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A NEUTRON DIFFRACTION STUDY
OF NICKELOUS OXIDE

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

By
David Owen Murray, B.A.

*****

The Ohio State University
1962

Approved by

[Signature]
Adviser
Department of Physics
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INTRODUCTION

Nickelous oxide (NiO) is one of a group of transition element oxides and halides that exhibit the property of antiferromagnetism below a characteristic transition temperature called the Néel temperature. A simple example of an antiferromagnet is a crystal composed of two sublattices with the magnetization direction of one sublattice antiparallel to that in the other. The percentage saturation of the alignment of these atomic moments is temperature dependent, and above the Néel temperature the material loses its antiferromagnetic property of magnetic correlation and exhibits paramagnetism. At the Néel point the sample will usually exhibit crystal lattice distortion, a specific heat anomaly, a susceptibility anomaly, and other evidences of a magnetic transition. Although some of these anomalies had been observed as early as 1914,\cite{1,2} it was not until 1932 that Néel proposed the concept of the antiferromagnet and developed an approximate theory for it.\cite{3} Since that time many experiments and theoretical calculations have been performed in attempts to understand antiferromagnetism.
It has been recognized that the important magnetic interaction which results in antiparallel magnetic moment arrangements in the transition element oxides is an indirect exchange interaction occurring between the two magnetic ions via an intervening oxygen ion. The electrons participating in the interaction are the magnetic electrons or the electrons of the unfilled 3d shell which produce the magnetic moment of the ion. The distribution of these electrons in the crystal may provide important evidence as to the nature of the antiferromagnetic bond.

A unique method of determining the magnetic electron distribution is available in the techniques of neutron diffraction wherein intensity measurements are made of the diffraction maxima arising when a monoenergetic beam of neutrons is incident upon a suitably oriented crystal. The positions of the diffraction maxima of a crystal are determined by the neutron (de Brogie) wavelength and the Bragg condition for coherent scattering.

The intensities of the diffraction maxima will exhibit a decrease with increasing scattering angle which is described by a magnetic form factor. This form factor is similar to the atomic form factor for x-ray scattering with the important difference that only the magnetic electrons contribute to the neutron scattering. The form factor dependence arises from the fact that the dimensions
of the electron cloud are comparable to the neutron wavelength. For forward scattering all parts of the electron cloud scatter in phase. As the scattering angle is increased interference effects due to the spatial extension of the atom come into play and the scattered intensity falls off. A determination of the form factor from investigations of the magnetic diffraction maxima thus gives information as to the distribution of the magnetic electrons.

Most of the early determinations of magnetic form factors were obtained from powder diffraction data. In comparison to single crystal measurements the powder method has the advantages that the data are relatively easy to obtain and analyse and that powder samples are generally available. On the other hand, the use of a single crystal allows the precision of the data to be improved because of the higher counting rates available in single crystal diffraction. Also a single crystal investigation permits any crystal reflection to be studied individually, whereas powder diffraction patterns have all reflections of the same scattering angle grouped into one diffraction peak.

In this work diffraction data obtained from a single crystal of NiO are utilized to determine the magnetic form factor of the Ni$^{4+}$ ion and the results compared with some recent calculations for Ni$^{4+}$. 
CHAPTER I

DIFFRACTION APPARATUS

Neutron Source

The neutron source for the diffraction measurements was the Battelle Research Reactor at West Jefferson, Ohio. This reactor is of the swimming pool type and operates at a power of 2 megawatts, yielding a thermal neutron flux of about $2 \times 10^{13}$ n/cm$^2$/sec in the reactor core. Access to the neutron flux was obtained through a beam tube which extended through the reactor wall and water shielding to within a few inches of the core. The neutrons were brought out of the beam tube through a 2-inch square collimating-channel 55 inches long. The first 16 inches of the beam tube was filled with graphite to reduce the fast neutron component of the flux. Graphite was used since it does not reduce the thermal neutron flux arriving at the reactor face as much as a non-moderating material. The external shielding, as shown schematically in Figure 1 and photographically in Figure 2, consisted of an iron plug to attenuate the $\gamma$-radiation, and paraffin blocks interspersed with layers of boric acid powder to absorb the neutrons.
Figure 1

Plan View of the Reactor Facility
Figure 2

Photograph of Diffraction Apparatus
The radiation emerging from the collimating channel is intercepted by the monochromator crystal which is set to reflect neutrons satisfying the Bragg condition,

$$\lambda = 2d \sin \theta .$$

In the above, $\theta$ is one-half the scattering angle, $d$ is the lattice spacing of the reflecting planes of the crystal, and $\lambda$ is the de Broglie wavelength of the neutrons. In the present case the scattering angle is fixed at approximately $22^\circ$ and a (111) reflection from a lead crystal gives a monochromatic beam of about 1.1 Å wavelength. The wavelength spread of the diffracted beam was approximately 0.05 Å and is attributed mainly to the angular divergence of the incident beam. The intensity of the monochromatized beam is estimated to be $5 \times 10^5$ n/cm$^2$/min. The monochromator crystal can be adjusted to obtain the maximum reflected neutron beam at the diffraction apparatus by means of three external controls. These controls provide for rotation of the crystal in a horizontal plane, tilt of the crystal with respect to the vertical, and a translation across the incident beam.

**Diffractometer**

The diffractometer consists of a crystal table and counter arm mounted with double axle rotation about a common vertical axis. Each of these motions is effected by
rotating one of two 360-tooth worm gears mounted on the rotation axis and attached to either the table shaft or the counter arm. The single thread worms are driven manually or by a motor coupled to the worms through separate solenoid clutches. The gearing from the motor to the table and counter arm is such that the counter arm is driven at twice the angular velocity of the table. This maintains the angular relation between crystal planes and the detector, as is customary with single crystal spectrometers. To scan a diffraction peak, i.e., to determine the intensity versus $\theta$ curve, for a reflection with a Bragg angle $\theta_B$, the crystal planes are set at $(\theta_B - \theta)$ and the counter at $2(\theta_B - \theta)$, where the two angles are measured with respect to the incident beam. The diffraction count is recorded at this position and then the clutches are automatically engaged to advance the counter and crystal to the next counting position. The size of the angular steps is controlled by a cam and microswitch arrangement on the table worm shaft and can be adjusted for either 0.10 or 0.05 degree intervals of the crystal table.

**Electronic Circuitry**

The neutron detectors used were $^{10}$B enriched BF$_3$ proportional counters (N. Wood Counter Laboratory). The neutrons are detected by the 2.3 Mev alpha particle from the high cross section reaction of thermal neutrons with
B^{10}. The monitor counter was 1 inch in diameter and contained BF\textsubscript{3} gas (11 per cent B\textsuperscript{10}) at 20 cm of Hg pressure. With the counter placed perpendicular to the neutron beam its efficiency was between 1 and 2 per cent. This counter was used to monitor the monochromatic neutron beam (a function of the reactor power) and to determine the time base for each diffraction count. The large diffraction counter, 2 inches in diameter by 10 inches long, was filled with BF\textsubscript{3} gas (96 per cent B\textsuperscript{10}) at a pressure of 60 cm of Hg and had an 80 per cent efficiency for thermal neutrons traveling through its length. This counter was shielded by a 2-inch layer of borated paraffin plus an inner 0.02-inch layer of cadmium, the latter shield being opaque to thermal neutrons.

The pulses from the counters enter presamplers located at the counters, are transmitted to Detectolab DA3 pulse amplifiers, amplified and registered by Detectolab DS2 scalers. The output of the diffraction counter scalers is registered continuously in scales of 2\textsuperscript{n} by a Streeter-Amet print-out recorder. The signal ending a counting interval originates in the preset monitor scalers and causes the recorder to print out the diffraction count. The scalers then reset and the magnetic clutches are actuated to move the counter and table to the next counting position.
**Crystal Mount**

For room temperature measurements the NiO crystal was mounted from a Supper goniometer head by means of a spring aluminum clamp. This assembly is shown in Figure 3 as used in conjunction with a General Electric crystal orieneter which mounted directly on the diffractometer table. The goniometer has two mutually perpendicular rotational arcs which are used to bring a crystal direction \([hkl]\) coincident with the goniometer axis and three translational adjustments which position the crystal at the center of the arcs. The orieneter has two rotational motions, a \(\phi\) rotation of 360° about the goniometer axis and a \(\psi\) rotation of 90° which positions the \(\phi\) rotation axis at some angle relative to the horizontal plane. The \(\phi\) and \(\psi\) rotations are used to bring any desired reflection plane vertical and thus enable the reflection to be observed by the proper rotation about the vertical (table rotation) axis.

