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Presented in Partial Fulfillment of the Degree Doctor
of Philosophy in the Graduate School of The Ohio State
University

By

Thomas Thornton Meek, B.S., M.S.

THE OHIO STATE UNIVERSITY
1977

Reading Committee:
Dr. W. D. Shook
Dr. C.H. Drummond III
Dr. D. McLachlan, Jr.

Approved By:

William B. Shook
Adviser
Department of Ceramic Engineering
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VITA

I, Thomas Thornton Meek, was born on December 26, 1944 in Scranton, Pennsylvania. I took my secondary education at Ruston High School, in Ruston, Louisiana. In 1966 I graduated from The Louisiana Polytechnic Institute with a Bachelor of Science degree in Electrical Engineering and in 1969 received the Master of Science degree in Ceramic Engineering from The University of Missouri at Rolla, Rolla, Missouri.

During the years 1971 to 1977 I have been a graduate student in the Ceramic Engineering Department at The Ohio State University.
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CHAPTER I
INTRODUCTION AND LITERATURE REVIEW

Structures of amorphous materials have long been of interest because of the direct relation between the structure and other properties of the material. For example optical transparency, electrical conductivity, viscosity, density, and diffusion are all very structure dependent. Various techniques have been employed to obtain accurate structural information on amorphous materials. The book by Wong and Angell (Glass Structure by Spectroscopy) along with publications by Wright, and Wright and Leadbetter provide an up-to-date survey of many of these techniques.

Two of the more commonly used methods for obtaining structural information are x-ray diffraction and neutron diffraction. Neutron diffraction studies have been carried out on the structure of vitreous silica by Breen, Delaney, Persiani, and Weber; Delaney and Weber; Carraro, Domenici, and Zucca, and Lorch.

Both x-ray diffraction and neutron diffraction techniques were used by Henninger, Buschert and Heaton to obtain radial distribution functions (RDF's) on vitreous silica. Their theoretical analysis consisted of using the approximate method put forth by Warren.
The early work done on the structure of vitreous silica largely employed x-ray diffraction methods. Probably the first important paper published on this structure was by Randall, Rooksby and Cooper in 1930. Their work presented the first x-ray study of vitreous silica, and their conclusion was that the structure consisted of an aggregate of very small crystals. Zachariasen in 1932 put forth the view that vitreous silica consisted of a three-dimensional network of randomly oriented SiO$_4$ tetrahedra. In 1936 Warren, Krutter, and Morningstar presented the first radial distribution analysis of vitreous silica using x-ray diffraction. Their work indicated that the structure of vitreous silica consisted not of an aggregate of small crystals, but of a continuous random network of SiO$_4$ tetrahedra. They thus confirmed Zachariasen's random network model.

The most recent x-ray diffraction work on the structure of vitreous silica resulted from the development by Warren of a direct method for analyzing x-ray diffraction data from an amorphous material with more than one kind of atom. Warren's student R. L. Mozzi carried out the first structure investigation of vitreous silica using the new pair distribution function (PDR) method. To date, his results are probably the best yet obtained on vitreous silica. Up to this time the x-ray diffraction studies on vitreous silica were interpreted
using the approximation that different atoms in a unit of composition have atomic scattering factor curves that are constant multiples of each other. This method was referred to as the approximate method and was introduced in the work of Warren, Krutter, and Morningstar. The development of the direct method enabled x-ray diffraction data to be analyzed without having to make the above assumption.

In the work of Warren and Mozzi on the structure of vitreous silica, it should be noted that diffraction data were obtained experimentally using the Warren-Marvel\textsuperscript{1} x-ray fluorescence technique. Prior to this, x-ray data on vitreous silica could not be obtained accurately in the region of high $k,k=12$ because of inability to correct for the modified component of x-ray scattering. $k$ here is defined as $4 \pi \sin \theta / \lambda$, where $\theta$ is the angle of incidence of the x-ray beam and $\lambda$ is the wavelength of the incident radiation. For low atomic number materials, such as silica, the magnitude of the inelastic scattering (Compton scattering) is many times that of the unmodified scattering at high $k$. Using the Warren-Marvel technique, Mozzi was able to eliminate most of the Compton scattering that took place at high $k$. The x-ray diffraction data that Mozzi then used were very accurate out to a $k$ of 20. Mozzi's experimental setup consisted of directing a primary beam of crystal-monochromated RhK$\alpha$ radiation upon the sample.
of vitreous silica. The scattered radiation, consisting of both the unmodified (same wavelength as incident radiation) and modified (Compton scattering, longer wavelength), then fell upon a sheet of molybdenum foil which was oriented $45^\circ$ to the beam. The molybdenum fluorescence K radiation was detected by a krypton filled counter at $90^\circ$ to the diffracted beam. The wavelength of the molybdenum K absorption edge is 0.620Å. It is thus apparent that the Compton component of the scattered radiation will be effectively eliminated at high $k$. The efficiency of this process is approximately 0.5%; however, intensities are sufficient to yield very good results.

Interpretation of the x-ray diffraction data yielded the following information about the structure of vitreous silica. Each silicon atom is tetrahedrally surrounded by four oxygen atoms with a Si-O bond of 1.62Å, a O-O bond of 2.65Å, and a Si-Si bond of 3.12Å. On the resulting PDF the first major peak corresponds to the Si-O bond length, the second major peak to the O-O bond length, and the third major peak to the Si-Si bond length. The angular distribution function $V(\alpha)$ showed a variation in the Si-O-Si bond angle $\alpha$ of $120^\circ$ to $180^\circ$ with a maximum at $144^\circ$.
In general, Mozzi's work supported the random network model for vitreous silica. His work however, made the model more precise.

Further work was done on the structure of vitreous silica at the University of Florida by Gokularathnam. His work examined the effect of heat treatment, water content, and fast neutron irradiation on the structure of vitreous silica. Heat treating a bulk sample of vitreous silica for 360 hours at 1450°C had no effect on the PDF of vitreous silica. However, if the same bulk sample was ground up into powder and heat treated, crystallization was shown to occur with time.

The effect of water content on the structure of vitreous silica was not clearly defined by Gokularathnam; however, his conclusion was that as water content increases in vitreous silica the structure exhibits a more crystalline nature.

His analysis of the effect of fast neutron irradiation of vitreous silica showed a broader distribution of the interatomic distances and a decrease in the Si-O-Si angle $\alpha$.

One of the more recent investigations of the vitreous silica structure using the Warren-Marvel x-ray fluorescence technique was carried out by Wicks. Generally his work confirmed Mozzi's results. He determined a Si-O bond length of 1.625\AA, and a O-O bond of 2.66\AA, with a Si-O-Si angle of 143°. The range of
\( \alpha \) was 130° to 180°. He also concluded that a random orientation (twist) about the Si-O bond directions exists.

One other commonly used technique to develop a structure for amorphous materials is the construction of models. This method has been applied to the structure of vitreous silica by Ordway;\textsuperscript{27} Evans and King;\textsuperscript{28} and Bell and Dean.\textsuperscript{29} In applying this technique, the following procedure is generally undertaken. A model of the structure is made by joining SiO\(_4\) tetrahedron units in a random manner. From this model the distribution of bond length and average number of neighbors are determined. This information essentially determines a proposed RDF for the model and can be compared to an experimentally obtained RDF using x-ray diffraction techniques.

Up to now the x-ray work carried out on the vitreous silica structure has employed wavelength spectrometers. Best results have been obtained by using the Warren-Marvel experimental approach. One serious drawback in using this approach however, is an overall process efficiency of only 0.5%. For every 200 unmodified quanta entering the receiving slit, only one count is recorded in the krypton counter. The present investigation was conducted utilizing energy dispersive x-ray analysis as the data gathering technique in an effort to improve the efficiency. It is hoped that better x-ray diffraction structural data can be obtained at high \( k' \) with this technique.
There are certain advantages in using an energy spectrometer over the conventional wavelength spectrometer. For example, a wavelength spectrometer can detect only a narrow window of energies at one time with limited collection efficiencies. This stems from geometrical constraints on the crystal, the specimen, and the detector positions. Also it should be noted that diffraction and focusing conditions of the wavelength spectrometer require very precise mechanical motions of the crystal and detector with respect to the x-ray source to be analyzed. For wavelength spectrometry the specimen has to be accurately located at a particular diffraction plane in space in order to avoid loss in intensity. For energy spectrometry neither diffraction nor focusing are required, and a solid state detector such as a silicon lithium (Si (Li)) doped one can respond to a wide range of x-ray energies whose coverage by a conventional wavelength spectrometer would require use of several crystals and detectors. With advances made recently in the area of solid state detectors, such as the Si(Li) detector used in this investigation, the use of energy spectrometry in structural analysis is possible. A comparison between the resolution capabilities of wavelength spectrometers is shown in Figure. It should be noted that for silver radiation, the only wavelength spectrometer that exhibits a resolution
FIGURE 1
(From Reference 9)

COMPARISON OF RESOLUTION BETWEEN WAVELENGTH AND ENERGY SPECTROMETERS AS A FUNCTION OF X-RAY ENERGIES
superior to the Si(Li) detector is the four inch LiF crystal spectrometer.

Very little structure work has been reported in the literature in which energy dispersive x-ray analysis is the data gathering technique. A recent analysis of the amorphous Ge$_{17}$Te$_{83}$ structure was reported by Betts, Bienenstock, Keating, and deNeufville.$^{31}$ Their work utilized zirconium filtered MoK$_\alpha$ radiation with a Picker diffractometer and a NEG solid-state detector. A pulse height analyzer with a window of 15 kev to 19 kev was used so that Compton scattering along with coherent radiation would be detected. The Compton correction was made by computer techniques during data analysis.

The structure of amorphous Se has been reported by Shimazu and Watanabe.$^{11}$ In their paper they indicated that the structure of vitreous silica had been determined; however, they gave no results. A technique was discussed concerning the elimination of the Compton scattering by using a half profile approach when recording the coherent (unmodified) peak area with a multichannel analyzer. This method of Compton correction will be discussed in Chapter 5.

It was decided that in order to properly evaluate this data gathering technique, a suitably well understood vitreous structure would be used as a reference. The structure of vitreous silica was chosen since it is the
basic structure for silicates and because intense interest has been directed toward understanding of this structure over the years.
CHAPTER II
THEORY

In this chapter three topics shall be discussed. First, a general derivation following closely that of Warren\(^2\) will be given describing x-ray scattering from an amorphous material with more than two kinds of atoms. Next, a discussion of diffuse scattering from an amorphous material and a single crystal will be presented; and last, errors will be discussed in the experimental measurement of x-ray diffraction information caused by x-ray beam penetration into the sample, incorrect multichannel analyzer energy calibration, and misalignment of the diffractometer.

Generally there are two methods used in the analysis of experimental x-ray diffraction data in terms of structure. One method consists of a theoretical calculation of the scattering pattern for various proposed models and then comparison with the observed pattern. The second method, discussed in the next section, consists of a Fourier transform from energy space into \(R\) space thereby obtaining structural information directly.
2.1 Scattering Off An Amorphous Material:

For this investigation the method used for data analysis is called "the exact method" for analyzing x-ray scattering from an amorphous sample with more than one kind of atom. The development given here follows closely that of Warren's treatment.

