td>3.32</td>
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<td>0.962</td>
<td>0.988</td>
</tr>
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<td>3.23</td>
<td>0.958</td>
<td>0.960</td>
<td>0.996</td>
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<td>0.972</td>
<td>1.00</td>
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<td>3.01</td>
<td>0.951</td>
<td>0.964</td>
<td>0.998</td>
</tr>
</tbody>
</table>

*Refer to Eqs. (7.2) - Eqs. (7.4) for definition of f', f^*, and f^0, and to Eq. (7.15) for definition of \( \Pi \).
## TABLE 28

Experimental, and Corrected Scattering Factors,*
Total Distortion Factor, $f^\circ /f^p$, and the
Distortion Factors for Discrete Displacements, $\Pi$, for the Na⁺ Ion in
50% NaCl - 50% NaBr

<table>
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<tr>
<th>$\sin \theta /\AA$</th>
<th>$f^p$</th>
<th>$f^\circ$</th>
<th>$f^\circ /f^p$</th>
<th>$\Pi$</th>
<th>$\Pi$</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>$\gamma=1.8$</td>
<td>$\gamma=1.0$</td>
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<tr>
<td>0.34</td>
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<td>5.81</td>
<td>6.47</td>
<td>0.914</td>
<td>0.917</td>
</tr>
<tr>
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<td>5.34</td>
<td>5.92</td>
<td>0.902</td>
<td>0.906</td>
</tr>
<tr>
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<td>4.88</td>
<td>5.43</td>
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<td>0.904</td>
</tr>
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<td>4.46</td>
<td>5.06</td>
<td>0.880</td>
<td>0.886</td>
</tr>
<tr>
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<td>4.14</td>
<td>4.76</td>
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<td>0.873</td>
</tr>
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<td>2.75</td>
<td>3.84</td>
<td>4.51</td>
<td>0.852</td>
<td>0.858</td>
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<td>4.31</td>
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<td>0.833</td>
</tr>
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<td>0.817</td>
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<td>3.15</td>
<td>3.96</td>
<td>0.795</td>
<td>0.802</td>
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<td>1.89</td>
<td>3.01</td>
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<td>0.790</td>
<td>0.798</td>
</tr>
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<td>3.70</td>
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<td>3.50</td>
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<td>0.764</td>
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<td>0.728</td>
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</tr>
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<td>0.93</td>
<td>2.07</td>
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<td>0.694</td>
<td>0.706</td>
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</table>

*Refer to Eqs. (7.2) - Eqs. (7.4) for definition of $f^p$, $f^\circ$, and $f^0$, and to Eq. (7.15) for definition of $\Pi$.}
TABLE 29

Experimental, and Corrected Scattering Factors,*
Total Distortion Factor, \( \frac{f^\Delta}{f_0^\Delta} \), and the
Distortion Factors for Discrete Displacements, \( \Pi \), for the Na\({}^+\) Ion in
25% NaCl - 75% NaBr

<table>
<thead>
<tr>
<th>( \sin \theta/A )</th>
<th>( f' )</th>
<th>( f^\Delta )</th>
<th>( f_0 )</th>
<th>( f^\Delta/f_0 )</th>
<th>( \Pi ) for ( \xi = 1.8 )</th>
<th>( \Pi ) for ( \xi = 1.0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>5.15</td>
<td>6.33</td>
<td>6.22</td>
<td>1.018</td>
<td>1.021</td>
<td>1.027</td>
</tr>
<tr>
<td>0.36</td>
<td>4.47</td>
<td>5.60</td>
<td>5.70</td>
<td>0.983</td>
<td>0.986</td>
<td>0.994</td>
</tr>
<tr>
<td>0.38</td>
<td>4.00</td>
<td>5.18</td>
<td>5.28</td>
<td>0.979</td>
<td>0.983</td>
<td>0.991</td>
</tr>
<tr>
<td>0.40</td>
<td>3.64</td>
<td>4.84</td>
<td>4.95</td>
<td>0.976</td>
<td>0.982</td>
<td>0.990</td>
</tr>
<tr>
<td>0.42</td>
<td>3.33</td>
<td>4.55</td>
<td>4.68</td>
<td>0.972</td>
<td>0.977</td>
<td>0.986</td>
</tr>
<tr>
<td>0.44</td>
<td>3.06</td>
<td>4.32</td>
<td>4.46</td>
<td>0.968</td>
<td>0.973</td>
<td>0.984</td>
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<tr>
<td>0.46</td>
<td>2.83</td>
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<td>4.27</td>
<td>0.965</td>
<td>0.970</td>
<td>0.982</td>
</tr>
<tr>
<td>0.48</td>
<td>2.63</td>
<td>3.96</td>
<td>4.10</td>
<td>0.965</td>
<td>0.974</td>
<td>0.983</td>
</tr>
<tr>
<td>0.50</td>
<td>2.44</td>
<td>3.80</td>
<td>3.96</td>
<td>0.960</td>
<td>0.967</td>
<td>0.980</td>
</tr>
<tr>
<td>0.52</td>
<td>2.28</td>
<td>3.68</td>
<td>3.83</td>
<td>0.962</td>
<td>0.968</td>
<td>0.983</td>
</tr>
<tr>
<td>0.54</td>
<td>2.13</td>
<td>3.57</td>
<td>3.71</td>
<td>0.962</td>
<td>0.968</td>
<td>0.986</td>
</tr>
<tr>
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<td>1.98</td>
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<td>3.61</td>
<td>0.956</td>
<td>0.963</td>
<td>0.982</td>
</tr>
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<td>0.948</td>
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<tr>
<td>0.60</td>
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<td>3.40</td>
<td>0.945</td>
<td>0.953</td>
<td>0.973</td>
</tr>
<tr>
<td>0.62</td>
<td>1.56</td>
<td>3.09</td>
<td>3.29</td>
<td>0.937</td>
<td>0.946</td>
<td>0.967</td>
</tr>
<tr>
<td>0.64</td>
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<td>3.15</td>
<td>0.934</td>
<td>0.943</td>
<td>0.966</td>
</tr>
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<td>1.32</td>
<td>2.86</td>
<td>3.06</td>
<td>0.933</td>
<td>0.943</td>
<td>0.968</td>
</tr>
<tr>
<td>0.68</td>
<td>1.21</td>
<td>2.75</td>
<td>2.95</td>
<td>0.932</td>
<td>0.943</td>
<td>0.968</td>
</tr>
</tbody>
</table>