When measurements of the diffracted intensities of many reflections are to be made of a single crystal, it is desirable to align the crystal accurately with respect to the orieneter. Once this is done the orieneter and table rotations can be used to position the crystal for any Bragg reflection readily. The goniometer is used to make this alignment.
Figure 3

The crystal, goniometer head and crystal orienter are shown. The two concentric goniometer adjusting arcs (± 25° rotation) are located behind the crystal. The goniometer mounts in the center of the φ rotation dial which has a 360° rotational motion. The ψ rotation is that associated with the large arc of the orienter and is shown in its 90° position.
The alignment procedure consisted of two parts: a preliminary alignment performed optically and the final alignment with the neutron beam. The optical alignment was accomplished with the aid of a telescope with crosshairs and entailed the centering of the crystal at the center of the goniometer arcs by means of the translational adjustments, and the rough adjustment of the [hkl] direction parallel to the goniometer axis. The diffraction peak associated with the [hkl] direction was then observed for the 0, 90, 180, and 270 degree positions of the $\phi$ rotation dial. The goniometer arcs were adjusted until this diffraction peak fell at the same table setting. This ensures that the [hkl] direction is parallel to the goniometer axis. A $\psi$ rotation of 90° was then made, putting the $\phi$ rotation axis vertical, and the $\theta$ setting for some reflection in this zone measured. This last measurement essentially determines the zero for the $\phi$ rotation. With care the error in the alignment would be less than 3' of angle for either $\phi$ or $\psi$ rotation.

**Cryostat**

The vacuum cryostat used to obtain the low temperature diffraction data for the NiO crystal is shown in the cross sectional view of Figure 4. The cylindrical aluminum vacuum wall is sealed at both ends by o-rings against brass end plates. The cryostat is evacuated
Figure 4

Cross Sectional View of Vacuum Cryostat
through the tube in the bottom o-ring plate. The thin wall monel tube extending through the top plate supports all of the low temperature components in the cryostat. The two tubes entering the cryostat inside of the monel tube are used to transfer coolant to the upper chamber of 1.5 liter capacity. The lower chamber has a volume of 0.5 liter and is filled via an external transfer tube. These chambers are fabricated from brass and all vacuum joints silver soldered. A thin aluminum radiation shield is suspended inside the vacuum wall to reduce the radiative heat leak to the low temperature components. The lower three removable shields are constructed from aluminum which has good heat conduction properties and small scattering and absorption cross sections for neutrons. The crystal holder mounts from the shaft which is supported from the inner heat shield. The crystal may be rotated about the axis of the shaft by engaging the coupling mechanism and turning the o-ring sealed drive shaft. This mechanism is shown in the photograph of Figure 5.

The vacuum was obtained by employing a mechanical pump to establish a rough vacuum of 10 microns, sealing off the cryostat, and admitting liquid nitrogen to the upper reservoir. A small volume (100 gram) of activated charcoal located at the top of the large reservoir then reduces the pressure to approximately $10^{-6}$ mm of Hg. The capacity of
Figure 5

The cryostat orienter assembly and NiO crystal are shown with the two inner radiation shields. The crystal and crystal holder mount on the smaller shield. The scale is in centimeters.
the charcoal was adequate to maintain this pressure for several days. Under these conditions the evaporation rate was measured to be 0.06 liters of liquid nitrogen per hour.

Before assembling the cryostat for an experiment, the crystal holder with its crystal in position was mounted on the inner shield, centered on the diffractometer table, and neutron reflections used to align the crystal with respect to the rotation axis of the crystal holder. The crystal and shield were then mounted in the cryostat, the crystal alignment checked, the cryostat evacuated and cooled, and the measurements taken.
CHAPTER II

MONOCHROMATOR CRYSTAL

Introduction

The function of the monochromator crystal, as mentioned in Chapter I, is to provide a monoenergetic neutron beam, or actually a beam of neutrons with energies, or wavelengths, closely grouped about a central energy.

Investigations of the suitability of various crystals for neutron monochromators have shown that metallic crystals such as lead and copper give more intense reflected beams than other common crystals. This occurs for three reasons: low absorption cross sections for neutrons, high coherent scattering cross sections, and relatively large mosaic spreads for these crystals. The first allows a large volume of the crystal to be utilized because of the large penetration depth, the second ensures that the reflection is strong, and the third factor has to do with "crystalline perfection" which will be discussed in Chapter III. However, it can be stated here that a crystal of low perfection (high mosaic spread) will reflect more neutrons for any given incident wavelength, but the total reflection will have a wider wavelength spread.
There are two forms of monochromators which are useful for neutron work. These are the reflection and transmission crystals shown in Figure 6. The transmission arrangement has the advantage that a smaller crystal is needed to intercept the incident beam. On the other hand, it has been demonstrated that with the larger reflection crystal it is possible to produce a more intense beam by cutting the crystal face at a small angle to the reflecting planes as shown in Figure 6. This will condense the reflected beam into a smaller area than the incident beam. Increases in beam intensity by a factor of two are feasible in this manner.

The large size and specific orientation necessary for the monochromator crystal makes it very difficult and expensive to obtain from commercial sources. It was therefore decided to produce these crystals in the laboratory. Because of its low melting point and convenient crystallization habit, the major effort was devoted toward producing suitable lead crystals. The various aspects of growing and evaluating these lead crystals are discussed in this chapter.

Crystal Growing Apparatus

The essential details of the vacuum furnace can be explained with the aid of Figure 7. Four separate heaters are wound on two 18-inch spiral grooved ceramic cores which
Figure 6

Reflection and Transmission Crystals
TRANSMISSION

REFLECTION

INCIDENT NEUTRONS

REFLECTING PLANES

REFLECTED NEUTRONS

2\theta
Figure 7

Cross Sectional View of Crystal Furnace
fit closely around an Inconel vacuum wall of 4-inch
diameter. The main heaters, A and B in the figure, consist
of 76 turns of 12-gauge nichrome wire. The two guard
heaters, G1 and G2, are made up of 11 turns of 24-gauge
nichrome. These latter two windings serve to reduce the
thermal loading of the main windings due to heat loss to
the cold ends. The upper main winding, A, is the high
temperature portion of the furnace in which the lead is
molten, and the lower winding, B, is the low temperature
portion into which the molten lead is lowered.

Four thermocouple positions are indicated in the
furnace drawing and are labeled TC 1, TC 2, TC 3, and TC 4.
These are Chromel P-Alumel (Leads and Northrup 20-gauge)
thermocouples used with ice baths for the cold junctions.
TC 1 and TC 4 are attached to the furnace wall and used to
adjust the power input to the two guard heaters.
Thermocouples TC 2 and TC 3 were each embedded in 50 grams
of iron and placed immediately outside of the two main
heaters. These thermocouples were used to adjust the power
input to heater windings A and B to give the desired
temperature gradient through the region in which the lead
solidified.

Asbestos insulation was used for lagging around the
windings. Water fed cooling coils soldered to the outside
aluminum jacket and to the ends of the furnace wall lessen
the heat flow to the room and also supply a constant thermal loading on the furnace, irrespective of the room temperature.

The lowering rod, supporting the crystal holder, is a 1/8-inch drill rod which enters the vacuum chamber through a sliding o-ring seal. This rod is lowered by the counterbalanced clock mechanism mounted from the wall. A wide range of lowering rates is possible by changing the synchronous drive motor and its associated worm gear drive.

The vacuum chamber is sealed at both ends by means of brass plates bolted to o-ring flanges soldered to the ends of the furnace wall. Three thermocouples for monitoring sample temperatures are brought through the bottom end plate via a wax seal.

The power for the various furnace windings is supplied by a Superior Electric Company IE 5101 line regulator. The two guard windings and the lower main winding are directly connected to three autotransformers which set the constant voltage to these windings. The voltage to the upper main winding is supplied by the voltage control circuit shown in Figure 8. The 1:1 isolation transformer, T1, serves to reduce electrical interference problems between the furnace windings and the thermocouple leads. The maximum furnace voltage, $V_F$, is adjusted by the variable transformer V1. This voltage is controlled downward, according to the demands of the
Figure 8

Schematic of Voltage Control Circuit
FURNACE WINDING

T1

T2

V1

V2

V3

110 VAC
furnace, by the series autotransformers V2 and V3 coupled to the output line by the 18:1 reduction transformer, T2. The mechanically driven autotransformer, V3, adjusts the control voltage, $V_c$, appearing across the output winding of T2. Thus, the resulting voltage supplied to the furnace is the difference between $V_f$ and $V_c$, neglecting losses in T1. The range of control of $V_c$ is set at 0-6 volts by adjusting V2.