Listed below are symbols used in this chapter:

- \( UC \) = unit of composition
- \( uc \) = sum over the atoms of the unit of composition
- \( N \) = number of units of composition in the sample
- \( V \) = volume of the sample
- \( N/V \) = number of units of composition per unit volume
- \( I_{eu} \) = the ratio of the actual scattered sample intensity to that of the classical intensity from a single electron.
- \( f_m \) = atomic scattering factor of atom \( m \)
- \( N_{ij} \) = average number of atoms in shell \( i \) at distance \( r_{ij} \) from atom of type \( j \).
- \( q_m(r) \) = fraction of atoms within sample of the surface of a sphere of radius \( r \) which is centered on atom \( m \).
\[ \rho_m(r_{mn})dV_n = \text{number of atoms (with each atom being multiplied by its } f_m) \text{ in a volume element } dV_m \text{ displaced } \vec{r}_{mn} \text{ from atom } m. \]

In considering scattering off an amorphous sample, it is first prudent to develop a general scattering equation for random orientation of the sample. Let vector quantity \( \vec{r}_m \) be the instantaneous position of each atom of type \( m \) located about an atom of type \( n \). The vector joining the two atoms then is \( \vec{r}_{mn} \). It is known that the scattered intensity from a sample containing atoms of type \( m \) and type \( n \) given in electron units takes the form:

\[
(2-1) \ I_{eu} = \sum_{m} \sum_{n} f_m f_n e^{(2\pi i/\lambda)(\vec{S} - \vec{S}_0) \cdot \vec{r}_{mn}} e^{-(2\pi i/\lambda)(\vec{S} - \vec{S}_0) \cdot \vec{r}_n}
\]

The incoming x-ray beam has a direction represented by vector quantity \( \vec{S}_0 \) and the direction to the point of observation is represented by vector quantity \( \vec{S} \). Represented in Figure 52 is the above information. It is seen then from Figure 2 that

\[
(\vec{S} - \vec{S}_0) \cdot \vec{r}_{mn} = 2\sin \theta \cdot r \cos \theta
\]

and letting \( k \) be defined as \( k = 4\pi \sin \theta / \lambda \) where \( k \) here is defined to be the wave number. Equation (2-1) can be reduced further by letting \( \vec{r}_{mn} = \vec{r}_m - \vec{r}_n \).

\[
(2-2) \ I_{eu} = \sum_{m} \sum_{n} f_m f_n e^{(2\pi i/\lambda)(\vec{S} - \vec{S}_0) \cdot (\vec{r}_m - \vec{r}_n)}
\]

and

\[
(2-3) \ I_{eu} = \sum_{m} \sum_{n} f_m f_n e^{(2\pi i/\lambda) \cdot (\vec{S} - \vec{S}_0) \cdot \vec{r}_{mn}}
\]
As shown in Figure 2 when $\bar{r}_{mn}$ is allowed to take any orientation in space with equal probability, then it is known that atom $m$ can reside with equal probability at any point on the sphere of Figure 2. The average value of the exponential term of equation (2-3) then can be written as:

\[
\left\langle e^{i(2\pi \bar{r}_{mn} \cdot (\bar{s} - \bar{s}_0))} \right\rangle = \frac{1}{4\pi r_{mn}^2} \int_{\phi=0}^{\pi} e^{i\vec{r}_{mn} \cdot 4\pi \sin\theta \cos\phi / \lambda} \frac{1}{2\pi r_{mn}^2} \sin\phi d\phi
\]

Remembering that $k = 4\pi \sin\theta / \lambda$, expression (2-4) can be reduced to:

\[
\left\langle e^{i(2\pi \bar{r}_{mn} \cdot (\bar{s} - \bar{s}_0))} \right\rangle = \frac{1}{4\pi r_{mn}^2} \int_{\phi=0}^{\pi} e^{ikr_{mn} \cos\phi} \frac{1}{2\pi r_{mn}^2} \sin\phi d\phi
\]

Upon integration of the integral shown in (2-5), expression (2-6) is obtained:

\[
\left\langle e^{i(2\pi \bar{r}_{mn} \cdot (\bar{s} - \bar{s}_0))} \right\rangle = \sin kr_{mn} / k r_{mn}
\]

Substituting expression (2-6) in expression (2-1) for every exponential term, it is seen that an equation is developed, representing the average unmodified intensity from an array of atoms which can take all orientations in space.
FIGURE 2

(From Reference 5)

THE RELATION BETWEEN THE $\vec{S} - \vec{S}_o$ VECTOR AND THE VECTOR $\vec{f}_{mn}$ FOR AN ATOM $n$ CENTERED AT $0$ AND AN ATOM $m$ AT THE INSTANTOUS POSITION $\vec{r}_{mn}$
Figure 2
Equation (2-7) is known as the Debye\textsuperscript{16} scattering equation. Throughout the derivation of expression (2-7) little was mentioned concerning the atomic scattering factors $f_m$ and $f_n$. It was assumed that for (2-1) the x-ray wavelength is much smaller than any of the absorption edge wavelengths in the atom and (2) that electron distribution in the atom takes on spherical symmetry. In this investigation it is known that the second assumption does not hold. It is necessary then to employ a dispersion correction. This correction is expressed as: 

\begin{equation}
(2-8) \quad f = f_o + \Delta f^1 + i \Delta f^{11}
\end{equation}

where $f$ now is the corrected scattering factor, $f_o$ is the uncorrected value found in the International Tables for X-ray Crystallography Vol. III,\textsuperscript{31} and $\Delta f^1$ and $\Delta f^{11}$ are the real and imaginary parts of the dispersion correction. Here $\Delta f^{11}$, the imaginary part, represents a small shift in phase of the scattered radiation. Angular dependence of $\Delta f^1$ and $\Delta f^{11}$ is small compared to $f_o$.

If a unit of composition UC is chosen, as for example silica, then it would consist of one silicon atom and two oxygen atoms. In considering x-ray scattering off a structure of two types of atoms, expression (2-1) then would become
Expression (2-9) is obtained by separating terms in expression (2-1) for which \( m = n \) and \( m \neq n \).

If now the term \( \rho_m (\vec{r}_{nm}) \, dV_n \) (defined above) is introduced, the \( \frac{1}{m} \) can be replaced by an integral over the sample volume.

\[
(2-10) \quad I_{eu} = \frac{1}{m} f_m^2 + \frac{1}{m} f_m \int_s [\rho_m (r_{mn}) e^{(2\pi i/\lambda)(\vec{r} - \vec{r}_0)} \cdot \vec{r}_{mn}] \, dV_n 
\]

Recognizing that the average value of \( \rho_m (\vec{r}_{nm}) \, dV_n \) is as follows:

\[
(2-11) \quad \langle \rho_m (\vec{r}_{nm}) \, dV_n \rangle = \frac{N}{V} \frac{1}{\nu_c} f_j \, dV_n
\]

where \( j \) here denotes the kind of atom. A term involving this average can now be added and subtracted from expression (2-10) yielding expression (2-12).

\[
(2-12) \quad I_{eu} = \frac{1}{m} f_m^2 + \frac{1}{m} f_m \int_s [\rho_m (\vec{r}_{nm}) - \frac{N}{V} \frac{1}{\nu_c} f_j \, dV_n] \times e^{(2\pi i/\lambda)(\vec{r} - \vec{r}_0)} \cdot \vec{r}_{mn} \, dV_n + \frac{1}{m} f_m \int_s \frac{N}{V} \frac{1}{\nu_c} f_j \, dV_n \times e^{(2\pi i/\lambda)(\vec{r} - \vec{r}_0)} \cdot \vec{r}_{mn} \, dV_n 
\]

The last term of expression (2-12) is negligible because it represents the small-angle intensity (intensity at scattering angles so small as not to be observable).
Also recognizing that for displacements of \( \vec{r} \)
(where \( \vec{r}_{nm} = \vec{r} \) and \( \rho(r) = \langle \rho_m(\vec{r}_{nm}) \rangle \)) of greater
than a few atomic dimensions,
\[
\rho_j(r) - \frac{(N)}{V} \leq f_j \rightarrow 0 ,
\]
and recalling that when \( \vec{r}_{nm} \) can take any orientation,
the average value of the exponential terms can replace
them, then expression (2-12) becomes:

\[
(2-13) \quad I_{eu} = \frac{1}{m} \sum f_m^2 + \frac{1}{m} \sum f_m \leq \frac{1}{n+m} \sum f_m \sin kr_{nm} k r_{nm} \\
- \frac{1}{m} \sum f_m \frac{1}{s} \sum \frac{N}{V} \leq f_j \leq \frac{1}{n+m} \sum \frac{1}{k r_{mn}} \int dV_n
\]

Two quantities defined above are now introduced:
\( N_{ij} \) and \( q_m(r) \); and spherical shells are denoted by \( i \) and
atom type by \( j \). It is seen that the \( \leq \frac{1}{n} \) can be replaced
by a sum over shells of neighbors and the integral
can be extended to infinity because \( q_m(r) \rightarrow 0 \) as
\( r \rightarrow \infty \). Thus expression (2-13) becomes:

\[
(2-14) \quad I_{eu} = N \leq \frac{1}{n} \sum f_j^2 + N \leq \frac{1}{n} \sum f_j \leq N_{ij} \leq f_i \frac{1}{k r_{ij}} \sum \sin kr_j \\
- \frac{1}{n} \sum f_j \leq \frac{1}{n} \sum f_m \int_0^\infty \frac{1}{k r} \int_0^2 \sin kr \, \int_0^2 \, dV_n
\]

Now taking the average value of \( q_m(r) \) to be \( \langle q_m(r) \rangle = q(r) \)
where this average is taken over all atoms \( m \), it is
seen from the definition of $q_m(r)$ that for $r = 0$, $q(r) = 1.0$ and, when $r$ equals the sample dimensions, $q(r) = 0.0$. Expression (2-14) can then be altered as shown in (2-15).

\[(2-15) \quad k \left( \frac{I_{eu}}{N} - \sum \frac{f_j^2}{U_j} \right) = \sum \frac{f_j}{U_j} \sum \frac{N_{ij}}{r_{ij}} f_i \sin kr_{ij} \]

\[- \frac{N}{V} \left( \sum \frac{f_j}{U_j} \right)^2 \int_0^\infty r q(r) \sin k r dr \]

Let us now call expression (2-15) the $k_i(k)$ equation where $k_i(k) = k\left(\frac{I_{eu}}{N} - \sum \frac{f_j^2}{U_j}\right)$.

It is now expedient to introduce two new factors: (1) a convergence factor $e^{-\alpha^2k^2}$ and (2) a sharpening factor $\frac{1}{\sigma(k)}$, $\alpha$ being defined as (\frac{1}{k_{max}}). Without multiplying the $k_i(k)$ expression by the convergence factor, equal weight would be given to the peaks and dips in the $i(k)$ curve at large values of $k$ where the experimental accuracy is not very good. A second reason for multiplying by a convergence factor is that termination of the $k_i(k)$ expression at some finite $k_{max}$ where the $k_i(k)$ curve has not converged will produce false termination satellites in the pair function curve. By multiplying by a convergence factor the magnitude of these satellites will be reduced.

Expression (2-15) is divided by a sharpening factor so as to sharpen the peaks and dips of the $k_i(k)$ curve at high $k$. The sharpening factor behaves as follows:
at \( k=0 \), \( g(k) = 1.0 \), as \( k \) increases \( g(k) \) decreases.

For this investigation, \( g(k) = f_e \) the scattering factor for an electron. The expression for the \( ki(k) \) curve then is:

\[
(2-16) \quad ki(k)e^{-\alpha^2k^2} = \left( \frac{Ie\omega}{N} - \frac{f_j^2}{\omega c} \right) e^{-\alpha^2k^2}g^2(k)
\]

or

\[
(2-17) \quad ki(k)e^{-\alpha^2k^2} = \frac{f_j}{\omega c} \sum_{i} N_i j f_i \frac{e^{-\alpha^2k^2}}{g^2(k)} \sin k r \delta_{ij}
\]

\[-\frac{N}{V} \left( \frac{f_j}{\omega c} \right)^2 e^{-\alpha^2k^2} \frac{1}{g^2(k)} 4\pi \int_0^\infty q(r) \sin kr \, k \, dk \]

If now expression (2-17) is multiplied by \( \sin kr \) and then integrated from \( k = 0 \) to \( k = k_m \) expression (2-18) follows:

\[
(2-18) \quad \int_0^{k_m} ki(k)e^{-\alpha^2k^2} \sin kr \, k \, dk = \frac{f_j}{\omega c} \sum_{i} N_i j f_i \int_0^{k_m} e^{-\alpha^2k^2} \frac{1}{g^2(k)} 4\pi \int_0^\infty q(r) \sin kr \, k \, dk
\]

It is evident through successive integration of \( \int_0^\infty q(r) \sin kr \, dr \) by parts that this function is negligible at small values of \( k \) and decreases rapidly as \( k \) increases. It is thus expedient to replace the last term of expression
(2-18) with a term having all of its slowly varying quantities replaced by their values at \( k=0 \). The last term in expression (2-18) then is:

\[
(2-19) \quad -\frac{N}{V} \int_{0}^{\infty} \left( \sum_{\mu \in \mathbb{C}} \frac{f_{\mu}}{c} \right)^{2} \frac{e^{-\alpha^{2}k^{2}}}{\mathcal{Q}^{2}(k)} 4\pi \int_{0}^{\infty} r_{Q}(r) \sin kr \, dr \\
= \frac{N}{V} \left( \sum_{\mu \in \mathbb{C}} z_{j} \right)^{2} 4\pi \int_{0}^{\infty} \int_{0}^{\infty} r_{Q}(r) \sin kr \, dr \, dk
\]

where the integral over \( k \) is now allowed to go to infinity.