*Refer to Eqs. (7.2) - Eqs. (7.4) for definition of \( f' \), \( f^\Delta \), and \( f_0 \), and to Eq. (7.15) for definition of \( \Pi \).
TABLE 30  

Experimental, and Corrected Scattering Factors,*  

Total Distortion Factor, $f^\Delta / f^0$, and the  
Distortion Factors for Discrete Displacements, $\Pi$, for the $X^-$ Ion in  
75% NaCl - 25% NaBr  

<table>
<thead>
<tr>
<th>$\sin \theta/\lambda$</th>
<th>$f'$</th>
<th>$f^\Delta$</th>
<th>$f^0$</th>
<th>$f^\Delta/f^0$</th>
<th>$\Pi_{\gamma=1.8}$</th>
<th>$\Pi_{\gamma=1.0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>9.95</td>
<td>11.94</td>
<td>12.70</td>
<td>0.941</td>
<td>0.945</td>
<td>0.952</td>
</tr>
<tr>
<td>0.36</td>
<td>9.39</td>
<td>11.52</td>
<td>12.20</td>
<td>0.944</td>
<td>0.947</td>
<td>0.956</td>
</tr>
<tr>
<td>0.38</td>
<td>8.83</td>
<td>11.09</td>
<td>11.76</td>
<td>0.944</td>
<td>0.948</td>
<td>0.958</td>
</tr>
<tr>
<td>0.40</td>
<td>8.29</td>
<td>10.67</td>
<td>11.39</td>
<td>0.937</td>
<td>0.942</td>
<td>0.953</td>
</tr>
<tr>
<td>0.42</td>
<td>7.60</td>
<td>10.29</td>
<td>11.05</td>
<td>0.932</td>
<td>0.937</td>
<td>0.950</td>
</tr>
<tr>
<td>0.44</td>
<td>7.35</td>
<td>9.96</td>
<td>10.74</td>
<td>0.927</td>
<td>0.933</td>
<td>0.945</td>
</tr>
<tr>
<td>0.46</td>
<td>6.91</td>
<td>9.64</td>
<td>10.43</td>
<td>0.924</td>
<td>0.930</td>
<td>0.944</td>
</tr>
<tr>
<td>0.48</td>
<td>6.48</td>
<td>9.32</td>
<td>10.14</td>
<td>0.918</td>
<td>0.925</td>
<td>0.939</td>
</tr>
<tr>
<td>0.50</td>
<td>6.05</td>
<td>8.96</td>
<td>9.87</td>
<td>0.908</td>
<td>0.917</td>
<td>0.933</td>
</tr>
<tr>
<td>0.52</td>
<td>5.64</td>
<td>8.63</td>
<td>9.60</td>
<td>0.900</td>
<td>0.908</td>
<td>0.925</td>
</tr>
<tr>
<td>0.54</td>
<td>5.24</td>
<td>8.30</td>
<td>9.33</td>
<td>0.889</td>
<td>0.898</td>
<td>0.916</td>
</tr>
<tr>
<td>0.56</td>
<td>4.86</td>
<td>7.97</td>
<td>9.06</td>
<td>0.880</td>
<td>0.888</td>
<td>0.909</td>
</tr>
<tr>
<td>0.58</td>
<td>4.49</td>
<td>7.62</td>
<td>8.79</td>
<td>0.867</td>
<td>0.876</td>
<td>0.898</td>
</tr>
<tr>
<td>0.60</td>
<td>4.12</td>
<td>7.27</td>
<td>8.53</td>
<td>0.852</td>
<td>0.862</td>
<td>0.884</td>
</tr>
<tr>
<td>0.62</td>
<td>3.79</td>
<td>6.96</td>
<td>8.29</td>
<td>0.839</td>
<td>0.850</td>
<td>0.873</td>
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<tr>
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<td>6.64</td>
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<td>0.837</td>
<td>0.862</td>
</tr>
<tr>
<td>0.66</td>
<td>3.19</td>
<td>6.34</td>
<td>7.83</td>
<td>0.810</td>
<td>0.821</td>
<td>0.847</td>
</tr>
<tr>
<td>0.68</td>
<td>2.92</td>
<td>6.06</td>
<td>7.68</td>
<td>0.790</td>
<td>0.802</td>
<td>0.830</td>
</tr>
</tbody>
</table>

*Refer to Eqs. (7.2) - Eqs. (7.4) for definition of $f'$,  
$f^\Delta$, and $f^0$, and to Eq. (7.15) for definition of $\Pi$. 