A block diagram of the apparatus which controls the position of V3 is shown in Figure 9. Besides the previously described thermocouple and control transformer, the apparatus consists of the following Leeds and Northrup equipment: a dc microvolt amplifier, 9835-B; a millivolt recorder, model S; an electronic control unit, model P.A.T. 60; and a servo-drive mechanism, 10267. The potentiometer shown is a high impedance, low drift instrument constructed in this laboratory. The total impedance of the potentiometer circuit is 130,000 ohms with a 1.3v El2 mercury cell used to supply the working current of $10^{-5}$ amp. An internally mounted Weston standard cell is used for standardization. To minimize thermal emf effects the potentiometer was constructed on an aluminum chassis and mounted in a cabinet packed with thermal lagging. The observed daily variation was $\approx 10$ microvolts in 100 millivolts and this was attributed entirely to thermal emf
Figure 9

Block Diagram of Furnace Control Apparatus
HOT JUNCTION  COLD JUNCTION

POTENTIOMETER

DC AMPLIFIER

SERVO MOTOR  CONTROL UNIT

V3  RECORDER
effects. The instrument adjusts in 1 millivolt steps up to 110 millivolts with a 10 turn slide wire which allowed readings to .001 millivolt.

The difference between the potentiometer emf and the thermocouple emf is amplified by the dc amplifier and used as the input to the control unit. The recorder is also driven by this signal, thereby affording a continuous record of the furnace operation. The control unit has three types of adjustable responses to the input signal: (1) a proportional output which depends on the amplitude (and sign) of the input signal, (2) a cumulative response which gives an output signal proportional to the integral of the input signal with respect to time, (3) a rate response which supplies an output proportional to the time rate of change of the input signal.

**Experimental Procedures**

The method employed here for growing lead crystals is essentially that due to Bridgeman. The molten metal is slowly lowered from the high temperature region into the low temperature region. As the lowering proceeds, the solidification "zone" moves upward in the lead sample, radiative heat transfer providing the major thermal contact between furnace wall and crystal holder. For the resultant crystal to have a single growth habit, it is essential (1) that the initial growth start from a single seed and
(2) that the growth not be hampered by a large number of competing or parasitic crystals as the growth proceeds. To enhance the probability of an initial single seed, a small tube with a large length to diameter ratio is attached to the lower end of the crystal holder. With this arrangement, although several crystal seeds may start at the bottom, the seed which begins with an "easy" direction of growth closest to the axis of the tube will prevail over the other crystallites by the time the solidification has reached the top of the tube and entered the main body of molten lead. The second effect, parasitic growth, is due mainly to impurities in the lead which act as seed centers.

The variables which can be adjusted for a crystal growth are the lowering rate and the temperatures of the upper and lower heaters. These will directly affect the rate of crystal growth and the temperature gradient at which the metal is crystallized. (The purity of the lead can also be considered a variable but will not be treated so here except in a qualitative manner.) A high temperature gradient through the solidification region is desirable since it will enhance the purification factor that is obtained when solidification occurs. However, a high temperature gradient results in poorer control of the furnace temperatures and also may introduce strains in the crystal. The effect of the lowering rate is not well understood, and in fact, contradictory reports on the
effect of lowering rate have been made. Andrade and Roscoe recommend the smallest practical lowering rate whereas Goss and Weintroub give evidence that too small a lowering rate results in poor crystals. One other word should be said on the matter of lowering rates; the lowering rate must not exceed the growth rate, which has an upper limit, since this would result in very favorable conditions for the production of new seeds above the solid-liquid interface.

The basic dimensions of the several crystal holders used were 11 inches in length and 2 inches in diameter. Four types of crystal holders were used: (1) brass cylinder, 1/32-inch wall; (2) stainless steel cylinder, 1/32-inch wall; (3) Vycor cylinder supported in steel cylinder; (4) steel cylinder with an internal .020-inch aluminum jacket. The first two holders are of the same design and differed only in the material used; the stainless steel was superior to the brass in corrosion resistance and in the smaller heat conduction occurring along the wall. These two holders had tapered bottom ends with the taper terminating in a small seeding tube (Figure 7). In order to facilitate the removal of the crystal from the holder the brass and steel containers were given an oxide coating by heating them in air and in some cases adding to this a graphite coating. These steps were necessary to prevent the lead from soldering to the metal,
in which case the soldered area would give rise to many seeds. The disadvantages of these holders were that contamination of the lead is likely and that removal of the crystal required some mechanical shock to be applied to the crystal. The Vycor holder was tapered at the bottom with a smaller tapered seed tube added to that. This holder gave excellent insurance against contamination, but was faulty in that the lead adheres strongly to the Vycor. This presented a problem in removing the Vycor and also required that a new holder be used for each run. This holder was also susceptible to breakage during the growing process. The fourth holder was designed so as to allow easy removal of the crystal. The thin aluminum jacket fitted loosely into the steel holder except at a sealing point just above the tapered end. The tapered steel end with seed tube was bolted to the steel cylinder with machine screws. The crystal was extracted by removing the holder tip and pushing out the aluminum sleeve which was then split away from the lead. This technique suffered only from the difficulty in forming a tight seal between the aluminum sleeve and steel wall. In addition to these holders, a small holder, 6 inches long and 1 inch diameter, was constructed in order to examine the effects of various experimental conditions economically.

The lead used for the crystals was granular lead of 99.99 per cent or greater purity. Antimony and tin
comprised the largest part of the impurity. Since the granular lead had about one half the density of the solid lead, it was necessary to cast an ingot previous to loading it into the furnace. The granular lead was melted and heated to 400-460°C in a stainless steel container situated in a vacuum bell jar. This melt was solidified, the dross was removed from the surface, the lead remelted and cast into an aluminum holder. A second method employed was to load the granular lead directly into the vacuum furnace using a holder such as the one shown in Figure 7 which has a hopper to hold the extra volume.

After the holder is loaded through the bottom of the furnace, the furnace is sealed and evacuated with an oil diffusion pump backed by a rotary oil pump. Once the vacuum is established the holder was raised slowly, to avoid vacuum loss due to outgassing, into the hot upper furnace. The lead was melted and kept at 410-500°C for 10 to 12 hours. The temperature was then reduced to the desired starting temperature (nominally 400°C) and the furnace allowed to stabilize. At this point the control circuitry was activated and the lowering motor started. At the end of the run the lead was allowed to cool gradually in the lower furnace.

Lowering rates of 0.25, 0.50, and 2 inches per hour were employed; the smaller two rates were most often used.
The temperature control of the furnace as indicated by the thermocouple record was within 0.1°C of the control point and, with the sample between the two windings, the control improved to 0.02°C due to the stabilization provided by the solidifying sample. The thermal gradient at the solidification point (327°C) was measured by means of iron-constantan thermocouples attached to the walls of the crystal holder. This gradient was usually set between 7°C C/in to 15°C C/in.

Analysis of Crystals

The first step in the evaluation of the perfection of a crystal was to etch the surface. Of several etching solutions tried for lead, the best performance was given by 10 gm of Fe₂(NO₃)₃ dissolved in 1 liter of a 4 per cent solution of nitric acid. The action of this solution was greatly enhanced by rapid stirring. In a few cases the surface of the crystal was very irregular upon removal from the holder and had to undergo a preliminary treatment in which a small layer was machined away. (This situation always arose when a Vycor holder was used.)

The orientation of the crystallographic axes in the lead crystal (face centered cubic, a₀ = 4.95A) was determined using the neutron diffraction apparatus to identify such Bragg reflections as (111), (220), and (200). The preferential direction of growth for lead is a (110)
crystal axis and if this direction coincides with the cylinder axis of the lead ingot (the growth direction) there would be (111), (111), and (001) axes perpendicular to the cylinder axis. The usual case was to have the (110) axis inclined 1 to 10 degrees relative to the cylinder axis with at least one of the (111) or (111) within 4° of a perpendicular to the cylinder axis.