It is known that the term:

\[
(2-19) \quad 4\pi \int_{0}^{\infty} r_{Q}(r) \sin kr \, dr
\]

is the Fourier transform of \( r_{Q}(r) \). Employing the inversion relation:

\[
(2-21) \quad f(r) = \frac{1}{2\pi^{2}} \int_{0}^{\infty} \phi(k) \sin kr \, dk
\]

it is seen that expression (2-22) develops.

\[
(2-22) \quad 2\pi^{2} r_{Q}(r) = 4\pi \int_{0}^{\infty} r_{Q}(r) \sin kr \, dr
\]

The last term of expression (2-18) then becomes:

\[
(2-23) \quad 2\pi^{2} r_{Q}(r) \frac{N}{V} \left( \sum_{\mu \in \mathbb{C}} z_{j} \right)^{2} = 2\pi^{2} r_{e} \sum_{\mu \in \mathbb{C}} z_{j}
\]
where \( \rho_e = \frac{N}{V} \sum_j z_j \) and is the average electronic density and \( z_j \) is the atomic number of the \( j \)th kind of atom. Assuming zero porosity, \( \rho_e \) can be calculated from the measured density in expression (2-23). It is recognized that for small values of \( r \), \( q(r) = 1.0 \). In this investigation, this approximation will be valid. Expression (2-18) can now be written as (2-24)

\[
(2-24) \quad \rho_e \rho_e \rho_e \sum_{i<j} \frac{N_{ij}}{r_{ij}} \int_{0}^{k_m} \frac{f_i f_j}{\sigma^2(k)} e^{-\alpha^2 k^2} \sin k r_{ij} \sin k r d r = 2 \pi^2 r \rho_e \rho_e \rho_e \rho_e z_j + \int_{0}^{k_m} k i(k) e^{-\alpha^2 k^2} \sin r k d k
\]

Warren in his development introduces a set of pair functions at this point. Waser and Schomaker earlier indicated the usefulness of pair functions in the exact treatment of amorphous scattering. They indicated that the number of interatomic interactions at a given distance could be found by a Fourier transform of the suitably modified interatomic part of the intensity function multiplied by \( r \). Here an atomic distribution function is obtained whose peaks have areas proportional to the number of atomic pairs involved in the interactions.
Expression (2-25) represents the pair function employed by Warren.

\[ P_{ij}(r) = \int_0^{k_m} \frac{f_i f_j}{g^2(k)} e^{-\alpha^2 k^2} \sin kr \sin kr \, dk \]

by a simple trigonometric identity it is known that

\[ \sin kr_i \sin kr = (\cos(r-r_{ij})k - \cos(r+r_{ij})k)/2 \]

It is expedient to represent the pair function as

\[ P_{ij}(r) = \Phi_{ij}(r-r_{ij}) - \Phi_{ij}(r+r_{ij}) \]

where \( \Phi_{ij}(r-r_{ij}) \) and \( \Phi_{ij}(r+r_{ij}) \) are called auxiliary functions. The variation of electronic density versus distances for each atom pair will be described by an independent auxiliary function, (for example vitreous GeO\textsubscript{2} would have three atom pairs: Ge - Ge, Ge-0, 0-0).

In solving expressing (2-25) it is seen that the job can be made simpler by recognizing that \( \Phi_{ij}(r+r_{ij}) \) is usually small enough to neglect, thereby allowing the representation of expression (2-25) as

\[ P_{ij}(r) = \Phi_{ij}(x) = \frac{1}{2} \int_0^{k_m} \frac{f_i f_j}{g^2(k)} e^{-\alpha^2 k^2} \cos kx \, dk \]
where \( x = r - r_{ij} \). In terms of pair functions

equation (2-24) can then be written in a final exact
form as:

\[
\begin{align*}
(2-29) \quad \sum_{\mu \neq \nu} \frac{N_{\mu \nu}^i}{r_{\mu \nu}^i} P_{\mu \nu}^i(r) &= 2\pi \int r_0 \sum_{\mu \neq \nu} \frac{N_{\mu \nu}^i}{r_{\mu \nu}^i} \times \\
&\quad + \int_{0}^\infty k e^{-\lambda^2 k^2} \sin \pi r k \, dk
\end{align*}
\]

Expression (2-29) is the expression used in
structure determination. The procedure followed is
first to make certain corrections to the raw experimental
uncorrected x-ray scattering data. The corrections
will be discussed in the Chapter V. Once corrected, the
right hand side of expression (2-29) can be solved for
various \( r \) values yielding an observed experimental
structure. The first few peaks represent the interatomic
distances \( r_{ij} \) between the relative atoms.

Next, the left hand side of expression (2-29)
is used to develop a proposed theoretical model. First
a pair function is developed for each pair of atoms
corresponding to the observed \( r_{ij} \) distances on the
experimental model. Peaks from a crystalline form
of the amorphous material are used to identify the peaks
on the experimental model. Using the \( r_{ij} \) values and
the same convergence and sharpening factors as for the
experimental model and approximating \( N_{ij} \), the number of
\( j \) type atoms in the \( i \)th shell, it is then possible to
solve the left hand side of expression (2-29) to yield a theoretical model. This model is compared to the experimentally observed model and refinements in $N_{ij}$ and $r_{ij}$ are then made, thereby yielding slightly different pair functions and a slightly different theoretical model. This procedure is continued until the two models agree sufficiently well.

It should be noted that since the observed model cannot distinguish between calculated models which give equally good comparisons, the determined structure is not unique.

2.2 Diffuse Scattering Off Of A Crystalline Material

In the first part of this section a general scattering theory\(^5\) pertaining to an amorphous material was outlined. Data obtained to make the Compton correction to structural data obtained from vitreous silica was gathered by scattering x-radiation off a BT cut (a cut made $49^\circ$ to the $z$-axis of silica) single crystal of silica. A treatment of this type x-ray scattering is therefore presented below.

In general, scattering off a single crystal takes the form of Bragg scattering when the Bragg relation is satisfied and diffuse scattering when it is not satisfied. Bragg's relation is given below as:

\[(2-30) \quad \eta \lambda = 2d \sin \Theta \]

This expression relates the incident x-ray wavelength on the crystal to the
distance between atomic planes and the angle the incident radiation makes with those planes. Bragg scattering will only take place when this relation is completely satisfied. For this work the x-radiation wavelength was held constant at either CuKα (1.54Å) or AgKα (0.5598Å). Thus in order to satisfy the Bragg relation the crystal was rotated such that θ varied and d varied and thus whenever the product sinθ times 2d equalled the x-radiation wavelength, or any whole number multiple of it (n), Bragg reflection would occur. To obtain Compton scattering information the BT cut crystal of silica was misoriented in an attempt to confine the scattering to just diffuse scattering. The scattering was taken to be both the Compton scattering and the background scattering. In this discussion then, only diffuse scattering will be of concern. Consider Figure 32 as representing a multichannel analyzer display of scattering off the BT cut single crystal using AgKα radiation at an angle such that Bragg's relation is not satisfied. Mc here represents the peak of the Compton scattering and M represents the peak of the coherent scattering. Mc (the Compton Peak) is located at a particular energy labeled Ec which is determined by the relation

\[ Ec = \frac{h \lambda_c}{m c} \]  

where
FIGURE 3
MULTICHANNEL ANALYZER DISPLAY OF
DIFFUSE SCATTERING OFF BT-CUT SINGLE
CRYSTAL SILICA
Figure 3
(2-32) \( \lambda_c = \lambda + \frac{\hbar}{M_e c} (1 - \cos 2\theta) \)

where \( \lambda \) is the characteristic wavelength of the silver radiation (0.559\( \AA \)), \( M_e \) is the mass \( \hbar/M_e c \) electron, and \( C \) is the speed of light, and \( \hbar/M_e c \) is called the Compton wavelength and is equal to 0.02426\( \AA \). If the shape of the Compton curve is assumed to be symmetrical and following a general Gaussian behavior, then certain information can be determined from Figure 3. Describing the Compton curve as a Gaussian distribution then yields the following expression:

(2-33) \( I = I_{MC} e^{-\mu (E - E_c)^2} \)

Here \( \mu \) is a constant which is dependent on the general shape of the Gaussian curve. \( \mu \) can be determined by considering the half height expression for Figure 3.

(2-34) \( I_{1/2} = I_{MC} e^{-\mu (E_{1/2} - E_c)^2} \)

(2-35) \( \frac{I_{MC}}{2} = I_{MC} e^{-\mu (E_{1/2} - E_c)^2} \)
and (2-36)

\[ e^{-\mu (E^2_c - E_c)^2} = \frac{I_{mc}}{2} \frac{1}{I_{mc}} = \frac{1}{2} \]

and (2-37)

\[ \mu (E^2_c - E_c)^2 = \ln 2 = 0.69315 \]

thus yielding (2-38)

\[ \mu = \frac{0.69315}{(E^2_c - E_c)^2} \]

Now using expression (2-33) to describe the behavior of Compton scattering with \( E \), the area associated with region 2 as shown in Figure 3, can be determined by integrating over the interval from \( E_1 \) to \( E_3 \).

\[ (2-38) \quad A_{\text{REGION 2}} = \int_{E_1}^{E_3} e^{-\mu (E - E_c)^2} dE \]

Region 2 then is that portion of the coherent peak thought to be due to Compton scattering. Expression (2-38) can only be evaluated through computer techniques using numerical analysis.

As mentioned earlier it was suggested that the area under the coherent peak is due strictly to Compton scattering plus background scattering. However, what is called background really contains a certain amount of structural information and this component of region 1 will be called \( A_1 \). Region 1 then is
\[ A_{\text{Bkg}} + A_I \]. The magnitude of \( A_I \) depends on the imperfect nature of the BT-cut crystal of silica. \( A_{\text{Bkg}} \) can be described as arising from two sources. First that portion which is extraneous, due to cosmic sources or in nearby equipment, will be present when the incident beam is off. The second component, which is due to the instrument itself, is largest at small angles and results from air scattering in the neighborhood of the sample and spurious effects from such objects as slits and collimators.

In calculating the area of region 2, it should be noted that Alexandropoulos\(^{28}\) has shown that area will vary from the BT cut single crystal to the vitreous silica sample. He showed that the ratio of coherent to incoherent scattering is different for vitreous and single crystal silica. He also showed that this ratio varied as a function of crystallographic planes in the same crystal as Figure 21 clearly suggests.

2.3 \( \text{Si(Li)} \) Detector Operation

The lithium-drifted silicon detector used in this investigation is the heart of the energy spectrometer. It is made by first diffusing lithium into one surface of a piece of p-type silicon to form a p-n junction. Next lithium atoms from the n-type region are made to migrate, or drift, through the silicon so as to compensate for the original p-type impurities. The result within the drift region is a net dopant of intrinsic proportions. Next the original p-type contact
is replaced by a thin gold surface barrier contact which is transparent to soft x-rays. When the Si(Li) detector is under reverse bias, a photon interacting within the intrinsic region frees electrons and holes. These then migrate through the electric field to their respective collecting electrodes. The collected charge is then one electronic charge \((1.6 \times 10^{-19}\text{coul})\) for every 3.5eV of incident photon energy.