### TABLE 31

**Experimental, and Corrected Scattering Factors,*  
Total Distortion Factor, $f^\Delta/f^\circ$, and the  
Distortion Factors for Discrete Displacements, $\Pi$, for the X Ion in  
50% NaCl - 50% NaBr**

<table>
<thead>
<tr>
<th>$\sin \theta /\lambda$</th>
<th>$f'$</th>
<th>$f^\Delta$</th>
<th>$f^\circ$</th>
<th>$f^\Delta/f^\circ$</th>
<th>$\Pi_{\lambda=1.3}$</th>
<th>$\Pi_{\lambda=1.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>13.01</td>
<td>15.52</td>
<td>15.64</td>
<td>1.003</td>
<td>1.015</td>
<td></td>
</tr>
<tr>
<td>0.36</td>
<td>12.29</td>
<td>15.10</td>
<td>15.12</td>
<td>0.998</td>
<td>1.002</td>
<td>1.015</td>
</tr>
<tr>
<td>0.32</td>
<td>11.64</td>
<td>14.53</td>
<td>14.65</td>
<td>0.992</td>
<td>0.999</td>
<td>1.010</td>
</tr>
<tr>
<td>0.40</td>
<td>10.97</td>
<td>14.14</td>
<td>14.22</td>
<td>0.994</td>
<td>1.000</td>
<td>1.013</td>
</tr>
<tr>
<td>0.42</td>
<td>10.29</td>
<td>13.52</td>
<td>13.32</td>
<td>0.982</td>
<td>0.988</td>
<td>1.005</td>
</tr>
<tr>
<td>0.44</td>
<td>9.57</td>
<td>12.90</td>
<td>13.42</td>
<td>0.960</td>
<td>0.968</td>
<td>0.965</td>
</tr>
<tr>
<td>0.46</td>
<td>8.84</td>
<td>12.32</td>
<td>13.02</td>
<td>0.951</td>
<td>0.959</td>
<td>0.978</td>
</tr>
<tr>
<td>0.48</td>
<td>8.15</td>
<td>11.76</td>
<td>12.64</td>
<td>0.930</td>
<td>0.937</td>
<td>0.959</td>
</tr>
<tr>
<td>0.50</td>
<td>7.55</td>
<td>11.23</td>
<td>12.25</td>
<td>0.917</td>
<td>0.926</td>
<td>0.947</td>
</tr>
<tr>
<td>0.52</td>
<td>7.01</td>
<td>10.78</td>
<td>11.38</td>
<td>0.907</td>
<td>0.917</td>
<td>0.940</td>
</tr>
<tr>
<td>0.54</td>
<td>6.57</td>
<td>10.47</td>
<td>11.50</td>
<td>0.910</td>
<td>0.921</td>
<td>0.946</td>
</tr>
<tr>
<td>0.56</td>
<td>6.06</td>
<td>10.00</td>
<td>11.13</td>
<td>0.897</td>
<td>0.909</td>
<td>0.935</td>
</tr>
<tr>
<td>0.58</td>
<td>5.65</td>
<td>9.66</td>
<td>10.76</td>
<td>0.883</td>
<td>0.911</td>
<td>0.938</td>
</tr>
<tr>
<td>0.60</td>
<td>5.28</td>
<td>9.37</td>
<td>10.41</td>
<td>0.890</td>
<td>0.912</td>
<td>0.944</td>
</tr>
<tr>
<td>0.62</td>
<td>4.92</td>
<td>9.13</td>
<td>10.09</td>
<td>0.905</td>
<td>0.913</td>
<td>0.952</td>
</tr>
<tr>
<td>0.64</td>
<td>4.61</td>
<td>8.84</td>
<td>9.73</td>
<td>0.909</td>
<td>0.924</td>
<td>0.958</td>
</tr>
<tr>
<td>0.66</td>
<td>4.31</td>
<td>8.52</td>
<td>9.45</td>
<td>0.911</td>
<td>0.926</td>
<td>0.955</td>
</tr>
<tr>
<td>0.68</td>
<td>4.07</td>
<td>8.47</td>
<td>9.29</td>
<td>0.912</td>
<td>0.928</td>
<td>0.938</td>
</tr>
</tbody>
</table>

*Refer to Eqs. (7.2) - Eqs. (7.4) for definition of $f'$,  
$f^\Delta$, and $f^\circ$, and to Eq. (7.15) for definition of $\Pi$.*
TABLE 32

Experimental, and Corrected Scattering Factors,*

Total Distortion Factor, $f^A/f^0$, and the Distortion Factors for Discrete Displacements, $\Pi$, for the $X^-$ Ion in 25% NaCl - 75% NaBr

<table>
<thead>
<tr>
<th>$\sin \theta^\lambda$</th>
<th>$f'$</th>
<th>$f^\lambda$</th>
<th>$f^0$</th>
<th>$f^A/f^0$</th>
<th>$\Pi$</th>
<th>$\Pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>15.75</td>
<td>19.00</td>
<td>18.57</td>
<td>1.02</td>
<td>1.025</td>
<td>1.032</td>
</tr>
<tr>
<td>0.36</td>
<td>14.67</td>
<td>18.05</td>
<td>18.03</td>
<td>1.001</td>
<td>1.005</td>
<td>1.011</td>
</tr>
<tr>
<td>0.38</td>
<td>13.68</td>
<td>17.24</td>
<td>17.53</td>
<td>0.983</td>
<td>0.986</td>
<td>0.996</td>
</tr>
<tr>
<td>0.40</td>
<td>12.77</td>
<td>16.53</td>
<td>17.05</td>
<td>0.969</td>
<td>0.974</td>
<td>0.983</td>
</tr>
<tr>
<td>0.42</td>
<td>11.95</td>
<td>15.88</td>
<td>16.58</td>
<td>0.957</td>
<td>0.962</td>
<td>0.973</td>
</tr>
<tr>
<td>0.44</td>
<td>11.19</td>
<td>15.28</td>
<td>16.11</td>
<td>0.947</td>
<td>0.952</td>
<td>0.965</td>
</tr>
<tr>
<td>0.46</td>
<td>10.50</td>
<td>14.79</td>
<td>15.62</td>
<td>0.946</td>
<td>0.953</td>
<td>0.965</td>
</tr>
<tr>
<td>0.48</td>
<td>9.84</td>
<td>14.29</td>
<td>15.13</td>
<td>0.944</td>
<td>0.950</td>
<td>0.964</td>
</tr>
<tr>
<td>0.50</td>
<td>9.22</td>
<td>13.80</td>
<td>14.64</td>
<td>0.943</td>
<td>0.950</td>
<td>0.965</td>
</tr>
<tr>
<td>0.52</td>
<td>8.64</td>
<td>13.34</td>
<td>14.15</td>
<td>0.944</td>
<td>0.951</td>
<td>0.968</td>
</tr>
<tr>
<td>0.54</td>
<td>8.06</td>
<td>12.90</td>
<td>13.68</td>
<td>0.943</td>
<td>0.950</td>
<td>0.970</td>
</tr>
<tr>
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<td>0.940</td>
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<tr>
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<td>0.940</td>
<td>0.949</td>
<td>0.970</td>
</tr>
<tr>
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<td>12.29</td>
<td>0.937</td>
<td>0.946</td>
<td>0.969</td>
</tr>
<tr>
<td>0.62</td>
<td>5.94</td>
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<td>11.85</td>
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<tr>
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<td>5.49</td>
<td>10.62</td>
<td>11.42</td>
<td>0.930</td>
<td>0.941</td>
<td>0.964</td>
</tr>
<tr>
<td>0.66</td>
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<td>11.12</td>
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</tr>
<tr>
<td>0.68</td>
<td>4.76</td>
<td>10.00</td>
<td>10.90</td>
<td>0.917</td>
<td>0.930</td>
<td>0.956</td>
</tr>
</tbody>
</table>