In some cases, a rocking curve and/or the etch pattern would show the lead to consist of several large crystals and the specimen would be discarded. A test of the uniformity and perfection of the crystal with respect to translation along the growth axis was next performed. This was accomplished by investigating the (220) reflection in transmission at intervals along the ingot. The neutron beam was stopped down so that only a narrow segment of the crystal perpendicular to the ingot axis was used for each measurement. In this transmission method the effective neutron absorption is the same for all volume elements in the incident beam. Thus a good idea of the crystalline perfection of that segment could be inferred from the shape and width of the diffraction peaks. Comparison of the diffraction peaks taken at different positions along the ingot yield evidence as to the uniformity of the crystal. For reasons explained below, a second type of experiment was also performed with the ingot axis vertical using a
narrow horizontal beam of neutrons. In this arrangement, the effective absorption is less for volume elements near the forward surface of the crystal. This complicates the interpretation of such diffraction peaks.

If the crystal was considered promising after the above investigations it was cast into a block of plastic material (Castolite Company, Philadelphia, Pennsylvania) preparatory to cutting. With a high speed band saw, a waste cut was made and the orientation of the crystallographic axes refined. The second cut was taken so as to expose one surface of the desired crystal. This surface was milled flat, etched and inspected for quality in the neutron beam using reflections from only the exposed face since the hydrogenous plastic was impervious to thermal neutrons.

A typical fault which appeared to some degree in all of the crystals was a lineage structure. Lineage may be defined as a structure in a crystal which consists of a number of small zones extending in the general direction of growth, and having slightly differing orientations with respect to the overall growth orientation. The disorientations occurring in this "fiberous" growth are rotations about the direction of growth. The photographs of Plate I indicate to some extent the kind of information on crystal lineage structure that can be obtained from etch
Plate I

1. The etch pattern of a (111) crystal face which lies approximately parallel to the growth direction is shown. The lineage structure appears as horizontal stripes. The dimensions of the exposed crystal are 11x1-1/2 inches.

2. The etch pattern shown here is of a face cut perpendicular to the growth direction. The two irregular shaped areas which show up at the bottom of the face are made up of 10 different lineage zones.

3. This is the same sample as above viewed from the side. Several lineage boundaries are visible and the dark strip in the middle is a single lineage zone.
patterns. Not all of the lineage zones can be seen in a photograph since their observation depends on the specular reflection of light. Thus what appears in a photograph to be a single lineage zone is usually made up of several zones. The etch patterns of many of the crystals showed the lineage zones to be small in the lower end of the crystal and to increase in size and disorientation toward the upper end of the crystal. This is the effect which is seen in the rocking curves of Figure 10 in which no evidence of lineage is detectable for the lower end reflection. These rocking curves were taken with the growth axis vertical since this experimental arrangement will better show up disorientations consisting of rotations about the growth axis.

Some observations can be made at this point concerning the effect of the various parameters on the growth of large single crystals of lead exhibiting negligible lineage structure.

Although the normal procedure was to maintain the purity of the lead as high as possible, several runs were made with reused lead of unknown but lesser purity. The crystals from these runs consisted of several (5-10) distinct crystals of greatly differing orientations.

Two growths were made with lowering rates of 0.5in/hr and 21n/hr and all other conditions the same. The etch patterns exhibited by these two crystals showed a
Figure 10

The two rocking curves shown are taken from different portions of the same lead sample and indicate the deterioration of crystal quality with increasing displacement from the bottom end or first grown portion of the crystal. The high sharp peak was taken 2 inches above the bottom end and the low broad peak was taken 6 inches from the bottom end.
LEAD ROCKING CURVES
(111)
greater lineage structure in the crystal grown at the higher rate. However, no appreciable difference could be detected between lineage structures of growths occurring at 0.5in/hr and 0.25in/hr.

It appears that the lineage structure is increased for lowering rates greater than 0.5in/hr and that increasing the impurity level results in the formation of new crystals. The fact that the lineage increases at the top or later grown portions of the crystal could be partly explained by an increase in the effective lowering rate for the top portions. This increased rate results from the freezing zone being shifted upwards as the lead is lowered and heats the lower furnace. Thus an improvement in the furnace would provide control of the lower furnace as well as the upper or would control the temperature difference of the two furnaces.

Several temperature gradients were tried for the crystal growths but no effect on the resulting crystal was observed. However, it was evident that the prolonged initial heating at a temperature >450°C is necessary in order to destroy crystalline structure that existed previous to melting.

Final Evaluation

The final test of the crystal was made after it was cut to shape and installed as a monochromator. The crystal
was adjusted by means of the external controls until the monitor counter indicated the crystal to be in its optimum reflection position.

An analysis of the reflected beam of neutrons with respect to its uniformity and magnitude of intensity, and with respect to its monochromaticity was made using a second crystal mounted on the diffraction apparatus. A (200) reflection from a LiF crystal, 2mmx7mmx7mm, was found suitable for this purpose. A rocking curve was taken for the crystal centered in the beam and then the effects on the rocking curve of translations of the crystal perpendicular to the beam were observed. Figure 11 illustrates the appearance of the parallel and antiparallel LiF rocking curves when the lead crystal is not a single crystal and thus reflects neutrons grouped about two or more wavelengths.

The use of the same crystal as an "analyser" for the different monochromator crystals enabled the intensities of the neutron beams produced by each to be intercompared, by comparing the integrated intensities from the rocking curves. Also the widths of these rocking curves provided a relative measure of the monochromaticity of the beam or the crystalline perfection of the lead.

Because of the poor uniformity of the lead crystals along their length it became advisable to abandon the "reflection" monochromator and to use instead the
Figure 11

LiF Rocking Curves for a Poor Quality Pb Crystal
LiF ROCKING CURVES
(200)

PARALLEL

ANTIPARALLEL

INTENSITY (NEUTRONS (25x6.4) MONITOR)

θ (DEGREES)
transmission case. This requires a smaller crystal, which could be obtained from the "good" end of the crystal specimen by cutting it perpendicular to its axis. The optimum thickness for this transmission cut was determined using various size slices from the sample. (The reflection case requires no such determination, since the neutrons enter and leave the same face.) These transmission crystals proved to be satisfactory in that they gave good neutron beams with intensities almost as high as the reflection crystals. The quality of the beam obtained with the good lead monochromator in transmission and analyzed with the LiF (200) reflection is shown in Figure 12.
Figure 12

LiF Rocking Curves for a Good Quality Pb Crystal
CHAPTER III

DIFFRACTION FROM A MOSAIC CRYSTAL

The diffraction of neutrons by a crystal is quite similar to the problem of x-ray crystal diffraction and basically differs only in the mechanism whereby the scattering originates. In particular the intensity of radiation scattered from an incident plane wave by an atom is given by

\[ I_s(r) = \frac{I_i}{r^2} b^2, \]  \hspace{1cm} (1)

where \( I_i \) is the intensity of incident radiation, \( r \) the distance from the atom to the point of observation, and \( b \) is the scattering length or amplitude of the atom. For the case of unpolarized x-rays coherently scattered by the electrons of an atom, the \( b^2 \) in Equation 1 is

\[ b^2 = \left( \frac{e^2}{mc^2} \right)^2 |f|^2 \frac{1 - (\cos 2\theta)^2}{2}, \]  \hspace{1cm} (2)

in which \( e \) and \( m \) are the electron charge and mass, \( c \) is the velocity of light, and \( 2\theta \) is the angle of scattering. The
The electronic form factor $f$ is, for a spherically symmetric charge distribution,

$$f(k) = \int_{0}^{\infty} U(r') \frac{\sin(kr')}{kr'} dr',$$

(3)

where $U(r')$ is the radial distribution of electron number density, $r'$ is the radial distance from the nucleus, and $k$ is equal to $(4\pi \sin \theta)/\lambda$, $\lambda$ being the wave length of the radiation. The electronic form factor is maximum for forward scattering ($\theta = 0$), where it has a value equal to the number of electrons in the atom, and decreases as $\theta$ increases.