The energy resolution of the model 7333E detector was briefly discussed earlier and will be expanded here.

For a Si(Li) spectrometer system the overall energy resolution is a function of electronic noise and statistical variation in the number of charge carriers produced within the intrinsic region for a given photon energy. The overall system resolution thus can be given by the expression

\[
(2-39) \text{ system resolution} = \left( (\text{Det Res})^2 + (\text{Elect Res})^2 \right)^{\frac{1}{2}}.
\]

In discussing detector resolution it will be necessary first to introduce a constant called the Fano factor. When x-rays of energy less than 1 MeV interact with a solid, the x-ray energy will be altered by one of three processes: the photoelectric effect, Compton scattering, and elastic scattering. In particular, for x-ray energies less than 50 kev (the investigation was carried out using 40 kev x-rays) the initial interaction is usually a photoelectric absorption followed by secondary ionization. Secondary ionization consists of
two competing processes (1) impact ionization producing electron-hole pairs and (2) optical phonon generation. The sum of the residual kinetic energy, the energy consumed by optical phonons, and the ionization threshold energy is the average energy \( \langle E \rangle \) required for the production of electron-hole pairs. For electron-hole pair production to occur, \( \langle E \rangle \) must be larger than the band gap energy for the detector material. For silicon \( E_g \) is 1.1 ev while at \( 300^\circ K \) \( E = 3.6 \) ev. The total number of charge carriers \( N = \frac{E}{\epsilon} \) does not obey Poisson statistics but is less than the predicted value because of the above competing processes. \( E \) here is the energy of the detected radiation. Fano introduced a factor \( F \) which considers the degree of correlation in successive ionizations and he derived the variance \( N^*F \). Thus, the expression for detector energy resolution at full width at half maximum is:

\[
(2.40) \quad \text{DET. RES (FWHM)} = 2.355 \left( \epsilon \times \frac{E}{\epsilon} \times F \right)^{1/2}
\]

where \( F \) for Si is thought to be about 0.12, \( \epsilon \) is the energy per ion pair and \( E \) is the energy of the detected radiation.
2.4 Errors In Measurement of Experimental Data

There are three significant types of errors\textsuperscript{27} that can affect accuracy of the experimental data. These are errors caused by a misaligned diffractometer, inadequate energy calibration of the multichannel analyzer and x-ray penetration into the sample.

If the sample is displaced a distance $d$ below the axis of the diffractometer, the error in $\theta$ is given by the expression:

\begin{equation}
(2-41) \quad \Delta \theta_d = \frac{d \cos \theta}{R}
\end{equation}

where $\theta$ is the x-ray beam angle of incidence on the sample and $R$ is the distance from the diffractometer axis to the detector slit. Typically $\Delta \theta_d$ is of the order of $0.01^\circ$.

The error in $\theta$ due to beam penetration can be written as:

\begin{equation}
(2-42) \quad \Delta \theta_p = -\frac{1}{4} \frac{\mu (1-f) \sin 2 \theta}{\mu l R}
\end{equation}

Where $R$ and $\theta$ are as defined above, $f$ is that fraction of the peak intensity on the high energy side of the peak center, and $1-f$ is the intensity fraction on the low energy side. $\mu l$ is the linear absorption coefficient, which
for vitreous silica is 15.614/cm. Taking \( f \) to be 0.5 and \( 2\theta \) to be 90° the maximum \( \Delta \theta_p \) is found to be 0.003°.

The error due to inadequate energy calibration can be expressed as:

\[
\sigma = \frac{FWMH}{(2.355N)^{1/2}}
\]

Where FWHM is the system energy resolution and \( N \) is the total counts in a Gaussian peak. \( \sigma \) represents the standard deviation in the measurement of the centroid of the peak. By using several calibration sources the error due to inadequate calibration can be made less than 10eV, thus nonlinearity should not cause a significant error. The effect of the errors discussed above is to broaden the coherent peak by some \( \Delta \theta \). For this investigation \( \Delta \theta \) is in the range of 0.013°.
CHAPTER III
EQUIPMENT

The equipment used in this investigation consisted of the following items.

1. General Electric XRD-5 X-Ray Diffractometer
2. Canberra 7333E Detector System
3. Canberra 1708 Preamplifier
4. Hewlett-Packard 3015 High Voltage Power Supply
5. Canberra 1713 X-Ray Amplifier
6. Canberra 1431 Single Channel Analyzer
7. Canberra 1481-L Lin-Log Ratemeter
8. Canberra 1776 Dual Counter/Timer
9. Canberra 1712 Scan Controller
10. Canberra 6027 Motor Drive Power Supply
11. Canberra 6025E Stepping Motor with a Model 3501 gear reducer and a 3532 GEXRD 2-Theta Adapter
12. Canberra 1488 Teletype Scanner
13. Model ASR-33 Teletype
14. Canberra 1400 Bin/Power Supply
15. Canberra Omega Multichannel Analyzer
In this section the function of each of the above items will be discussed briefly. Most of the information presented in Chapter III was obtained from the Canberra System Manual\textsuperscript{33} which accompanied the equipment when it was purchased.

3.1 GE XRD-5 X-RAY DIFFRACTOMETER

This equipment served as the x-ray source with two x-ray tubes being used, a copper tube and a silver tube. The goniometer served to rotate the specimen through the desired 2-Theta range. The specimen was mounted in a holder mounted on the goniometer and high voltage was supplied to the x-ray tube by a high voltage power supply included with the GE XRD-5.

3.2 SEMICONDUCTOR X-RAY SPECTROMETER

The semiconductor x-ray spectrometer used in this investigation can best be described as an instrument which utilizes the proportionality between the energy of an x-ray, the number of free electron-hole pairs created in a semiconductor by that x-ray, and the resulting motion of these carriers thus providing a means for determining the energy of the x-ray. Items two through fifteen as listed on page 38 comprise the energy spectrometer used in this investigation.

SERIES 7333E Si(Li) DETECTOR SYSTEM

The detector used was a model 7333E Canberra Si(Li) detector. It was housed in a model 7901-5 5 liter capacity dewar. Liquid nitrogen was used
as the cooling agent. The detector area is \(30\text{mm}^2\), thickness 3mm, and is located 3mm from a 1mm thick beryllium window. Detector operating voltage is -500 volts DC and minimal preamp reset rate is 5 seconds at quiescent (no source voltage). Using the K\(\alpha\) line (5.894 kev) of a calibrated Fe-55 source, the energy resolution of the Si(Li) detector was determined to be 169ev at FWHM (full width at half maximum) and 314ev at FWTM (full width at tenth maximum). These data were obtained using the above detector in conjunction with a Canberra Model 1713 amplifier, a Model 8100 Canberra Multichannel Analyzer, and a Model 3001 Canberra high voltage power supply. A count rate of 1000 cts/sec or greater was maintained throughout while data were taken to determine spectrometer resolution.

**PREAMPLIFIER MODEL 1708**

The preamplifier used with this system is maintained at LN\(_2\) temperature (-320°F) so as to minimize electronic noise. The basic component of the preamplifier is an FET which is charge sensitive and employs pulsed-optical feedback to enhance its low noise performance.

The preamplifier operation is as follows: by changing the current through a heater in the preamplifier the temperature of the FET is finely adjusted (to around -320°F) for minimum electronic noise. A capacitative feedback (CF) integrates the charge liberated by photon interaction in the detector. This
then produces a step voltage output proportional to the charge. Continued photon interactions produce more steps until an upper limit of preamplifier output is reached. When this occurs, the reset generator fires, forcing current through a light emitting diode which is optically coupled to the input FET. The FET gate impedance is then momentarily reduced by the resultant light pulse and the feedback capacitance is then discharged leaving the output voltage at its initial setting of -2 volts.

**MODEL 6516 H.V. POWER SUPPLY**

This power supply is used to provide the Si(Li) detector bias of -500V DC. The power supply is all semi-conductor, constant voltage/current limited, and designed to furnish a maximum 3000VDC at 6 milliamperes. Its output is highly stable, very well regulated and insensitive to ambient temperature variations. Its load regulation is less than 0.01% (or 16mv whichever is greater) output voltage change for a full load to no load change in output current. Line regulation is less than 0.01% or 16mv output voltage change for a 10% change in the normal line voltage. Ripple and noise characteristics are less than 2mVRMS, 5mv peak-peak and stability is less than 0.05% + 5mv total drift for 8 hours after 30 minutes warm-up with 3°C ambient variation. The unit may be operated in the temperature range of 0°C to 55°C. The design of this power supply
employs the piggy-back regulator concept, that of a highly regulated low voltage supply in series with a less well regulated high voltage power supply.

**MODEL 1713 X-RAY SPECTROSCOPY AMPLIFIER**

This spectroscopy amplifier is designed to optimize energy resolution in spectroscopy applications with Si(Li) detectors operating at count rates up to 80% duty cycle. The amplifier response will accept signal inputs of either polarity.

This spectroscopy amplifier employs a baseline restorer which effectively eliminates (1) baseline undershoots following a linear signal, (2) correlated noise, and (3) nonlinear response at low amplitude signals. Because the overload recovery time for the Si(Li) pulsed optical preamplifier used with this system is very rapid, this x-ray spectroscopy amplifier can be used with pulsed optical preamplifiers and Si(Li) detectors without using gating or pulse pile-up rejection systems. System resolution is enhanced, especially in high count rate experiments, because of the output signal's ultra-low noise contribution and clear return to the baseline. The change observed in detector resolution when used with a pulsed optical preamplifier and model 1713 x-ray spectroscopy amplifier is 0.56% for a count rate change from 1K to 20K cts/sec.

The active filter used in the model 1713 causes pulse shaping which forces a monotonic return to the
baseline preventing secondary under or over-shoots.
The model 1713 has selectable shaping time constants of 1.0, 2.0, 4.0, 6.0, 8.0, 12.0 sec.

**MODEL 1431 SINGLE CHANNEL ANALYZER**

This device examines the output from the model 1713 x-ray spectroscopy amplifier and either accepts or rejects an input pulse depending on preselected requirements of the analyzer. If the pulse is accepted, it is stored and, after a preselected count time has passed, the total number of acceptable pulses is printed out. This single channel analyzer offers three modes of operation: (1) dual discriminator, (2) SCA with 100% window, and (3) SCA with 10% window.

Each mode will be discussed beginning with the dual discriminator mode. In this mode, the upper level discriminator (ULD) and the lower level discriminator (LLD) controls are completely independent, as are the ULD and LLD outputs. Each output will fire if the input pulse is greater than the corresponding ULD or LLD setting. However, the ULD setting must be greater than the LLD setting. In this mode both the ULD and the LLD settings are referenced to ground. The range for each is 25mv to 10 volts.

The 100% $\Delta E$ mode is generally used with detectors of coarse resolution. Here, the upper level (ULD/$\Delta E$) control selects an energy window width from 0% to 100% of the full scale (10 volts). This window is
referenced to the baseline LLD setting. An SCA output then is generated whenever an input pulse is greater than the LLD setting, but less than the sum of LLD plus $\Delta E$.

The last mode of operation, the 10% $\Delta E$ mode, is generally used with detectors of high resolution, such as a Si(Li) detector. Operation in this mode is exactly the same as in the 100% $\Delta E$ mode except that for an output to be generated, the input pulse must be greater than the LLD setting but less than the sum of LLD plus $\Delta E$, where the ULD/$\Delta E$ here is a window from 0% to 10% of full scale (normally 10 volts).

For improved performance at high count rates the model 1431 SCA has a built-in DC restorer. This enables pulse pair resolution of 0.5 sec with output pulse widths set at 0.4 sec.