*Refer to Eqs. (7.2) - Eqs. (7.4) for definition of $f'$, $f^\lambda$, and $f^0$, and to Eq. (7.15) for definition of $\Pi$. 

given lattice site which must be individually considered and the other factor being given by Eq. (2.28) for the more distant lattice sites that may be satisfactorily treated by the elastic theory approximation. If the former factor is designated as $\pi_i$ and the latter factor as $E_i$, then

$$\left< \exp \frac{i\mathbf{k} \cdot \mathbf{u}_i}{L} \right>_p = \left( f_i^A \right)_p \left( f_i^O \right)_p = (E_i)_p \left( \pi_i \right)_p,$$

(7.15)

where $p$ designates the concentration of the solid solution and $i$ designates whether the sites are those of cations or anions. In this section the method of calculation of $(E_i)_p$ will be presented. With the values of this factor determined, the values of $(\pi_i)_p$ are calculated by Eq. (7.15) for each ion in each solid solution from the total distortion factors obtained from the experimental measurements. Finally, in the following section, values of $(\pi_i)_p$ will be calculated from the form of Eq. (2.23) appropriate for the NaCl type lattice assuming mean displacements of various magnitudes for the nearest-neighbor sites, and these calculated values of $(\pi_i)_p$ will be compared with the experimental values obtained here.

It was shown in Chapter II that $E(x)$ in Eq. (2.28) may be set equal to unity for the range of $\sin \theta/\lambda$ covered in this research with negligible error. Also, in Chapter VI, it was shown that the lattice constants of the NaCl-NaBr solid solutions obey Vegard's rule precisely within experimental accuracy. With these simplifications, Eqs. (2.28) and (2.29) may be combined to give
for the sodium chloride lattice in which there are four negative ion
defect sites, \( \psi \), per unit cell,

\[
(E_1)_p = \exp \left[ -\frac{(2\pi \psi)}{\sqrt{2}} \left( \frac{1}{r_{oi}} \right) \left( \frac{1}{r_p} \right) \frac{(1-p)}{(\sin \theta)^2} \right], \tag{7.16}
\]

\[
= \exp -A_{ip} (\sin \theta \lambda)^2
\]

where \( p \) is the fraction of total negative sites occupied by bromide ions, \( r_{oi} \) is the radius in angstroms of the smallest shell containing
defect sites which produce displacements of an ion of type \( i \) located
at the center of the shell that are treated by the elastic theory,

and where

\[
\Delta V_\alpha = \frac{1}{4} \left[ (a_0)^3_{NaBr} - (a_0)^3_{NaCl} \right], \tag{7.17}
\]

and

\[
V_p = \left[ (1-p)(a_0)^3_{NaCl} - p(a_0)^3_{NaBr} \right]^3, \tag{7.18}
\]

with \( a_0 \) being the unit cell length in angstroms of the respective
component. Also, in Eq. (7.16), \( \gamma \) is a factor defined by

\[
\gamma = 3(1-\sigma)/(1+\sigma), \tag{7.19}
\]

where \( \sigma \) is the Poisson ratio for the crystal.

In the following section the values of \( \Pi_i \) are calculated for
only the first or nearest-neighbor shell of defect sites around an
anion lattice site and for the first two shells of defect sites around
a cation lattice site. Therefore, by reference to Figures 34 and 35,
it is evident that the appropriate values of \( r_0 \) to be used in Eq. (7.16)
for the radii for the second shell of defect sites around an anion site
and for the third shell of defect sites around a cation site are

\[
(r_0)^- = (a_0)_p, \tag{7.20}
\]

\[
(r_0)^+ = \sqrt{5/2} (a_0)_p. \tag{7.21}
\]
It was mentioned in Chapter II that the fact $\delta$, defined in Eq. (7.19), must be employed in Eq. (7.16) when the distorted crystal under consideration is of finite size but has stress-free surfaces. However, it has been pointed out by Eshelby (13) that for a real crystal that is distorted because of internal displacement disorder, it is probably not very accurate to consider that the surfaces of the crystal are free of internally produced stress, and, therefore, there is some ambiguity as to the proper value that should be chosen for in such a crystal. It is clear from the analysis presented by Eshelby that the maximum possible value of $\gamma$ will be given by Eq. (7.19), and the minimum possible value will be unity. In view of this uncertainty, the values for the elastic distortion factor, $E_1$, have been calculated in every case both for $\gamma$ equal to unity and for $\gamma$ equal to its maximum value of 1.30. The value of 1.80 is obtained from Eq. (7.19), assuming a value of 1/4 for $\sigma$ for each of the solid solutions. Since the value of $\sigma$ is exactly 1/4 for an isotropic medium, it will introduce negligible error in assuming this same value for the solid solutions of interest here because of the cubic symmetry of these lattices.