Whereas the coherent scattering of x-rays by an atom is entirely due to an electric interaction with all the electrons of the atom, the scattering of neutrons results from a nuclear interaction as well as from a magnetic interaction with the magnetic (unpaired) electrons of the atom. The interaction with the nucleus involves specific nuclear forces not well understood and therefore the nuclear scattering amplitude must be determined for each nucleus. Nuclear scattering is in general isotropic because of the high localization of nuclear matter relative to the neutron wave length. Tables of the neutron scattering parameters for the nuclei are given in the literature.\(^{12}\)
The coherent magnetic scattering amplitude for neutrons scattered by an atom with effective electron spin $S_{\text{eff}}$ is given by Halpern and Johnson \(^\text{13}\) as,

$$ p = \frac{e^2}{mc^2} \gamma' f_{S_{\text{eff}}} \quad (4) $$

In Equation 4, $\gamma'$ is the neutron magnetic moment in nuclear magnetons, $e^2/mc^2$ has the same value as for x-ray scattering, and $f$ is the relative magnetic form factor obtained from Equation 3 with $U(r')$ equal to the radial probability density of magnetic electrons. The magnetic form factor is therefore unity in the forward direction.

Because of the vector nature of the magnetic scattering interaction there is an additional geometric factor, $q$, to describe the coherent scattering from a system of aligned magnetic moments in a crystal lattice. If $\alpha$ is the angle between the atomic magnetic moment direction and the normal to the scattering plane, then the intensity of magnetic scattering is given by Equation 1 with $b^2 = p^2q^2$ where $q^2 = \sin^2\alpha$.

As can be seen from the preceding, the nuclear-neutron scattering is isotropic whereas both the x-ray and magnetic scattering are functions of $\theta$. The nuclear scattering amplitude is therefore described with a single parameter. The angular dependence of the magnetic
scattering is of major interest here, since it is intimately related to the distribution of magnetic electrons. In addition, the magnetic scattering dependence on orientation \( (q) \) is a very important tool in the determination of magnetic structures of solids.

The transition from the case of scattering by a single atom to that of scattering by a lattice of atoms parallels the treatment given in texts on x-ray diffraction\(^{14,15} \) and the neutron case has been treated separately in various works.\(^{13,16,17,18} \)

A mosaic crystal is defined as a crystal made up of many small perfect crystals which have slight disorientations with respect to one another. These "mosaic blocks" are usually considered to have a Gaussian distribution of orientations with respect to their mean. The standard deviation of the Gaussian distribution is called the mosaic spread and is a measure of the crystalline perfection. These blocks will reflect as "optically independent" units; that is, the intensities rather than the amplitudes of the scattered wave from these blocks is additive.

For such a crystal the integrated intensity or integrated reflection, which is proportional to the area under a diffraction peak plot of intensity versus
scattering angle, can be expressed as

\[ P = I_o Q V A \quad (\text{n/sec}). \quad (5) \]

\( I_o \) is the intensity incident upon the crystal, \( V \) is the volume of the crystal, and \( A \) the absorption correction term,

\[ A = \frac{1}{V} \int_V \exp(-\mu t) dV, \quad (6) \]

wherein \( \mu \) is the linear absorption coefficient and \( t \) the total absorption path for the neutrons arriving at \( dV \) and exiting thence to the counter. The quantity \( Q \) is

\[ Q = \frac{\lambda^3 N^2}{\sin 2\theta} |P|^2, \quad (7) \]

with \( N \) the number of unit cells per cm\(^3\), \( \lambda \) the neutron wavelength, \( \theta \) the Bragg scattering angle, and \( P \) the crystal structure factor for the unit cell. For scattering from a particular plane with Miller indices \( h, k, l \), for which nuclear scattering alone is effective, the crystal structure factor may be written as

\[ F_{\text{nucl}} = \sum_j b_j \exp \left[ -2\pi i(hx_j + ky_j + lz_j) \right] e^{-W_j}, \quad (8) \]

in which the sum is over the atoms with scattering
amplitudes $b_j$ located in their equivalent positions $(x_j, y_j, z_j)$ in the unit cell. For reflections in which only magnetic scattering occurs, Equation 8 will have $b_j$ replaced by $p_jq_j$, defined by Equation 4. The exponential term, $e^{-W_j}$, is the Debye-Waller correction for the effect of thermal vibration and for a monatomic cubic crystal is

$$W = B \left( \frac{\sin \theta}{\lambda} \right)^2,$$

(9)

$$B = \frac{6h^2}{Mk \Theta} \left( \frac{\phi(x)}{x} + \frac{1}{4} \right),$$

(10)

where $h$ is Plank's constant, $k$ is Boltzman's constant, $N$ is the mass of the atom, and $\Theta$ is the characteristic Debye temperature of the crystal. The function $\phi(x)$, where $x$ is the ratio of the Debye temperature to the crystal temperature is defined as

$$\phi(x) = \frac{1}{x} \int_x^\infty \frac{\xi d\xi}{e^\xi - 1}.$$

(11)

For diatomic molecules the usual procedure is either to use the above equations with the two atom masses supplying a different correction term for each atom, or to use an average mass which gives the same correction for each atom.
If the two atoms have greatly different masses both above treatments fail and the practice is to fit the data by a suitable choice of $B$ of Equation 9 for each atom.

**Structure of NiO**

The crystalline structure of NiO above its Néel temperature of $\approx 520^\circ K$ is face centered cubic (NaCl). At the Néel temperature it undergoes a small rhombohedral distortion (a contraction along a body diagonal) which increases with decreasing temperature; the rhombohedral axial angle is approximately $60^\circ 04'$ at room temperature. The usual crystal will consist of many regions of four types of twins in which a region (twin domain) of one kind will have its rhombohedral axis in the [111], [111], [111], or [111] direction. Because of the smallness of the deformation from the cubic cell it is convenient to index the reflections on a face center cubic cell rather than the rhombohedral one. The onset of the crystal deformation is coincident with the antiferromagnetic ordering.

The first measurement of the magnetic structure was obtained by neutron diffraction from a powder sample and showed that the magnetic unit cell dimension must be double that of the chemical cell. It was also proposed that the crystallographically unique (111) planes were ferromagnetic sheets and that alternate (111) planes had parallel and
antiparallel arrangements of their spins. The original experiments indicated a magnetic axis in a (100) direction but results from later measurements showed that the Ni\textsuperscript{++} spins lie in the (111) planes.\textsuperscript{23} Any direction in the (111) plane is allowable from the powder data.

The above magnetic structures were arrived at by assuming a single magnetic axis in the unit cell although it was recognized that four independent magnetic sublatticed axes are possible.\textsuperscript{22} Recent work\textsuperscript{24,25,26,27} with relatively untwinned single crystals of NiO has shown that each magnetic cell has a single axis of alignment and confirmed the results of the earlier investigations. The direction of the magnetic moments in the (111) plane cannot be unambiguously assigned. Current evidence\textsuperscript{26,27} indicates the existence of three kinds of magnetic spin domains within each twin domain; the direction of the spin alignment being [\textit{\textit{il}0}], [\textit{10\textit{i}}] and [0\textit{i}1] for the spin domains in the [\textit{\textit{il}1}] twin domain.

NiO Structure Factor

If the equivalent positions of the 32 nickel and 32 oxygen atoms of the unit cell are substituted into the structure factor expression of Equation 8, the result for
the nuclear reflections is

$$F = 32(b_n e^{-Wn} + b_o e^{-Wo}),$$

for $h, k, l$ all even, and

$$h + k + l = 4m,$$  \hspace{1cm} (12)

or

$$F = 32(b_n e^{-Wn} - b_o e^{-Wo}),$$

for $h, k, l$ all even (but not zero), and

$$h + k + l = 4m - 2,$$  \hspace{1cm} (13)

and $F \equiv 0$ for all other cases. The subscripts $n$ and $o$ refer to the nickel and oxygen atoms and $m$ is a positive or negative integer. The structure factor for the magnetic reflections becomes

$$F = 32 p q e^{-Wn},$$

for $h, k, l$ all odd, and

$$h - k, h - l, l - k = 4n,$$  \hspace{1cm} (14)

with $n$ a positive or negative integer, and $F \equiv 0$ for all other cases. The nuclear reflections occurring with the
The structure factor of Equation 12 are the so-called sum reflections and those of Equation 13 the difference reflections of the face centered cubic lattice with the usual Miller indices multiplied by 2 because of the larger cell. The conditions to be fulfilled by the Miller indices for a magnetic reflection (Equation 14) are to be interpreted for an untwinned crystal and therefore only $1/4$ of all possible combinations of odd indices are allowed. However, when all four kinds of twins are present in the crystal, all reflections with odd indices will be observed with strengths dependent upon the volume occupied by each twin. In this connection, it is convenient to label the domains as (111), (111), (111) and (111) domains which occupy fractional volumes $\mathcal{V}_1$, $\mathcal{V}_2$, $\mathcal{V}_3$, and $\mathcal{V}_4$, respectively, and where the $\mathcal{V}_1$ domains have the [111] as their unique rhombohedral axis, $\mathcal{V}_2$ domains the [111] and so on. The presence of these twins will effectively reduce the volume of the crystal for a given magnetic reflection. The effective volume to be used in the expression for integrated intensity (Equation 5) will be

$$v_1 = \mathcal{V}_1 v.$$  

The absorption correction volume integral will still be over the physical crystal volume since it is assumed that these twins are randomly distributed in the volume.
The selection rules given in Equation 14 for the Miller indices apply to (111) domain type reflections but may be modified for the three other domain types by replacing the appropriate index by its negative.