**MODEL 1481 LIN/LOG RATEMETER**

The lin/log ratemeter is used in the spectrometry system to show at rate counts are being stored in the SCA. This ratemeter, as the name implies, offers count rates displayed in either linear form or logarithmic form. In the linear mode, the model 1481L has a range of 10 counts per second to 500,000 counts per second. In the logarithmic mode, the model 1481L has a range of 10 counts per second to $10^5$ counts per second.
The model 1481L Lin/Log Ratemeter converts an average number of pulses per second that occur at its input to an analog output voltage. The conversion can be either linear or logarithmic. The front panel meter indicates the count rate by using the analog output to deflect the meter.

**MODEL 1776 DUAL COUNTER/TIMER**

This device consists of two independent six decade scalers and an internal crystal-controlled time base. There are two presetable counting channels (A and B), which permit preset count and preset time operation, either separately or simultaneously. This Counter/Timer may act as a system master to control the time of counting experiments on the basis of preset count and time or just time. The device may also serve just as a dual channel system slave, operating at counting rates up to 25MHZ. Data which has accumulated in the two internal scalers is printed out by means of the model 1488 Teletype scanner, which will be discussed later in this section. Channel A can be operated by an internal time base or driven by an external time base. Channel B is a second scaler which is presetable and independent of Channel A. The B Channel scaler counts and displays the B count input signals.
MODEL 1712 SCAN CONTROLLER

The function of this component of the energy spectrometer is that of system master programmer. It drives the model 6025 stepping motor which rotates the goniometer through its 20 range. At each 20 + \( \Delta 20 \) the scan controller initiates data accumulation and then prints out data at the end of a preset count time. The drive signal to the stepping motor is coupled through the motor power supply. Scanning is controlled by three thumbwheel assemblies. Two thumbwheel switch assemblies control the upper and lower scan limits (0° to 399.99 degrees 20). The third thumbwheel switch assembly controls the \( \Delta 20 \) or the step scan mode (from 0.01 degree to 9.99 degrees \( \Delta 20 \)).

The scan controller may be operated in three different modes: (1) step scan, (2) continuous scan, and (3) peak-see. For the present investigation it was operated in the step scan mode. In this mode the controller is set to the actual position of the goniometer axis. It may then track future goniometer movement. The scan cycle is initiated by depressing the start push button. The controller then drives the stepping motor to the first data point ( \( \Delta 20 \) increment). At this time a start pulse is sent to the system counter (the 1776 dual counter/timer) which counts until a preset time limit is reached. Printout of the accumulated data is then accomplished by the print
controller, the model 1488 Teletype Scanner. When all the data have been printed out, the Teletype Scanner sends an end of printout command to the scan controller. The stepping motor is then driven to the next data point, thus starting the next data gathering cycle.

When the scan limit is reached (maximum 20 setting for the goniometer) and the last data printout cycle is finished, the scan controller will retrace to the original 20 setting.

**MODEL 1488 TELETYPE SCANNER**

This device causes the data stored in the model 1776 Dual Counter/Timer to be printed out on an ASR-33 teletype. Data are recorded in both punched paper tape form and printed form. Single cycle and recycle operation is also controlled by the model 1488 Teletype Scanner. The interval between data accumulation cycles can be controlled through the external timing input on the Teletype Scanner. For this investigation, this mode of operation was not used, but the scan controller was used to control this interval.

**MODEL 6027 MOTOR DRIVE POWER SUPPLY**

The motor power supply furnishes power to the 4-phase precision 6025 stepping motor which is used to rotate the goniometer through the desired 20 range.
MODEL 60255 PRECISION STEPPING MOTOR

This device is used to rotate the goniometer employed on the GE XRD-5 x-ray diffractometer through a preset 2θ range in steps or increments of Δ2θ which are also preset. The unit is driven by the 1712 scan controller through the motor power supply.

MODEL AEC-320-5A BIN POWER SUPPLY

The bin power supply provides ±12/±24vDC to the various components of the energy spectrometer discussed earlier. It is mounted at the rear of the modular instrumentation and each 12 and 24 volt output may be operated simultaneously at maximum current rating.

MODEL 807 PULSER

This device is not a normal component part of the energy spectrometer. It is, however, used for initial set up of the system. The pulser provides a source of positive or negative pulses that can be used as an input to the model 1713 spectroscopy amplifier thus eliminating the need for the Si(Li) detector/preamplifier to be used during initial system setup. The model 807 pulser can be used to evaluate amplifier noise and linearity. It also can be used to calibrate pulse height analyzers and to generally check the overall system operation before beginning an experimental run.
The Canberra omega multichannel analyzer used with experimental setup B provided 1024 channels of intensity information over the entire energy range of from 0 kev to 45 kev. A region of interest was selected on the MCA and the area in this region of interest was determined by the MCA and displayed. Coherent and background intensity data were obtained using the Omega MCA.
CHAPTER IV
EXPERIMENTAL PROCEDURE

In the experimental portion of this study it was necessary to obtain samples of vitreous silica and germania, polycrystalline silica and germania, and single crystals of silica. X-ray diffraction data were obtained on these samples using two experimental configurations. Henceforth these will be referred to as either experimental setup A or experimental setup B. Figure 4 shows the component parts of both arrangements.

Table 1 gives, in summary form, the important x-ray diffraction runs made during the course of this investigation. This table will be referred to when discussing the various experimental runs.

This chapter is divided into two major sections: the first deals with a description of the experimental samples and the second, a description of the manner in which each run was carried out.

4.1 Sample Preparation

Several samples of vitreous silica were purchased from Amersil Inc. (650 Jerneees Mill Rd., Sayerville, New Jersey). The trade name of the vitreous silica
FIGURE 4
SCHEMATIC DIAGRAM OF EXPERIMENTAL
SETUPS A AND B
Setup A

GE-XRD5 → Si(Li) Detector → PreAmp

Lin-Log Ratemeter → SCA → X-Ray Amp.

Dual Counter Timer → Motor P.S. → Teletype Scanner

Setup B

GE-XRD5 → Si(Li) Detector → PreAmp

ASR-33 Teletype → MCA → X-Ray Amp.

Figure 4
TABLE 1

LIST OF EXPERIMENTAL X-RAY DIFFRACTION RUNS

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>Rad.</th>
<th>Mode</th>
<th>2θ Range</th>
<th>Cnt-Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ultrasil</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>20 sec</td>
</tr>
<tr>
<td>2</td>
<td>Ultrasil</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>3</td>
<td>Ultrasil</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>4</td>
<td>Ultrasil</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>5</td>
<td>Ultrasil</td>
<td>CuKα</td>
<td>10% ΔE</td>
<td>5°-145°</td>
<td>360 sec</td>
</tr>
<tr>
<td>6</td>
<td>S.Xytal</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>20 sec</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>BT-SiO₂</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>8</td>
<td>S.Xytal</td>
<td>CuKα</td>
<td>10% ΔE</td>
<td>5°-145°</td>
<td>360 sec</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Ultrasil</td>
<td>CuKα</td>
<td>MCA</td>
<td>5°-145°</td>
<td>100 sec</td>
</tr>
<tr>
<td>10</td>
<td>Ultrasil</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>20 sec</td>
</tr>
<tr>
<td>11</td>
<td>Ultrasil</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>12</td>
<td>Ultrasil</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>13</td>
<td>Ultrasil</td>
<td>AgKα</td>
<td>10% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>14</td>
<td>Ultrasil</td>
<td>AgKα</td>
<td>MCA</td>
<td>5°-59.5°</td>
<td>100 sec</td>
</tr>
<tr>
<td>15</td>
<td>Ultrasil</td>
<td>AgKα</td>
<td>MCA</td>
<td>60°-99.5°</td>
<td>300 sec</td>
</tr>
<tr>
<td>16</td>
<td>Ultrasil</td>
<td>AgKα</td>
<td>MCA</td>
<td>100°-145°</td>
<td>400 sec</td>
</tr>
<tr>
<td>17</td>
<td>S.Xytal</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>20 sec</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>S.Xytal</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run</td>
<td>Sample</td>
<td>Rad.</td>
<td>Mode</td>
<td>2θ Range</td>
<td>Cnt-Time</td>
</tr>
<tr>
<td>-----</td>
<td>--------------</td>
<td>------</td>
<td>--------</td>
<td>-----------</td>
<td>----------</td>
</tr>
<tr>
<td>19</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>20</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>21</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>22</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>23</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>24</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>25</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>26</td>
<td>Powder SiO₂</td>
<td>AgKα</td>
<td>10% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>27</td>
<td>Powder SiO₂</td>
<td>AgKα</td>
<td>10% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>28</td>
<td>GeO₂-Glass</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>29</td>
<td>GeO₂-Glass</td>
<td>CuKα</td>
<td>LLD, ULD Open</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>30</td>
<td>GeO₂-Powder</td>
<td>CuKα</td>
<td>100% ΔE</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>31</td>
<td>GeO₂-Powder</td>
<td>CuKα</td>
<td>LLD, ULD Open</td>
<td>5°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>32</td>
<td>GeO₂-Glass</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>33</td>
<td>GeO₂-Glass</td>
<td>AgKα</td>
<td>LLD, ULD Open</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>34</td>
<td>GeO₂-Powder</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>35</td>
<td>GeO₂-Powder</td>
<td>AgKα</td>
<td>LLD, ULD Open</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>36</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
<tr>
<td>37</td>
<td>BT-SiO₂</td>
<td>AgKα</td>
<td>100% ΔE</td>
<td>30°-145°</td>
<td>120 sec</td>
</tr>
</tbody>
</table>
sample used is Tl6 Ultrasil and its physical dimensions are 2 in x 0.125 in x 1 in. Each sample, as purchased, was ground and polished.

Single crystals of quartz were borrowed from the Geology and Mineralogy Department of The Ohio State University.

Polycrystalline samples of silica were made by mixing 10 micron and 50 micron silica and then compressing the mixture at 3500 psi. No binder was used so handling these samples was difficult. The samples were 1-inch diameter discs having a thickness of 0.125 inch.

Two germania glass samples were made by using electronic grade germania and heating it in platinum crucibles at 1115°C for 30 hours. After 12 hours and again after 24 hours at that temperature, the samples were removed and stirred with a platinum stirrer to remove bubbles. At the thirtieth hour, the samples were slowly cooled to 1000°C and held there for six hours and then slowly returned to room temperature. The resulting samples were rectangles of approximate size 1.5 in x 0.125 in. x 0.75 in. One of the glass samples was then cut using a diamond saw and mounted in a quick-setting translucent plastic resin called Quickmount. The specimen was then ground and polished.

The polycrystalline samples of germania (using electronic grade germania) were made in the same manner as the polycrystalline powder silica samples.
4.2 **Experimental X-Ray Diffraction Runs:**

Structure data were obtained on a vitreous silica sample (Ultrasil) using CuKα x-radiation and AgKα x-radiation. Runs 1-5, and run 9 were carried out using CuKα x-radiation and runs 11-16 employed AgKα x-radiation.

Before using experimental setup A, a silicon standard was used to calibrate the single channel analyzer (SCA). The lower level discriminator and upper level discriminator were set by orienting the silicon standard on its 111 plane and then adjusting the LLD and the ULD to give a maximum deflection on the rate meter and then backing off slightly. In this manner an energy window was established in which only the area of the coherent peak within this window would be determined. The energy window was set so as to filter out as much Compton radiation (inelastic scattering) as possible and still yield meaningful unmodified scattering data. The count time using setup A was 120 sec. except for runs 1 and 5 for CuKα radiation and run 10 using AgKα radiation. Data for runs 1 and 10 were taken for a count time of 20 sec and in run 5 the count time used was 360 sec. A count time of 20 seconds did not yield data as statistically accurate as did the 120 second count time. Run 5 used a count time of 360 seconds because the SCA was being operated in a high resolution mode (10%ΔE) thus requiring a longer time to yield statistically accurate data.
Generally the 2θ range over which intensity data were taken was from 5° to 145°; however, for runs 12 and 13 the range was from 30° to 145°. The shorter 2θ range for the AgKα data still provided a large overlap of Cu and Ag information.