The values of the elastic distortion factors, $(E_1)_p$, calculated from Eq. (7.16) using the parameters appropriate for the cation and anion in each of the solid solutions as given above in the text, are tabulated at intervals of $(\sin \theta/\lambda)$ for the range experimentally covered in Tables 33 and 34 for the cases $\gamma=1.00$ and $\gamma=1.80$,\ldots
TABLE 33

Elastic Distortion Factors, 
\((E_j)_{p*} \text{ for } y = 1.00\) 
\((\Delta V_o = 3.3876)\)

<table>
<thead>
<tr>
<th>(p^2)</th>
<th>(r_o^2)</th>
<th>(V_p^2)</th>
<th>(A)</th>
<th>(X^- (r_o = a_o))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75%NaCl</td>
<td>50%NaCl</td>
<td>25%NaCl</td>
<td>75%NaCl</td>
</tr>
<tr>
<td>.25</td>
<td>6.3863</td>
<td>6.4792</td>
<td>6.5724</td>
<td>.25</td>
</tr>
<tr>
<td>.50</td>
<td>136.36</td>
<td>194.63</td>
<td>203.14</td>
<td>.50</td>
</tr>
<tr>
<td>.75</td>
<td>0.09286</td>
<td>0.11684</td>
<td>0.08277</td>
<td>.75</td>
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</table>

\(\sin\theta\)

<table>
<thead>
<tr>
<th>(\sin\theta)</th>
<th>(\beta)</th>
<th>(\beta)</th>
<th>(\beta)</th>
<th>(\beta)</th>
<th>(\beta)</th>
<th>(\beta)</th>
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<td>$\text{Cl}^-$ $(r_0 = a_0)$</td>
<td></td>
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<tr>
<td>--------------------------------</td>
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</tr>
<tr>
<td></td>
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<td>50% NaCl</td>
<td>25% NaCl</td>
<td>75% NaCl</td>
<td>50% NaCl</td>
<td>25% NaCl</td>
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<td>0.9958</td>
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<td>0.9944</td>
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<td>0.9950</td>
<td>0.9931</td>
<td>0.9926</td>
<td>0.9945</td>
</tr>
<tr>
<td>$\sqrt{r_0}$ = 0.46</td>
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<td>0.9924</td>
<td>0.9946</td>
<td>0.9932</td>
<td>0.9915</td>
<td>0.9940</td>
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<tr>
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</tr>
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<td>0.9936</td>
<td>0.9920</td>
<td>0.9899</td>
<td>0.9922</td>
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<tr>
<td>$\sqrt{r_0}$ = 0.52</td>
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<td>0.9906</td>
<td>0.9882</td>
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<td>0.9879</td>
<td>0.9914</td>
<td>0.9892</td>
<td>0.9864</td>
<td>0.9904</td>
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<td>$\sqrt{r_0}$ = 0.60</td>
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<td>0.9855</td>
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<td>$\sqrt{r_0}$ = 0.62</td>
<td>0.9890</td>
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<td>0.9902</td>
<td>0.9877</td>
<td>0.9845</td>
<td>0.9890</td>
</tr>
<tr>
<td>$\sqrt{r_0}$ = 0.64</td>
<td>0.9883</td>
<td>0.9852</td>
<td>0.9895</td>
<td>0.9869</td>
<td>0.9835</td>
<td>0.9883</td>
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<td>$\sqrt{r_0}$ = 0.66</td>
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<td>0.9843</td>
<td>0.9889</td>
<td>0.9861</td>
<td>0.9825</td>
<td>0.9876</td>
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<tr>
<td>$\sqrt{r_0}$ = 0.68</td>
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<td>0.9833</td>
<td>0.9882</td>
<td>0.9852</td>
<td>0.9914</td>
<td>0.9868</td>
</tr>
</tbody>
</table>
respectively. At the head of each column is given the value of $A_{fp}$, defined by Eqs. (7.16), that was used for that set of calculations, as well as the appropriate values of $r_o$, $v_p$, and $p$ employed to compute its value. It is seen from these tables that even for the case, $\gamma = 1.00$, the predicted decrease in scattering power of an ion due to its elastic displacement by all defect sites located at a distance equal to or greater than $r_o$ does not exceed about 5 percent at the largest values of $(\sin \theta / \lambda)$ measured, and for the case, $\gamma = 1.80$ (which probably represents the physical situation more accurately), the decrease in scattering power does not exceed 2 percent.

In Tables 27 through 32 are tabulated the experimental values of $(\Pi_i)_p$ for $\gamma = 1.00$ and $\gamma = 1.80$, obtained by dividing the experimental total distortion factors, $(f_i^o)/(f_i^o)_p$ given in the tables by the corresponding values of $(E_i)_p$ which are given in Tables 33 and 34. It can be seen by comparison of the values of $f_i^o/(f_i^o)$ in Tables 27 through 32 with the corresponding values of $E_i$ in Tables 33 and 34 that the elastic theory factor does not nearly account for the magnitude of the effects observed for the larger values of $(\sin \theta / \lambda)$. In fact, a comparison of the corresponding values of $\Pi_i$ and $E_i$ in these tables at the larger values of $(\sin \theta / \lambda)$ discloses that for several cases the displacements caused by the first several shells of defect sites produces by far the largest contribution to the experimental total distortion factor, even if
is equal to unity. These points will be considered further in the following section.