The evaluation of the $q^2$ factor will depend on the precise direction of the magnetic axis within a given twin domain. If $\mathbf{K}$ is a vector describing the alignment direction of the spins lying in the (111) plane, then

$$ q^2 = \frac{\sin^2 \alpha}{\sin^2 \beta + \cos^2 \beta \sin^2 \phi}, $$

in which $\alpha$ is the previously described angle; $\beta$ the angle from the reflecting plane's normal, $[hkl]$, to the (111) plane, and $\phi$ is the azimuthal angle, measured in the (111) plane, of $[hkl]$ with respect to $\mathbf{K}$. If the spin domains possess random orientations of $\mathbf{K}$, the total $q^2$ for the crystal must be averaged over all directions in the (111) plane. For this case

$$ q^2 = 1 - \frac{\cos^2 \beta}{2}, $$

or

$$ q^2 = \frac{1/2 + (h + k + l)^2}{6 (h^2 + k^2 + l^2)}, \quad (15) $$

in terms of the Miller indices of a reflection. These same expressions will also hold in the case of equally populated 3-fold symmetric spin domains previously discussed.
CHAPTER IV
ANALYSIS OF DATA

Introduction

The NiO crystal used for this study was kindly supplied by Dr. Y. Nakazumi (Tochigi Chemical Industrial Company Limited, Osaka, Japan) who grew the crystal by a flame fusion method described in the literature.

Preliminary diffraction measurements were performed on the crystal to determine an appropriate size and shape to which the crystal could be reduced so as to avoid large extinction effects for the nuclear reflections and yet give appreciable intensities for the weaker magnetic reflections. The crystal was then ground and polished to a rectangular parallelepiped, 8.8mm x 7.4mm x 2.0mm in size, with the crystallographic directions shown in Figure 13.

In the following, reference to the integrated reflection of (hkl) will be used to denote the experimental value obtained from

\[ P = \sum_{1}^{n} C(\theta_1) - n\bar{E}, \]

(16)
Figure 13

The dimensions of the NiO crystal and the normals, \( h \), [011], and [011] to the crystal faces are shown. The cube axes \( k \) and \( l \) lie 45° above and below the [011] in the plane defined by the \( h \) axis.
wherein \( C(\theta_1) \) is the counting rate in units of neutrons/\( 64^2 \) monitor counts observed at a crystal setting \( \theta_1 \) which falls within the diffraction peak, \( n \) is the total number of such observations equally spaced in \( \theta \), and \( \overline{B} \) is the average background counting rate under the peak.

**Absorption and Extinction Correction**

The evaluation of the volume integral for the absorption correction (Equation 6) was accomplished by deriving closed form expressions for the various types of reflections and programming the IBM 704 computer at the Ohio State University Numerical Computation Laboratory to calculate the absorption factor for each observed reflection.

In the derivation of the integrated reflection (Equation 5) the usual assumption made is that within the volume of the crystal the attenuation of the beam is entirely due to absorption. At a Bragg reflection position there are two processes, additional to the linear absorption already discussed, which decrease the diffracted beam intensity. These are called primary and secondary extinction.\(^{14}\)

Primary extinction arises when the mosaic blocks are large enough to appreciably attenuate the beam due to reflection in a single block. The analysis of the data
for this kind of extinction is very difficult and fortunately this situation rarely occurs.

Even though the mosaic blocks are sufficiently small to avoid primary extinction, the intensity of the diffracted beam will be decreased as a result of attenuation by coherent scattering of the beam entering or leaving the crystal. This is secondary extinction and it can be shown\(^2\) that the attenuation of the incident and reflected beams is equivalent to increasing the linear absorption coefficient, \(\mu_0\), by a factor proportional to \(Q\), so that

\[
\mu = \mu_0 + gQ. \tag{17}
\]

The factor, \(g\), varies inversely with the mosaic spread and will be a constant for a given crystal if the mosaic blocks have an isotropic distribution of orientations.

The linear absorption coefficient \(\mu_0\) is readily determined by transmission measurements through a known thickness of crystal. For this crystal the observed value of \(\mu_0\) was 0.70 ± .01 cm\(^{-1}\).

The value of \(g\) was obtained from measurements of the same Bragg reflection in two different crystal orientations. The difference in intensities measured in this manner results from the different absorption paths,
since all other factors affecting the integrated intensity are unchanged. The ratio of the two integrated intensities is therefore

\[
\frac{P}{P'} = \frac{A}{A'}
\]

where the prime indicates a geometrically different crystal orientation. A and A' were then computed for various values of \( \mu \) and the value which gave the measured ratio was taken as the effective absorption coefficient of the reflection. Equation 17 then yielded a value for \( g \). Table 1 gives the results thus obtained.

### Table 1

<table>
<thead>
<tr>
<th>hkl</th>
<th>( \mu ) (cm(^{-1}))</th>
<th>( \mu - \mu_o ) (cm(^{-1}))</th>
<th>( 10^{-2}Q ) cm(^{-1})</th>
<th>( g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0.93 ± 0.05</td>
<td>0.23 ± 0.06</td>
<td>0.14</td>
<td>165 ± 40</td>
</tr>
<tr>
<td>222</td>
<td>0.98 ± 0.03</td>
<td>0.28 ± 0.04</td>
<td>0.18</td>
<td>155 ± 25</td>
</tr>
<tr>
<td>044</td>
<td>3.5 ± 0.1</td>
<td>2.8 ± 0.1</td>
<td>1.30</td>
<td>210 ± 5</td>
</tr>
<tr>
<td>444</td>
<td>4.0 ± 0.2</td>
<td>3.3 ± 0.2</td>
<td>1.08</td>
<td>300 ± 20</td>
</tr>
</tbody>
</table>
Unfortunately the ratio of absorption factors is rather insensitive to $\mu$, making it necessary to determine the intensity ratio with great accuracy. The (044) and (444) data show the limitation of this method of correcting for extinction when the $gQ$ term becomes comparable to or larger than $\mu_0$. The intensity measurements in this work are therefore restricted to reflections with $Q$ values equal to or less than those of the (111) and (222). This eliminates all nuclear sum reflections. A method developed by Hamilton\(^{30}\) would allow this restriction to be removed but requires a different computer program for the absorption calculation. The value, $g = 159$, obtained from the (111) and (222) measurements was adopted for this work.

Temperature Correction

The thermal vibration factor in the temperature correction term can be inferred from the diffracted intensities of a single peak measured at two temperatures. If $P_1$ and $P_2$ denote the integrated intensities at temperatures $T_1$ and $T_2$, the ratio of $P_1$ to $P_2$ is, by Equation 5, 7, 9, 12, and 13

$$\frac{P_1}{P_2} = \left( \frac{b e^{-B D} n + b e^{-B D} o}{b e^{-rBnD} + b o e^{-rBoD}} \right)^2,$$

where

$$D = \left( \frac{\sin \theta}{\lambda} \right)^2,$$
and $B_n$, $B_o$ and $rB_n$, $rB_o$ are the thermal vibration factors for the nickel and oxygen atoms at temperatures $T_1$ and $T_2$, respectively. The plus sign is used for nuclear sum reflections and the minus sign for the nuclear difference reflections. In this development it is assumed that the nickel and oxygen thermal vibrations have the same temperature dependence and that they have no large anisotropies. Any set of three intensity ratios will then be sufficient to determine the three parameters $B_n$, $B_o$, and $r$. However, since the variation of $P_1/P_2$ is small with respect to variation of $r$, the data were analyzed using the temperature variation of the thermal factor given by

$$r = \frac{B_n(T_2)}{B_n(T_1)} = \frac{B_o(T_2)}{B_o(T_1)},$$

$$= \frac{[\varphi(x_2)/x_2 + 1/4]}{[\varphi(x_1)/x_1 + 1/4]}, \quad (19)$$

as derived from Equation 10.