For experimental setup A the Cu and Ag x-ray tube operating conditions were the same. Filament current was set at 8 ma and excitation voltage at 40kv. The 2θ was always set at 0.1° for experimental setup A and the data recorded on the ASR-33 Teletype was always the 2θ setting, the count time, and the total count. These data were printed out and punched out on paper tape by the ASR-33.

Runs 9, 14-16 were conducted using experimental setup B. The multichannel analyzer used in obtaining the data was not energy calibrated; however, preliminary work was carried out using a model 8081 Canberra multichannel analyzer which was energy calibrated in the following manner. An iron 55 calibrated sample was used having an FeKα peak at 5.894kev and an FeKβ peak at 6.489kev. These peak positions by channel were not recorded; however, by using a known peak energy position, that of AgKβ radiation, a simple ratio and proportion will give the FeKα and FeKβ channel positions to within 10 ev. By using this method the FeKα peak channel position is:
The error here being:

\[
\text{Error} = \frac{860}{25.23} \quad \text{or Error in channels being 0.68 channels}
\]

At various 20 positions the peak position of AgKα Compton scattering was calculated and verified experimentally through gathering intensity data at these 20 positions and then observing the peak positions of the Compton and the coherent scattering. The familiar relation:

\[
(4-1) \quad \Delta \lambda = 0.02426 (1-\cos 2\theta)
\]

was used in determining the wavelength or energy shift at the particular 20 positions.

Before taking intensity data using experimental setup B, a region of interest was defined within which the area would be determined. This region was taken to be the right half profile of the coherent peak at a low enough 20 position so as to minimize the contribution due to Compton scattering. The half profile was selected so as to include as little Compton scattering information at high k as possible. It was assumed here that the shape of the coherent peak is symmetrical and that the contribution due to Compton scattering would be larger in the lower energy half of the coherent peak than in the higher energy half. This technique was first
reported in the literature by Shimazu and Watanabe. Background information was recorded at the same time as coherent scattering data by approximating the area of the background scattering as rectangular as shown in Figure 3.

Runs 6-8 were conducted to obtain Compton and background data using CuKα radiation. A single crystal of silica (slightly misoriented in the -x direction as shown in Figure 5) was used in run 6. A BT-cut single crystal of quartz was used in runs 7 and 8.

Runs 17-27 and runs 36 and 37 provided Compton and background information using AgKα radiation. Runs 17 and 18 employed the same single crystal of silica as used in run 6 and misoriented in the same manner as in run 6. All the other runs except runs 26 and 27 (which used a polycrystalline powder sample of Quartz) were carried out using various BT-cut single crystals of quartz. In all of these runs the sample was misoriented in the -x direction except in runs 36 and 37. Figure 5 shows the sample orientation. The x-ray beam is in the x-a plane and the sample is rotated in the x-y plane about the a axis.

Runs 28 through 35 were conducted to obtain structural, Compton, and background intensity information on vitreous germania. X-ray information was obtained using the SCA in two modes, first the LLD and the ULD were set to filter out the incoherent scattering and
FIGURE 5

ORIENTATION OF BT-CUT SINGLE CRYSTAL OF SILICA IN SAMPLE HOLDER
then the LLD and ULD were opened to allow the incoherent intensity to be obtained along with the coherent intensity. All the germania data were gathered using experimental setup A.
CHAPTER V
DATA REDUCTION AND RESULTS

5.1 Corrections Made To Data:

The x-ray diffraction data obtained from the Ultrasil sample of vitreous silica and the glass sample of germania were corrected for background, polarization, multiple scattering, and Compton scattering. An x-ray beam will become polarized upon being scattered off a sample. The correction for this polarization is given in expression 5-1, and shown in Figure 6.

\[ PF = \frac{1}{2} \left( 1 + \cos^2 2\theta \right) \]

Here \( \theta \) is the angle of scatter of the x-ray beam with no monochromator used, and PF is defined as the polarization factor. The correction is made by dividing the raw intensity data by PF. It is noted that PF is a function only of scattering angle.

The next correction made to the vitreous silica intensity data was that of multiple scattering. Warren and \( \omega \)ozzi\(^2\) developed an excellent method, shown before, for making this correction. Expression (5-2) shows this general relation.
FIGURE 6
POLARIZATION CORRECTION
FIGURE 6
Here \( \frac{I(2)}{I(1)} \) is the ratio of doubly and singly scattered intensity and \( B \) is the sum of the square of the total number of electrons present in a unit of composition, UC, \( (B = \sum_{j} \frac{Z_j^2}{u_j}) \). \( Q(2\theta, q, b) \) is determined from a table given in Warren and Mozzi's paper and \( J(P) \) is calculated from expression 5-3. \( A_i \) and \( U_i(m) \) are the atomic weight and mass absorption coefficients of the atoms of the unit of composition.

\[
(5-3) \quad J(P) = B \left[ q + (1-q)/(1 - b \sin^2 \theta) \right]
\]

Through picking a suitable value of \( q \) and \( b \), a curve representing \( J(P) \) versus \( \theta \) is plotted over a curve of the sum of the square of the atomic scattering factor of a unit of composition of the sample \( \sum_{j} f_j^2 \). When \( J(P) \) approximates \( \sum_{j} f_j^2 \) then the proper values of \( q \) and \( b \) have been determined. Once these have been determined then \( Q(2\theta, q, b) \) can be found, and expression (5-2) can be solved yielding a curve of \( \frac{I(2)}{I(1)} \) versus \( \theta \) (the angle of incidence of the x-ray beam). Figure 7 shows the correction used for multiple scattering.

\( \frac{I(2)}{I(1)} \) ranged from 9\% to 11\% over the region of \( k \).
FIGURE 7

MULTIPLE SCATTERING CORRECTION
greater than 15. The correction is made using expression 5-4.

\[ I_{\text{corrected}} = I(1) - I(1) \times \frac{I(2)}{I(1)} \]

The correction for multiple scattering was calculated for CuK\(\alpha\) radiation incident on vitreous silica by Mozzi\(^3\) and found to be negligible; therefore only the AgK\(\alpha\) data was corrected for multiple scattering. The graph of \(\frac{I(2)}{I(1)}\) should show a maxima and then tail off, however Figure 7 shows a maxima and then a dip. The region from 29 greater than 130° shows an increase in \(\frac{I(2)}{I(1)}\), probably because of a slight error in matching \(J(29)\) with \(\frac{\gamma f_j}{\mu c}\) in this region.

Background and Compton corrections were made together since the background was measured in both the Compton run and the vitreous silica run. As mentioned earlier, background is composed of an extraneous part and a part which arises from the instrument itself. The extraneous component is due to cosmic sources or other nearby equipment and is present with the x-ray beam off. The instrumental background is due to air scattering in the neighborhood of the sample and spurious effects from slits, collimators, etc. The instrumental background is large at small angles. Figure 8 shows the experimentally measured
Compton intensity scattered off the BT-cut single crystal of silica using CuKα radiation. The region of low k (k \leq 3.0) is largely due to instrumental background scattering. The data of Figure 8 was smoothed and is shown in Figure 9. The data of Figure 9 was used to make the correction for background and Compton due to CuKα radiation (1.54\,\text{\AA}). The experimental setup A was used to obtain the data of Figure 9 using a count time of 120 seconds. The probable error for the data ranged from 0.61\% to 2.52\%. The relation used for determining the probable error is:

\[
E_N = \frac{6.7}{\sqrt{N}}\% 
\]

Where \(N\) is the total number of counts. It should be noted that the probable error implies that the probability of the error being above or below \(E_N\) is 0.5. Three times the probable error yields a 96\% probability that the measured error is correct. The Compton data after being corrected for polarization was subtracted from the raw intensity data that had been corrected for polarization.

It was also necessary to correct the AgKα sample intensity data for Compton and background. A multichannel analyzer was energy-calibrated in the manner described in Chapter IV and Ultrasil sample peaks observed at a 2θ of 142° were identified by determining their energy.
FIGURE 8

COMPTON AND BACKGROUND FROM A SILICA SINGLE CRYSTAL USING CuKα RADIATION
FIGURE 9
DATA OF FIGURE 8 SMOOTHED
FIGURE 9
The AgKα peak was observed in channel 360 which corresponded to an energy of 25.23 kev or 200 ev larger than the calculated energy for this peak. Using the expression:

\[
E = \frac{hc}{\lambda} = \frac{6.6256 \times 10^{-27} \times 3 \times 10^{10} \times 6.26 \times 10^{11} \times x}{\lambda \times 10^{-8}}
\]

The calculated value of \( E_{K\alpha} \) = 25.03 kev or 0.7% lower than the observed Kα peak position. The Kα Compton wavelength shift was calculated using the expression:

\[
(5-7) \quad \Delta \lambda = \frac{h}{m_e c} \left(1 - \cos 2\theta\right)
\]

Where \( \frac{h}{m_e c} = 0.02426 \lambda \)

Thus \( \Delta \lambda_{K\alpha} = 0.2426 \left(1 - \cos 142^\circ\right) \)
and \( \Delta \lambda_{K\beta} = 0.0433 \lambda \)

Thus the energy of the Kα Compton peak was determined by expression (5-6) to be 23.024 kev and the observed peak position was 23.179 kev. The error here is 0.66%.

By using the ratio involving the Kβ peak channel and the observed Kα peak channel, the energy of the observed Kα peak can be determined as follows:

\[
(5-8) \quad \frac{E_{K\beta}}{E_{K\alpha}} = \frac{k\beta \text{ channel}}{k\alpha \text{ channel}}
\]
Using the observed values for $E_{KB}$, $K\alpha$ channel, and $K\beta$ channel, then the observed $E_{K\alpha}$ was determined to within an error of roughly 10 ev.

$$\frac{25.23\text{ kev}}{E_{K\alpha}} = \frac{360}{763}$$

Or $E_{K\alpha} = 22.22\text{ kev}$

The observed $E_{K\alpha}$ of 22.33 kev was larger than the calculated $E_{K\alpha}$ by 110 ev or 0.5%. Calculating the $K\alpha$ Compton peak position in the same manner led to an observed peak position for $E_{K\alpha}^{\text{Compton}} = 20.77\text{ kev}$ or 160 ev larger than the calculated $E_{K\alpha}^{\text{Compton}}$ giving an error of 0.8%.