D. Distortion Factor for Discrete Displacements

The values of the experimental distortion factors, $\Pi_1$, which were determined from this research are given in Tables 27 through 32. Also the experimental values of $1 - \Pi_1$ are plotted in Figures 32 and 33 as functions of $(\sin \Theta/\Lambda)^2$, where the x-points denote the values obtained by letting $\gamma = 1.30$ in Eq. (7.16) for the elastic factor correction and the 0-points denote the values obtained for $\gamma = 1.00$, for each of the types of ions and concentrations. As was described in the previous section, the values of these distortion factors are corrected for the effect of the elastic displacement of the ion by all of the defect sites except for the first shell of sites for the case of an anion and except for the first two ordinal shells of defect sites for the case of a cation.

In this section values of $\Pi_1$ will be calculated from the appropriate form of Eq. (2.23) for comparison with the experimental values, assuming displacements of various magnitudes for the cation and anion by the ions in these first several shells of sites. Since the unit cell of sodium chloride is centrosymmetric, the form of the characteristic function of the displacement given by Eq. (2.26) can be employed. Expanding $\mathbf{K} \cdot \mathbf{u}_{1t}$ in terms of the components of $\mathbf{u}$ along
Fig 32 Modified Distortion Factor for Positive Ion.
Fig. 33 Modified Distortion Factor for Negative Ion.
Fig 34 Unit Cell with Anion at Center
Fig 35  Unit Cell with Cation at Center
the lattice coordinates in \( \mathbf{a}_0 \) (2.23), we obtain

\[
\Pi_1 = \prod_{\text{pairs},t} \left\{ 1 - 2p(1-p) \left[ 1 - \cos 2\pi \left( \frac{h}{a_{\text{latt}}} u_{ix,t} + k u_{iy,t} + l u_{iz,t} \right) \right] \right\},
\]

(7.22)

where \( u_{is,t} \) for \( s = x, y, z \) is the ratio of the \( s \)-component of the vector \( \overline{u}_{it} \) to the length of the unit translation vector of the lattice, \( a_0 \). Equation (7.22) is a product of factors, with one factor for each pair of opposed defect sites, \( t \), that are to be treated, where two sites are said to be opposed if they are carried into one another by the operation of inversion. Since the distortion being studied in this research is caused by substitutional disorder, \( \overline{u}_{it} \) may be here interpreted as the displacement of a lattice ion of type \( i \) due to the substitution of a bromide ion for a chloride ion at a defect site, \( t \), in the sodium chloride lattice. Because of the symmetry of the sodium chloride lattice, all of the cation lattice sites are equivalent, as are all of the anion lattice sites. Furthermore, each of the defect sites in these first shells is located on an axis of symmetry with respect to the lattice site, as may be seen in Figures 34 and 35. Therefore, since the direction of the displacement with respect to a particular isolated defect site must also be along that respective symmetry axis, the directions of all individual displacements which are treated here are known, whence only their magnitudes need to be considered. Thus for the scalar displacement, \( u_{n}^\pm \), of a positive or negative ion due to a defect located at a site \( t \) in the shell of ordinal number \( n \), we can write

\[
u_n^\pm = \left| \overline{u}_{st} \right| = \left[ u_{xt}^2 + u_{yt}^2 + u_{zt}^2 \right]^{1/2}, \quad (7.23)
\]
as the magnitudes of the displacements caused by all defect sites in a given shell are the same.

By reference to Figure 35 it is apparent that the coordinates of the displacements of the positive ion by the negative ions in the six sites of the first shell are given by

1. \( u_{xt} = \pm u_1^+ \), \( u_{yt} = 0 \), \( u_{zt} = 0 \);
2. \( u_{xt} = 0 \), \( u_{yt} = \pm u_1^+ \), \( u_{zt} = 0 \);
3. \( u_{xt} = 0 \), \( u_{yt} = 0 \), \( u_{zt} = \pm u_1^+ \).

The distortion factor, given by Eq. (7.22), for these three pairs of opposed sites is

\[
\Pi_1^+ = \left\{ \begin{array}{c} 1-2p(1-p) \left[ 1-\cos 2\pi h u_1^+ \right] \\ x \left\{ 1-2p(1-p) \left[ 1-\cos 2\pi k u_1^+ \right] \\ x \left\{ 1-2p(1-p) \left[ 1-\cos 2\pi l u_1^+ \right] \right. \right. \right\} \right\}.
\]

Similarly, the coordinates of the displacements of the positive ion by the negative ions in the eight sites of the second shell are given by

1. \( u_{xt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{yt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{zt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \);
2. \( u_{xt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{yt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{zt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \);
3. \( u_{xt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{yt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{zt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \);
4. \( u_{xt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{yt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \), \( u_{zt} = \pm \frac{u_2^+/\sqrt{3}}{\sqrt{3}} \).

In each row, either all upper signs, or all lower signs are to be used, and these choices give the coordinates of the displacements.
for the two members of the opposed pair. The distortion factor for these four pairs of sites is

\[ \Pi_2^+ = \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi/\sqrt{3}\right)(h \cdot k - l) \right\} u_2^+ \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi/\sqrt{3}\right)(h \cdot k - l) \right\} u_2^+ \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi/\sqrt{3}\right)(h \cdot k - l) \right\} u_2^+ \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi/\sqrt{3}\right)(h \cdot k - l) \right\} u_2^+ \] (7.25)

Of course, the total distortion factor for the positive ion, \( \Pi_{12}^+ \), due to displacements caused by the first two shells of defect sites is given by

\[ \Pi_{12}^+ = \Pi_1^+ \Pi_2^+ \] (7.26)

By reference to Figure 34, it is seen that the coordinates of the displacements of the negative ion by the negative ions in the twelve sites of the first shell are