Measurements for NiO were made at $77^\circ K$ and $298^\circ K$ using the cryostat described in Chapter II. These measurements were mostly of nuclear difference reflections since these are most sensitive to the values of $B_n$ and $B_o$ in Equation 18. The results obtained by this method were
$B_n = 0.5 \pm 0.1 \times 10^{-16} \text{cm}^2$ and $B_o = 0.6 \pm 0.1 \times 10^{-16} \text{cm}^2$ with $r = 0.46(T_2<T_1)$. These values, when compared to the Debye-Waller values for $B_n$ and $B_o$ of $0.26 \times 10^{-16} \text{cm}^2$ and $0.95 \times 10^{-16} \text{cm}^2$ calculated by Equation 10, demonstrate the necessity of an experimental determination of the thermal vibration factors when the masses of the atoms involved are quite different.

Another evaluation of $B_n$ was made by examining two rather weak magnetic reflections, $(\bar{1}33)$ and $(333)$, at $77^\circ K$ and $298^\circ K$. For magnetic reflections Equation 18 reduces to

\[
\frac{P_1}{P_2} = M^2 \exp \left[ - (1 - r)B_n D \right],
\]

since $b_o$ is zero for magnetic reflections. $M$ is the ratio of the spontaneous sub-lattice magnetization at the two temperatures and was calculated to be 0.90 for a Brillouin function\textsuperscript{31} with $S = 1$ and $T_N = 520^\circ K$. With the Debye-Waller value of $r$ as previously used, the calculation gives $B_n = 0.4 \pm 0.2 \times 10^{-16} \text{cm}^2$.

Further discussion of the thermal vibration parameters will be presented in the section on nuclear calibration.
Coincident Reflections

It sometimes occurs, when scanning over a Bragg reflection, that the crystal is so oriented that conditions for another reflection (coincident reflection) are simultaneously satisfied. This situation can best be demonstrated with the aid of the reciprocal lattice as shown in Figure 14 (only a plane is represented here). In this figure, \( \mathbf{s}_0/\lambda \), drawn from point \( P \) to the reciprocal lattice origin, \( 0 \), defines the direction of the incident beam (\( \mathbf{s}_0 \) is a unit vector). The "sphere of reflection" is defined as the sphere with radius \( 1/\lambda \) centered on point \( P \) and has the significance that any reciprocal lattice point lying on the surface of this sphere corresponds to a Bragg reflection. In particular, the point \( M_1 \) will give rise to a reflection, \( R_1 \), in the direction of \( \mathbf{s} \) where \( \mathbf{s} \) is a unit vector. This is readily ascertained from the geometry and reciprocal lattice construction since

\[
|\mathbf{s}_0 - \mathbf{s}_1| / \lambda = |\mathbf{s}| / \lambda,
\]

reduces to

\[
2 \sin \theta / \lambda = 1/d_{hkl},
\]

which is the Bragg reflection condition for scattering at angle \( 2 \theta \), the angle of \( \mathbf{s} \) relative to \( \mathbf{s}_0 \).
Figure 14

Coincident Reflection Representation in
Reciprocal Lattice Space
As represented in Figure 14, a second point, $M_2$, lies on the sphere of reflection and corresponds to a reflection, $R_2$, which reflects neutrons along the path, $PM_2$. The usual effect of this situation on the integrated intensity of $R_1$ would be to decrease the observed intensity due to the increased extinction of the incident beam by the $R_2$ reflection. This will be labeled Process A.

It is also possible that the reflection represented by a vector drawn from $M_2$ to $M_1$ is allowed. (This may be determined by noting that a translation of the origin to $M_2$ will give the $M_2M_1$ vector Miller indices of $h_1 - h_2$, $k_1 - k_2$, $l_1 - l_2$.) If this reflection, $R_{21}$, is allowed the intensity of $R_1$ will be enhanced by reflection of the $R_2$ beam into the $R_1$. This will be denoted as Process B. If $R_{21}$ is allowed, then the inverse reflection, $R_{12}$, exists and will decrease the intensity of $R_1$ by scattering into $R_2$. This will be called Process C.

It is thus possible that the observed intensity of the $R_1$ reflection will be enhanced or diminished according to the relative strengths of the three unique reflections. It will be convenient to denote the strengths of these reflections by $Q(R_1)$, $Q(R_2)$, and $Q(R_{12})$, where $Q$ is defined in Equation 7. If the $R_{12}$ reflection is weak or forbidden, the resulting observed intensity will be lower than normal because of Process A. To judge the effects of Process B
and Process C upon the $R_1$ intensity it is important to note that Process B predominates over Process C whenever the double reflection into $R_1$ (via $R_2$ and $R_{21}$) is greater than the reflection out of $R_1$ (via $R_{12}$). Because $Q(R_{12}) = Q(R_{21})$, this will occur when $Q(R_1) < Q(R_2)$, and results in an enhanced $R_1$ intensity. On the other hand, Process C is predominant when $Q(R_2) < Q(R_1)$ and results in a diminution of the $R_1$ intensity. The magnitude of these two effects will vary with the strength of $R_{12}$ and also with the size of the inequality between $Q(R_1)$ and $Q(R_2)$. Process A will also be present in the two above cases and always affects the $R_1$ intensity in the same sense as does Process C.

In the preceding discussion no allowance has been made for the angular divergence and wavelength composition of the incident beam. The incident beam in Figure 14 should be drawn as a pencil of rays converging to the origin, $O$, from a region around the point $P$. A specific group of these rays is selected for reflection by $R_1$ and another group is selected for reflection by $R_2$. Only one ray will be common to both the $R_1$ and $R_2$ group and this is the one which is shown in Figure 14. Thus not all of the beam components reflected by $R_1$ are affected by the simultaneous $R_2$ reflection and therefore the net effect of any coincident reflection is smaller than the simple explanation indicates.
Due to the complexity of the processes occurring, quantitative analysis is not feasible and the practice is to avoid the problem by suitable selection of crystal orientation.

To determine if coincident reflections were present when an intensity measurement was made a computer program was compiled which would derive the indices of the interfering reflections from the input data of crystal orientation, indices of the reflection under observation, and the experimental constants. This program essentially calculates the angles which the incident and reflected beam make with the reflection planes of a possible coincident reflection, \((hkl)\). These two angles are then subtracted from the Bragg angle of \((hkl)\), and if either difference lies within a preset angular range, e.g., \(\pm 1.5\) degrees, the reflection is identified as a coincident reflection. Upper limits are set on the magnitude of \(h^2 + k^2 + l^2\) for the magnetic and nuclear reflections so that only reflections which have appreciable strengths are inspected for coincidence.

In the course of magnetic intensity measurements a marked intensity anomaly appeared in the \((73\overline{1})\) reflections as is demonstrated by the experimental data reproduced in Figure 15. The ratios of the integrated intensities of \((3\overline{1}7)\) to \((37\overline{1})\) to \((\overline{1}73)\) are 4:1.5:1. The other three reflections of the \((73\overline{1})\) set have intensities
Figure 15

Diffraction Curves of $\langle 3\bar{1}7 \rangle$
approximately equal to the (\(\bar{1}73\)). If an estimate is made of the form factor and the magnetic structure of Chapter III is assumed, the reflections of the \(\langle 73\bar{1} \rangle\) set should have equal intensities on the order of that observed for \((\bar{1}73)\). If the observed intensities resulted from an error in the assumed magnetic structure other sets of \(\langle hkl \rangle\) reflections would substantiate this fact. Since this was not observed, the effect in the \(\langle 73\bar{1} \rangle\) set was assumed to result from coincident reflections.