If the data were analyzed using the $AgK\alpha$ observed peak position as the reference with this channel corresponding to the calculated $E_{K\alpha}$ then the observed $E_{KB} = 25.033\text{ kev}$, $E_{KB}^{\text{Compton}} = 22.97\text{ kev}$, and the observed $E_{K\alpha}^{\text{Compton}} = 20.61\text{ kev}$. As can be seen, the peaks are well identified; converting the peak positions from energy to wavelength results in the observed values of $\lambda_{\beta} = 0.49701\text{Å}, \lambda_{\beta}^{\text{Compton}} = 0.54165\text{Å}$, $\lambda_{\alpha} = 0.56024\text{Å}, \lambda_{\alpha}^{\text{Compton}} = 0.60367\text{Å}$. These observed positions compare favorably with the calculated values of $\lambda_{\beta} = 0.49701\text{Å}, \lambda_{\beta}^{\text{Compton}} = 0.54038\text{Å}, \lambda_{\alpha} = 0.56024\text{Å}$, and $\lambda_{\alpha}^{\text{Compton}} = 0.60367\text{Å}$. The above results are listed in Table 2 below.
<table>
<thead>
<tr>
<th>Peak</th>
<th>Channel</th>
<th>$E_{\text{cal}}$</th>
<th>$E_{\text{obs}}$</th>
<th>cal</th>
<th>obs</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_B</td>
<td>860</td>
<td>25.03 kev</td>
<td>25.23 kev</td>
<td>0.49701</td>
<td>0.49318</td>
</tr>
<tr>
<td>K_{BC}</td>
<td>789</td>
<td>23.024</td>
<td>23.179</td>
<td>0.54038</td>
<td>0.53682</td>
</tr>
<tr>
<td>K_{\alpha}</td>
<td>763</td>
<td>22.22</td>
<td>22.33</td>
<td>0.56024</td>
<td>0.55723</td>
</tr>
<tr>
<td>K_{\alpha c}</td>
<td>708</td>
<td>20.61</td>
<td>20.77</td>
<td>0.60367</td>
<td>0.59908</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>Channel</th>
<th>$E_{\text{cal}}$</th>
<th>$E_{\text{obs}}$</th>
<th>cal</th>
<th>obs</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{\alpha}</td>
<td>763</td>
<td>22.22</td>
<td>22.22</td>
<td>0.56024</td>
<td>0.56024</td>
</tr>
<tr>
<td>K_{\alpha c}</td>
<td>708</td>
<td>20.61</td>
<td>20.609</td>
<td>0.60367</td>
<td>0.60367</td>
</tr>
<tr>
<td>K_B</td>
<td>860</td>
<td>25.03</td>
<td>25.033</td>
<td>0.49701</td>
<td>0.49701</td>
</tr>
<tr>
<td>K_{BC}</td>
<td>789</td>
<td>23.024</td>
<td>22.97</td>
<td>0.54038</td>
<td>0.54165</td>
</tr>
</tbody>
</table>
Figures 10 - 22 show Compton data obtained using AgK radiation (0.559 Å). The data of Figures 10, 11, 12, 13, 15 and 16 were averaged and used as the Compton correction after it was smoothed. All the data shown were obtained using a BT-cut single crystal of silica. In order to check repeatability the data of Figures 10, 11 and 12 were obtained by placing a BT-cut crystal in the sample holder, misorienting it in the manner discussed in Chapter IV, and collecting data for three runs without disturbing the sample. The data of Figure 13 were obtained by removing the sample and then replacing it in the same position and repeating the run. The major peaks evident on Figure 17 from left to right represent scattering off the 102 plane, the 004 plane, the 320 plane and third order scattering off the 110 plane. The calculated d spacings for the peak positions are tabulated in Table 3.

TABLE 3
IDENTIFICATION OF DIFFRACTION
PEAKS OBSERVED IN COMPTON RUNS 1-9

<table>
<thead>
<tr>
<th>2θ</th>
<th>θ</th>
<th>Sinθ</th>
<th>d_{hkl}</th>
<th>d_{hkl} card file</th>
<th>Card File hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.14°</td>
<td>11.57°</td>
<td>0.2</td>
<td>2.796315</td>
<td>2.841</td>
<td>102</td>
</tr>
<tr>
<td>37.6°</td>
<td>18.8°</td>
<td>0.327</td>
<td>1.737152</td>
<td>1.730</td>
<td>004</td>
</tr>
<tr>
<td>47.89°</td>
<td>23.95°</td>
<td>0.406</td>
<td>1.377741</td>
<td>1.379</td>
<td>320</td>
</tr>
<tr>
<td>53.59°</td>
<td>29.30°</td>
<td>0.489</td>
<td>1.143892</td>
<td>3.53</td>
<td>110(N=3)</td>
</tr>
</tbody>
</table>
FIGURE 10

COMPTON RUN #1 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AgKα RADIATION
FIGURE 10

IEU (X10^2)

0.00  40.00  80.00  120.00  160.00  200.00  240.00  280.00

5.00  10.00  15.00  20.00  25.00

FIGURE 10
FIGURE 11
COMPTON RUN #2 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AgKα RADIATION
FIGURE 12
COMPTON RUN #3 USING A 3T-CUT SINGLE CRYSTAL OF SILICA AND AgKα RADIATION
FIGURE 13

COMPTON RUN #4 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AgKα RADIATION
FIGURE 14

COMPTON RUN #5 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AgKα RADIATION
FIGURE 15
COMPTON RUN #6 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AGKα RADIATION
FIGURE 15
FIGURE 16

COMPTON RUN #7 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AgK\alpha RADIATION
FIGURE 16
FIGURE 17
COMPTON RUN #8 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AgKα RADIATION
FIGURE 17
FIGURE 18

COMPTON RUN #9 USING A BT-CUT SINGLE CRYSTAL OF SILICA AND AgKα RADIATION
FIGURE 19

COMPTON RUNS 1-9
FIGURE 20

COMPTON RUNS 1-9 AVERAGED
FIGURE 21

COMPTON RUNS 1-9 SMOOTHED
FIGURE 21

[Graph showing data points and curves]
FIGURE 22

DATA OF COMPTON RUNS 1-4, 6 AND 7

AVERAGED
Figure 19 shows the nine Compton runs obtained with experimental setup A and Figure 20 shows the average of the nine runs. The probable error for the data of Figure 19 ranged from 1.1% to 2.1%. Figure 22 represents the data used in making the Compton correction to the AgKα Ultrasil intensity data. Figure 22 represents the data of Figures 10, 11, 12, 13, 15, and 16 averaged. These data were subtracted from the raw AgKα Ultrasil data before any corrections had been made. It should be noted that the peak occurring at k = 9.1 in Figures 10, 11, 12 and 13 was smoothed before averaging with the data of Figures 15 and 16. The data of Figure 22 also includes the background correction. The magnitude of the experimentally determined Compton was at high k about 70% of the magnitude of the experimentally determined Ultrasil sample intensity. The calculated Compton at high k (k ≥ 19) is about six times the normalized sample intensity.

5.2 Sample Intensity Data

Figures 23-28 represent the CuKα intensity data recorded off a sample of vitreous silica. Figure 27 is the average of the data shown in Figures 23, 24 and 25. All of these data were taken using experimental setup A and all of the data discussed thus far were gathered over a count time of 120 seconds. The probable error for the data of Figures 23-25 ranges from 0.44% to 1.53%. Figure 28 represents the data of Figure 27.
smoothed and corrected for polarization, background, and Compton. The data of Figure 28 were used for the CuKα radiation intensity from the Ultrasil sample of vitreous silica. Figure 26 shows the data of Figure 23, 24 and 25 plotted versus k. It should be observed that little variation is seen from run to run. Figure 28 compares well to the data of Mozzi; however the ratio of the first peak to the third peak is only 60% of the ratio in Mozzi's curve. The peak positions occur in essentially the same position, however.

Figure 29 shows the average of two AgKα Ultrasil runs. Figure 30 shows Figure 29 smoothed and corrected for background, polarization, multiple scattering and Compton. These data were obtained with experimental setup A. The probable error ranged from 0.31% to 1.62%. The data of Figure 30 were used for AgKα information from a vitreous silica sample.

The data of Figures 28 and 30 were combined to form the data of Figure 31. The region from $7 \leq k \leq 8$ was a region in which the CuKα and AgKα data were overlapped. The data below $k = 7$ was CuKα data and the data for $k \geq 8$ was AgKα data. The data of Figure 31 were adjusted by an algorithm to linearize the k axis. This operation did not affect peak positions or heights in any way as illustrated in Figure 32, which shows the linearized data. The need to linearize the k axis is seen when the data is Fourier transformed.
from $k$ space to $R$ space. If the $k$ axis is nonlinear 
($k = \frac{4\pi \sin \theta}{\lambda}$) then $\Delta k$ will also be nonlinear, 
thus resulting in low frequency oscillation in the 
transformed $R$-space.

Experimental setup 3 was used to obtain the data 
of Figures 34 and 35. Figure 34 represents the 
corrected and normalized CuKα intensity data and 
Figure 35 represents the corrected, and normalized 
AgKα intensity data taken from the sample of vitreous 
silica. The data of Figure 34 was taken over a count 
time of 100 seconds and showed a probable error of 
from 0.30% to 0.96%. The data of Figure 35 was 
collected over three count times. For the region 
$5^\circ \leq \theta \leq 59.5^\circ$ the count time was 100 seconds, 
for $60^\circ \leq \theta \leq 99.5^\circ$, the count time was 300 seconds 
and for $100^\circ \leq \theta \leq 145^\circ$ the count time was 400 
seconds. The probable error ranged from 0.34% to 
1.48%. Data for experimental setup 3 was taken using 
the half profile method described by Shimazu and 
Watanshè in their paper on the amorphous structure 
of 3e. Since the effect of the high energy side of 
the Compton peak would be most evident in the low 
energy side of the coherent peak, it was thought that 
by measuring only the high energy half of the coherent 
peak a better separation could be obtained between the
FIGURE 23
ULTRASIL RUN #1 USING CuKα RADIATION
FIGURE 23
FIGURE 24
ULTRASIL RUN #2 USING CuKα RADIATION
FIGURE 25
ULTRASIL RUN #3 USING CuKα RADIATION
FIGURE 26
ULTRASIL RUNS 1-3
FIGURE 26
FIGURE 27

ULTRASIL RUNS 1-3 AVERAGED
FIGURE 28
DATA OF FIGURE 27
SMOOTHED AND CORRECTION
FIGURE 29
AVERAGE OF TWO ULTRASIL RUNS USING
AgKα RADIATION
FIGURE 30
DATA OF FIGURE 29
SMOOTHED AND CORRECTED
FIGURE 30
FIGURE 31
CORRECTED CuKα AND AgKα ULTRASIL
DATA WITH LINEAR K-AXIS
FIGURE 32
CuKα AND AgKα ULTRASIL DATA OVERLAP
FIGURE 33
DATA OF FIGURE 32 NORMALIZED ABOUT $\omega c f_j$
WITH CALCULATED COMPTON CURVE
FIGURE 33
FIGURE 34
CORRECTED AND NORMALIZED X-RAY INTENSITY
FROM ULTRASIL SAMPLE OF VITREOUS SILICA
USING AgKα RADIATION AND EXPERIMENTAL
SETUP B
FIGURE 35
CORRECTED AND NORMALIZED X-RAY INTENSITY
FROM ULTRASIL SAMPLE OF VITREOUS SILICA
USING AgKα RADIATION AND EXPERIMENTAL
SETUP B
Compton and coherent scattering. Figure 36 shows a typical multichannel analyzer display using AgKα radiation at a high 2θ. As shown in the figure the background correction was made directly by assuming that a rectangular area describes the background. Expression 5-3 shows the background correction for a region of interest (the region over which the area of the coherent peak is determined). The region of interest extends from channel x to channel y, where channel x is the low energy end of the region and channel y is the high energy end. Thus (5-3) is:

\[ I_{BK} = I_y (y-x) \]

The data obtained using experimental setup 3 was taken over a range of \( 5^\circ \leq 2\theta \leq 145^\circ \) with \( \Delta 2\theta = 0.50^\circ \) for both CuKα and AgKα radiation. The larger \( \Delta 2\theta \) was used because the data had to be taken by hand. It is felt though that little accuracy was lost in going to the larger \( \Delta 2\theta \) since the work of Mozzi used the same \( \Delta 2\theta \) of 0.5°.

The CuKα data were corrected for background, and polarization, and the AgKα data were corrected for background, polarization, and multiple scattering.

The data collected on the vitreous germania structure were collected using experimental setup A.
FIGURE 36
DRAWING OF TYPICAL MCA DISPLAY
Figure 36
They were treated in the same manner as the silica data discussed earlier.