1. \( u_{xt} = \pm u_1^\prime/\sqrt{2} \), \( u_{yt} = \pm u_1^\prime/\sqrt{2} \), \( u_{zt} = 0 \);
2. \( u_{xt} = \pm u_1^\prime/\sqrt{2} \), \( u_{yt} = \pm u_1^\prime/\sqrt{2} \), \( u_{zt} = 0 \);
3. \( u_{xt} = \pm u_1^\prime/\sqrt{2} \), \( u_{yt} = 0 \), \( u_{zt} = \pm u_1^\prime/\sqrt{2} \);
4. \( u_{xt} = \pm u_1^\prime/\sqrt{2} \), \( u_{yt} = 0 \), \( u_{zt} = \pm u_1^\prime/\sqrt{2} \);
5. \( u_{xt} = 0 \), \( u_{yt} = \pm u_1^\prime/\sqrt{2} \), \( u_{zt} = \pm u_1^\prime/\sqrt{2} \);
6. \( u_{xt} = 0 \), \( u_{yt} = \pm u_1^\prime/\sqrt{2} \), \( u_{zt} = \pm u_1^\prime/\sqrt{2} \).

The distortion factor for these six pairs of opposed sites is

\[ \Pi_1^- = \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi\right)(h \cdot k) \right\} u_1^- \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi\right)(h \cdot k) \right\} u_1^- \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi\right)(h \cdot k) \right\} u_1^- \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi\right)(h \cdot k) \right\} u_1^- \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi\right)(h \cdot k) \right\} u_1^- \]

\[ \times \left\{ 1-2p(1-p) \right\} \left\{ 1 - \cos\left(2\pi\right)(h \cdot k) \right\} u_1^- \] (7.27)
It will be noted that $u^+_1$, $u^+_2$, and $u^-_1$ in these equations are the ratio of the magnitudes of the displacements to the length of the lattice translation vector, $a_0$.

The values of the distortion factors, $\Pi^+_{12}$ and $\Pi^-_1$, can now be calculated from Eq. (7.24), (7.25), and (7.27) for the various reflections assuming displacements, $u^+_1$, $u^+_2$, and $u^-_1$, of such magnitudes that the best correlation is obtained with the experimental distortion factors previously determined. Since the evaluation of $\Pi^+_{12}$ requires the knowledge of two parameters, $u^+_1$ and $u^+_2$, the further assumption will be made that the displacement, $u^+_2$, is proportional to that of $u^+_1$ in the same ratio as given by the elastic theory approximation. The ratio of the radii of the shells containing these sets of sites is $r^+_2/r^+_1 = \sqrt{3}$, whence, to this approximation,

$$u^+_2 = (1/3)u^+_1$$

(7.28)

It should be mentioned that even though this assumption is probably not too accurate, it is the only reasonable assumption that can be made considering the accuracy of the experimental data, and even if its value is considerably in error the resulting error in $\Pi^+_{12}$ will be quite small because of the relatively minor importance of $\Pi^-_2$, as is shown in Table 35.

It has been previously mentioned that the values of $\Pi^+$ and $\Pi^-$ are defined only for those values of $\sin \theta/\lambda$ corresponding to integral values of $h,k,l$, and the validity of the procedure of treating the experimental structure factors of the solid solutions as smooth functions of $\sin \theta/\lambda$, as has been done, must be considered.
The deviation of the calculated values of $\Pi$ from a smooth curve will be greatest for the largest displacements, $u$, that are encountered. Accordingly, in Table 35 are tabulated the values of $\Pi^+$ for the positive ion in the solid solution containing fifty percent sodium bromide which are calculated for eight reflections by Eqs. (7.24) and (7.25), for the assumed displacements $u_1 = 0.14 \AA/a$ and $u_2 = 0.14 \AA/3a$.

**TABLE 35**

Calculated Distortion Factors of the Positive Ion

<table>
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<tr>
<th>Reflection</th>
<th>$(\frac{\sin \theta}{\lambda})^2$</th>
<th>$\Pi_1^+$</th>
<th>$\Pi_2^+$</th>
<th>$\Pi_{12}^+$</th>
<th>$1-\Pi_{12}^+$</th>
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<td>0.1191</td>
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<td>0.8069</td>
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<td>0.9532</td>
<td>0.6842</td>
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</tbody>
</table>

When these calculated values of $1-\Pi_{12}^+$ were plotted as a function of $(\sin \theta/\lambda)^2$, it was found that a straight line could be drawn through the points such that no point lies off of the line by more than 2.0 percent of its value. This corresponds to a maximum deviation of 0.5 percent from a smooth curve for any calculated value of $\Pi_{12}^+$. 
and this in turn will cause a maximum deviation of 0.1 percent for any value of $F_{even}$ and 0.3 percent for any value of $F_{odd}$ from a smooth curve. Since the experimental uncertainty is one percent or greater for all but one of the structure factors determined for this solid solution as is indicated in Table 12, the procedure which was adopted of drawing smooth curves through the experimental points and thereby considering the effective scattering factors of the ions as being continuous and smooth functions of $(\sin \theta / \lambda)$ is seen to be justified. It will be noted that the deviation of the calculated distortion factors from a smooth curve for the positive ion in the other two solid solutions studied and for the negative ion in all of the solid solutions will be considerably less than for the example just given because of the smaller displacements of the ions.

The values of the distortion factors calculated by Eqs. (7.23), (7.24), and (7.26) for the ions in the solid solutions studied are shown by the solid lines in Figures 32 and 33 for various assumed displacements of the ions. For the curves of the distortion factors of the positive ions, $\Pi_{12}^+$, the magnitude of the displacements caused by the second shell of defects, $u_2^+$, are assumed to be one third as large as $u_1^+$, for each of the values of $u_1^+$ indicated on the graphs in Fig. 32.