The resulting SCA and ECA Ultrasil and vitreous germania sample intensity data were now in a form such that Warren's exact method could be used for data analysis. It should be noted that although vitreous germania is not mentioned, it was analyzed in exactly the same way as the vitreous silica data. Vitreous silica was the reference material in this investigation and the material whose structure was best known. The intensity curve shown in Figure 33 was first normalized about the \( \sum f_j^2 \) curve. Different normalization constants were used for CuK\( \alpha \) and AgK\( \alpha \) data; however, the AgK\( \alpha \) data was normalized so as to cause the high k region to oscillate about the \( \sum f_j^2 \) curve. Once this was done, the CuK\( \alpha \) data were normalized such that a good match could be made in the region \( 7 \leq k \leq 8 \). The range of the intensity data was \( 0 \leq k \leq 21.48 \). The region of k over which the best normalization of the AgK\( \alpha \) data could be made was \( 17 \leq k \leq 21.43 \). Once a satisfactory normalization of the data was achieved, then the resulting \( k_i(k) \) curve and PDF
curve were determined using Warren's exact method as described in Chapter 2. Figure 37 shows a typical ki(k) curve obtained in this investigation. It has been terminated to zero so as to minimize termination error. The curve shows that the Ultrasil sample intensity data has been normalized properly about \( \frac{f_j}{f_c} \). If a proper normalization had not been accomplished, the ki(k) curve would have oscillated about a k-axis at some angle to the observed k-axis.

Figure 38 shows a typical Pair Distribution Function for vitreous silica obtained by Fourier transforming the data of Figure 37.

The PDF is similar to but not as accurate as the PDF obtained by Mozzi. The region of \( R \) less than 2\( \bar{\alpha} \) shows low frequency oscillations. For this particular PDF these low frequency oscillations are due to a localized error in the ki(k) curve of Figure 37 at about \( k = 3.69 \). Figure 39 shows the PDF corrected for this low frequency oscillation. It should be noted that the manner in which the ki(k) curve is terminated will greatly affect the region of apparent error. Also a slight change in normalization will change the region of localized error in the ki(k) curve.
FIGURE 37

$k_i(k)$ CURVE FOR VITREOUS SILICA USING EXPERIMENTAL SETUP A
5.3 Discussion of Results

It is felt that the inability to remove the low frequency oscillations in the experimentally observed PDF results from an inability to accurately make the Compton correction to both the CuKα and the AgKα data. It was decided to reproduce as closely as possible Mozzi's PDF from the intensity curve given in his dissertation. This PDF shall be referred to as the modified PDF. It should be noted that the 0-0 peak position as shown in Figure 38 is at 2.45\(\AA\) whereas in Mozzi's PDF it occurs at 2.65\(\AA\). The difference between the modified PDF and the observed PDF was determined and converted into a Compton curve which would yield the modified PDF. The modified Compton curve is shown plotted over the Compton correction in Figure 41. It is seen that the largest error in measuring Compton occurred for AgKα radiation. Figure 41 shows only the AgKα Compton. The region of greatest variation is from \(k = 10\) to \(k = 14\). It is in this region that a diffraction peak occurs in the AgKα Compton data of Figures 10, 11, 12 and 13. It would appear that this region yields the least accurate Compton information as Figure 41 also indicates.

Figure 42 shows the resulting MCA ki(k) curve and Figure 43 the resulting MCA PDF for vitreous silica. Here the low frequency oscillations are due to a localized error in the ki(k) curve between \(k = 4.4\) to
FIGURE 38
PAIR FUNCTION FOR VITREOUS SILICA
USING EXPERIMENTAL SETUP A
FIGURE 39

FIGURE 38 CORRECTED FOR LOW R SINUSODIAL OSCILLATION ERROR
FIGURE 40

PAIR FUNCTION FOR VITREOUS SILICA

SIMILAR TO MOZZI'S
FIGURE 41
COMPTON AND BACKGROUND OF FIGURE 22
AND COMPTON AND BACKGROUND NECESSARY TO
YIELD RESULTS SIMILAR TO MOZZI'S
FIGURE 42

$\kappa_i(k)$ CURVE FOR VITREOUS SILICA USING
EXPERIMENTAL SETUP B
FIGURE 43

PAIR FUNCTION FOR VITREOUS SILICA

USING EXPERIMENTAL SETUP B
\[ k = 5.2 \]. It should be noted that the observed peak positions for Si-O, O-O, and Si-Si occur roughly in the same position as do Mozzi's. The 0-0 peak here occurs at 2.62Å as compared with Mozzi's 2.65Å.

Figures 44-46 are drawings from photographs (given in Appendix A) taken at 20 values of 35°, 65°, and 145° using CuKα radiation. It can be seen from these figures that in taking the MCA data for CuKα using the half peak area technique the CuKα Compton peak never was separated from the CuKα coherent peak. By using this technique though, it is clear that less error is encountered at each 2θ measurement using the MCA method than in using the SCA method where the entire Compton was measured at each \( \Delta 2\theta \). Figure 48 illustrates the point just made. The shaded area represents the Compton due to CuKα radiation. The manner in which the lower level and upper level discriminator are set would result in a region similar to ABC being used to determine the coherent radiation from the sample. As can be seen the measurement would include a large portion of the Compton. Now if this Compton component could be measured experimentally and subtracted, all would be well; however, what is most probably seen when using a single crystal and misorienting it, is shown in Figure 47. It is believed that no matter what the orientation of the sample, coherent scattering of the incoming x-ray beam will take place; this peak will, then have in it the Compton.
FIGURE 44

DRAWING OF MCA DISPLAY USING CuKα

RADIATION, $\theta = 30^\circ$ ULTRASIL SAMPLE
Figure 44
FIGURE 45

DRAWING OF MCA DISPLAY USING

CuKα RADIATION, 2θ = 65°, ULTRASIL SAMPLE
FIGURE 46
DRAWING OF MCA DISPLAY USING
CuKα RADIATION, 2θ = 145°, ULTRASIL SAMPLE
Figure 46
The presence of a coherent peak for the misoriented BT-cut silica now represents an element of error in the experimental method for measuring Compton. It should at this point also be mentioned that the work of Alexandropoulos, discussed in Chapter 2, has shown that the magnitude of Compton scattering is structure dependent and in a single crystal is also dependent on orientation of the crystal. It thus appears that the magnitude of Compton scattered off the BT-cut single crystal is not the same as the Compton scattered off the vitreous silica structure resulting in yet another error in this correction.

For the SCA work the LLD and ULD remain unchanged during both the Ultrasil sample intensity measurements and the BT-cut crystal Compton measurement. The MCA approach yields more accurate structural information. In considering the SCA approach, the LLD could be set at point B yielding a half profile area measurement; however, in making the Compton measurement the background area still cannot be effectively measured and subtracted. This approach would however, yield better SCA data than the approach used.

At this point it can be stated that the MCA approach has yielded superior structural data on vitreous silica. The MCA approach avoids the problem of the structure dependency of Compton scattering and diffuse
FIGURE 47
EXPERIMENTAL SETUP A AND B
DATA COLLECTION
Figure 47
scattering and makes the background scattering correction at the same time as the coherent peak area measurement. This technique, however, clearly has a built in Compton error that increases with 2θ and cannot be separated out by using experimental setup A or B.

Figures 48 - 50 shows MCA runs take at 2θ values of 35°, 65° and 145° for AgKα radiation. It is generally thought that the Compton correction is hardest to make for AgKα radiation. This is evident from Figures 48 - 50 especially for 2θ values greater than 50°. By using experimental setup A to measure the coherent peak area for 2θ = 65°, the following would result. Figure 51 shows that a larger Compton error would be measured than by the MCA technique. Again the LLD could be placed at point B, thus approximating the half profile technique; however, the area due to the background scattering could not effectively be determined. By making a second run to measure the Compton with the LLD placed at A and the ULD placed at C with the BT-cut crystal misoriented as discussed in Chapter 4, a curve similar to Figure 51 would result. As the misorientation in the -x direction increased, the resulting intensity would decrease as indicated in Figure 52. The Compton measured is not the area under the dashed curve of Figure 52 but the area under the coherent peak as well. Also as indicated by Alexandropoulos the Compton area will not be the same
FIGURE 48

DRAWING OF MCA DISPLAY USING

AgKα RADIATION, 2\(\theta\) = 35°, ULTRASIL SAMPLE
FIGURE 49
DRAWING OF MCA DISPLAY USING
AgKα RADIATION, 2θ = 65°, ULTRASIL SAMPLE
Figure 49
FIGURE 50

DRAWING OF MCA DISPLAY USING
AgKα RADIATION, 2θ = 145°, ULTRASIL SAMPLE
FIGURE 51
TYPICAL COHERENT PEAK USING AgK\(\alpha\) RADIATION AND MEASUREMENT OF K\(\alpha\) PEAK AREA USING EXPERIMENTAL SETUP A AND B
Figure 51
FIGURE 52
EFFECT OF TILTING THE DT-CUT SINGLE CRYSTAL OF SILICA ON THE COMPTON AND COHERENT PEAKS
as that seen at a corresponding 2θ position using the vitreous silica sample. Thus what is measured is the Compton scattering, background, and coherent diffuse scattering. By further misorienting the BT-cut single crystal of silica the magnitude of the peaks of Figure 52 is simply reduced. It is felt that substantial error exists in making the Compton correction over all k for experimental setup A, and less but still significant Compton error exists in the MCA data.
CHAPTER VI
CONCLUSIONS

The conclusions reached in this investigation are as follows:

1. Experimental setup A cannot be used to obtain accurate structural data on materials of low atomic weight such as vitreous silica.

2. The limiting parameter of experimental setup A is its inability to make an accurate measurement of the Compton correction necessary to yield accurate structural information.

3. Experimental setup B provides accurate structural information on low atomic weight materials such as vitreous silica.

4. It is unclear as to whether or not a Compton correction can be obtained to yield as accurate structural information as was obtained by Mozzi and Warren in their work on vitreous silica. It is felt that experimental setup B cannot match Mozzi's and Warren's data on this structure for reasons outlined in the Chapter V.

5. In order to use energy dispersive x-ray analysis to obtain accurate structural data, experimental setup B
will have to be modified so as to allow more accurate Compton data collection.
A possible experimental method that could be used to overcome the deficiencies in experimental setups A or B is outlined in a paper by S. Ergun, W. Braun and E. Fitzer. Their work considered the elimination of the Compton component of diffusely scattering materials. The way they were able to resolve the Compton scattering was as follows. In their experimental setup they used silver radiation which was monochromated by using a bent LiF single crystal. The monochromated radiation then was passed through a beta filter and then through a ruthenium filter. The ruthenium filter has a K absorption edge of 0.5605Å meaning that all wavelengths shorter than this will not be transmitted. Thus in placing the filter before the sample, the AgKα, radiation of wavelength 0.5594Å would be absorbed allowing only the AgKα, to be incident on the sample. This then would yield a coherent peak composed only of AgKα, and a Compton peak due only to AgKα,.

Now by placing the ruthenium filter between the sample and the detector, the following would be seen on a NCA display. The radiation now incident on the sample...
would be \( \text{AgK}_\alpha \), and \( \text{AgK}_\beta \). The scattered radiation then would pass through the Ru filter with the \( \text{AgK}_\alpha \) radiation being filtered out. Again the detector would measure the \( \text{AgK}_\beta \) coherent intensity and the Compton due to \( \text{AgK}_\alpha \); but, this time the Compton due to \( \text{AgK}_\alpha \) would be also measured since this would be a longer wavelength than the Ru (K edge) of 0.5605 Å. Next the experiment could be run with no ruthenium filter present and the results of the second experiment could be subtracted from the third experiment yielding the coherent scattering due only to \( \text{AgK}_\alpha \). This scheme appears promising as a way to use energy dispersive x-ray analysis in glass structure determination. It also is not clear at this time whether the radiation used need be monochromatic or not.
REFERENCES


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APPENDIX A

PICTURES USED FOR FIGURES

44-46, 48-50
FIGURE 53
PICTURE USED FOR FIGURE 44
WCA - CuKα, 2θ=35°
FIGURE 54

PICTURE USED FOR FIGURE 45

MCA - CuKα, 2θ=65°
FIGURE 55
PICTURE USED FOR FIGURE 46
MCA - CuKα , 2θ=145°
FIGURE 56

PICTURE USED FOR FIGURE 48

MCA - AgKα, 2θ = 35°
FIGURE 57

PICTURE USED FOR FIGURE 49

MCA - AgKα, 2θ = 65°
FIGURE 58
PICTURE USED FOR FIGURE 50
MCA - AgKα , 2θ = 145°