In view of the inherent uncertainty in the values of the experimental distortion factors, the agreement between the experimental values and the calculated values in each case is quite good for the range of $(\sin \theta / \lambda)$ covered, as is also the agreement of the trend of
the trend of the variation of the experimental values with \((\sin \theta/\lambda)\)
with that which is theoretically predicted. It will be noted in
these figures that because of the uncertainty in the experimental
results, it is not completely clear whether the values of the dis-
tortion factors determined with \(\gamma=1.00\) or those determined with
\(\gamma=1.80\) are in better agreement with the calculated curves, since
the values of the experimental distortion factors can be seen to be
relatively insensitive to this variation in \(\gamma\).

It should be mentioned that the values of the experimental
distortion factors which were determined at values of \((\sin \theta/\lambda)\) of
0.34, 0.36, 0.34, 0.36, and 0.33 are subject to rather large error
because of the necessity of extrapolating the curves through the
structure factors beyond the experimental points, as can be seen in
Figures 27 through 31. It will be noted that the quantities \(1-\prod_i\)
which are plotted in Figures 32 and 33 are a measure of the
fractional decrease in the scattering power of the ion due to the
distortion, and since the magnitude of \(1-\prod_i\) for the ions studied are
mostly in the range below 0.1, the deviation from linearity of the
experimental values plotted in the figures can be attributed entirely
to the error inherent in the values obtained for the structure
factors. In particular, the scatter in the experimental values of
\(1-\prod^+\) for the sodium ion in the solid solution containing 25 percent
sodium bromide is undoubtedly due in part to the error introduced
by having to correct the experimental structure factors of this
material for the effect of partial decomposition.
It should be emphasized, however, that the trend shown in the variation of the experimental distortion factors with increasing \((\sin \theta / \lambda)\), and the approximate values which they attain at the higher values of \((\sin \theta / \lambda)\) are with the possible exception of those values for the sodium ion in the solution containing 25 percent sodium bromide, significantly greater than the experimental uncertainty in their determination. Furthermore, it is significant that the experimental values of \(1 - \Pi_i\) which have been determined are, in each case, much larger than can be accounted for by the sole employment of the elastic theory approximation. Of particular interest is the very large mean displacement of \(0.13 \text{ Å}\) experienced by the sodium ion in the solid solution containing 50 percent sodium bromide, since this displacement is essentially the same, within experimental accuracy, as the value of \(0.14 \text{ Å}\) as given by Pauling (56) for the difference in the radii of the bromide ion and the chloride ion.

Of course, it is also reassuring that in no case is it necessary to require a displacement which exceeds this difference in radii of the bromide and chloride ions in order to account for the observed decrease in scattering power.

E. Discussion of Results

The general theory presented by Zachariasen regarding x-ray scattering by a disordered lattice as well as the detailed theoretical treatment due to Taylor both predict a decrease in the intensity of
the Laue-Bragg reflections because of local distortion about the
defect sites without significant broadening of these reflections.

However, prior to this investigation, there has appeared no con­
cclusive experimental evidence which would confirm this predicted
effect either qualitatively or quantitatively. It is believed that
the results of the present research, therefore, offer the first
unambiguous qualitative confirmation of the effect, as well as
allowing for conclusions of a semi-quantitative nature regarding the
magnitudes of the local distortion.

The formula derived by Huang for the elastic distortion factor,
as given by the square-root of the expression on page 9 of the text,
predicts values of 0.386 and 0.913 for the distortion factor for
p=0.50 and p=0.25 or 0.75, respectively, for the ions in the solid
solutions under investigation at \((\sin \theta/A) = 0.68\). These values of
\(E\) are the same as would be predicted for the elastic contribution
to the distortion factor as given by Eq. (7.16) for the corresponding
values of \(p\) and \((\sin \theta/A)\) if one sets \(f\) equal to unity and \(r_0\) equal
to \(a_0/2\) for the calculation. The latter condition implies, of course,
that the displacement of a cation by any defect site (including
nearest-neighbor sites) may be adequately treated by the elastic
theory approximation. It is clear that the decrease in scattering
power or intensity predicted by the elastic theory approximation is
not nearly sufficient to account for the magnitude of the observed
decrease for the cation in the solid solution containing 50 percent
sodium bromide. Thus it is seen to be mandatory in order to interpret
all of the experimental results to consider the larger discrete displacements which are undergone by the ions in the immediate vicinity of the defect sites, employing the accurate method of treatment developed by Taylor. It is noteworthy also that the relative decrease in the scattering power of the ions for the various reflections due to the local distortion as predicted by the theory of Taylor is in reasonable accord with that which is experimentally determined.

The close agreement between the magnitude of the displacement of the sodium ion in the 50 percent solid solution and the magnitude of the difference in radii of the bromide and chloride ions is very interesting. This may indicate that the assumption made by Taylor that the displacements produced by the various defects are independent of one another and vectorially additive may be reasonably true even for a solid solution of this concentration.

It will be noted that the mean displacements of the positive ion in the solid solutions containing 25 and 75 percent sodium bromide are only about one half as large as the displacement of the sodium ions in the 50 percent solid solution. This is undoubtedly due to the greater tendency of two negative ions of the same type to oppose a given sodium ion in the former two solid solutions such that no net displacement of the cation is produced. An abundance of such configurations will, of course, lower the mean displacement that is measured.
It is possible that within the precision of determination there is no significant difference in the displacements of the negative ions in the three solid solutions investigated. It is not surprising that the displacement of the negative ion in the 50 percent solid solution is much less than that of the cation since the nearest-neighbor anion-anion pairs are not in contact as are the nearest-neighbor cation-anion pairs.

Although the preceding discussion has been of a very qualitative nature, it has only intended to suggest that there is no apparent disagreement between the numerical results obtained in this study and those that might be expected or anticipated.
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