The results of the coincident reflection calculation for the \(\langle 73\bar{1} \rangle\) set showed that a \((111)\) \(R_2\) reflection was in a reflection position for both \((3\bar{1}7)\) and \((37\bar{1})\) with the \((408)\) and \((480)\) serving as \(R_{21}\) reflections. Since the \((111)\) reflection is a factor of 10 larger than the normal \(\langle 73\bar{1} \rangle\) reflections, the \((3\bar{1}7)\) and \((37\bar{1})\) should both be enriched by the Process B. As the plots of Figure 15 show, the \((3\bar{1}7)\) reflection exhibits a considerable enhancement, but the \((37\bar{1})\) is much less affected by the coincidence. This must be ascribed to a small misalignment of the crystal which partially destroys the coincidence of the \((37\bar{1})\) with the narrow \((111)\) reflection (as is evidenced by the asymmetry of \((37\bar{1})\) peak). Since the crystal settings to obtain the \((3\bar{1}7)\) and \((37\bar{1})\) reflections are symmetric with respect to \([111]\), exact alignment should equalize the two reflection curves with a result somewhere between the two.
Further study of this problem was made by mounting the crystal to rotate about a [311]. Rotation about this axis is the \( \phi \) rotation (Chapter I), with the zone axis being [011] at \( \phi = 0^\circ \) and the rotation being taken positive about the [311]. A sequence of integrated intensities were obtained for the relatively weak (311) from \( \phi = 0^\circ \) to \( 90^\circ \) in 1° steps. Smaller intervals were used in some regions. These integrated intensities are plotted in Figure 16, in which the gradual decrease of intensity with increasing \( \phi \) is caused by an increase in the effective absorption path length. The accuracy of the points is \( \pm 2 \) per cent. There are approximately 80 coincident reflections occurring through this range of \( \phi \), and many of them overlap. It is difficult to isolate the various coincident effects except the one occurring at \( 81^\circ \). This is another case in which Process C predominates and results from the (400) reflection reinforcing the (311) via the (111). The abruptness of the onset of coincidence as the crystal is rotated is demonstrated in Figure 17 which is a plot of the diffraction data taken in the vicinity of \( \phi = 81^\circ \).

The reason for the small effect of most coincident reflections is demonstrated by the (133) and (888) reflection as shown in Figure 18. Both reflections occur in the [011] zone and therefore can be observed with no reorientation of the crystal. No Process B or C is
Figure 16

$(3\bar{1}\bar{1})$ Coincident Reflection Study
311 INTENSITIES

INTEGRATED INTENSITY
(NEUTRONS + 16 / 642 MONITOR / 0.05°)

φ (DEGREES)

400 { COINCIDENCE

111
Figure 17

The $(3\overline{1}1)$ diffraction peaks in the vicinity of $\phi = 81^\circ$ are shown. The exact interference position of the $(400)-(111)$ double reflection is at $81.0^\circ$. The diffraction peak at $81.7^\circ$ is beyond the range of any coincident reflection effects.
INTENSITY (NEUTRONS / 65000 MONITOR)

3π DIFFRACTION PEAKS
Figure 18

The reduced intensity of the (888) diffraction peak caused by the simultaneous occurrence of the smaller (133) diffraction peak is demonstrated. The vector representation of the experimental situation shows the relative orientation of the incident neutron beam; the (133) normal, an; the (133) diffracted beam, a; the (888) normal, bn; and the (888) diffracted beam, b.
DIFFRACTION PEAKS
(888 AND 733)

INTENSITY (NEUTRONS/5x643 MONITOR)

RELATIVE θ (DEGREES)
expected, since the coupling reflection is the very weak (559) magnetic reflection. The effect of (133) on the (888) is small but evident by the dip in the (888) reflection curve. The effect of the (888) upon the (133) can not be seen, since as the (888) is rotated through its interference position, other coincident reflections are also occurring. However, it can be observed that the large angular width of high angle diffraction peaks will generally reduce the effect of coincidence upon the narrower diffraction peaks.

Since it is usual to make diffraction measurements by orienting the crystal in one convenient position, the coincident reflection effect, when not a large one, will go unnoticed. With the large wavelength spread and angular divergence of the beam used here, the frequency of occurrence of coincident reflection effects will be higher than in a case where the quality of the incident beam is much better. However, improving the quality of the beam (and thus reducing the intensity) would for practical purposes render the observation of weak magnetic reflections impossible. Coincident reflections are especially troublesome in the case of weak magnetic reflections since even a small fraction of a nuclear reflection added to the small magnetic intensity through a Process C will cause an appreciable error in the measured
intensity. The (317) reflection shown in Figure 15 clearly illustrates this effect.

Calculations were made for all of the measured reflections to determine if any coincident reflections were present. When a serious interference problem was indicated the intensity was remeasured using a different crystal orientation or using a crystallographically equivalent reflection.

**Nuclear Intensity Data**

The integrated intensity formula of Equation 5 can be evaluated for the magnetic reflections, except for the $p^2$ term occurring in $Q$, provided the incident neutron intensity $I_\circ$ is known. A determination of $I_\circ$ and the experimental integrated intensities would thus allow an evaluation of the absolute value of $p^2$ to be made. Since all of the parameters involved in the nuclear scattering formula are known, the nuclear intensity data can be used to evaluate the incident beam intensity. For the purpose of calibration it is convenient to define an instrumental constant, $C = P_\circ/QA$, for a diffraction peak of observed integrated intensity $P_\circ$. The constant $C$ is therefore proportional to $(I_\circ\cdot V)$ of Equation 5.

The integrated intensities of some selected nuclear peaks are shown in Table 2 along with the calculated absorption-extinction correction, $Q$ factors, and the
TABLE 2
NUCLEAR CALIBRATION DATA

<table>
<thead>
<tr>
<th>hkl (relative)</th>
<th>A ( \times 10^{-3}\text{cm}^{-1} )</th>
<th>Q₁ ( \times 10^6 )</th>
<th>C₁ ( \times 10^{-3}\text{cm}^{-1} )</th>
<th>Q₂ ( \times 10^6 )</th>
<th>C₂ ( \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>222 2380</td>
<td>0.71</td>
<td>1.81</td>
<td>1.31</td>
<td>1.85</td>
<td>1.29</td>
</tr>
<tr>
<td>622 1310</td>
<td>0.84</td>
<td>0.94</td>
<td>1.39</td>
<td>1.02</td>
<td>1.29</td>
</tr>
<tr>
<td>666 980</td>
<td>0.74</td>
<td>0.63</td>
<td>1.56</td>
<td>0.74</td>
<td>1.32</td>
</tr>
<tr>
<td>1022 990</td>
<td>0.82</td>
<td>0.63</td>
<td>1.57</td>
<td>0.74</td>
<td>1.33</td>
</tr>
<tr>
<td>1066 1020</td>
<td>0.76</td>
<td>0.62</td>
<td>1.65</td>
<td>0.79</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Mean 1.50
Mean 1.31
resulting calibration constant C. The $Q_1$ and $C_1$ columns are based on the thermal vibration parameters $B_n = 0.5 \times 10^{-16} \text{cm}^2$ and $B_0 = 0.6 \times 10^{-16} \text{cm}^2$ obtained from the low temperature measurements. As can be seen, the $C_1$ values systematically increase from the $C_1$ value of the (222) reflection to the $C_1$ value of (10,6,6). The values listed in the $Q_2$ and $C_2$ columns were arrived at by a trial and error process of adjusting the thermal vibration parameters. The values of $B_n$ and $B_0$ determined in this manner are $B_n = 0.5 \times 10^{-16} \text{cm}^2$ and $B_0 = 0.8 \times 10^{-16} \text{cm}^2$. These are the values adopted for analysis of the magnetic intensity data. The discrepancy in the magnitude of the oxygen thermal parameter is probably due to the assumption of equal temperature dependence for the nickel and oxygen thermal vibrations. It is important to note that the thermal correction term to be applied to the magnetic data depends only on the nickel vibration parameter which is found to be $0.5 \times 10^{-16} \text{cm}^2$ by either determination.

The calibration constant used is the average value of the $C_2$ column of Table 2; that is, $C = 1.31 \pm 0.07 \times 10^6 \text{ neutron-cm/64}^2 \text{ monitor (for 0.125}^\circ \text{ intervals in the numerical integration). This corresponds to } I_o = 3.5 \times 10^5 \text{ neutrons/cm}^2/\text{min which compares well with that estimated from the monitor counting rate and counter efficiency.}
Pertinent diffraction data for the NiO sample and constants of the diffractometer are collected in Table 3.

**Magnetic Intensity Data**

As was pointed out in Chapter III, the observed intensity of any magnetic reflection depends upon the fractional volume occupied by the twin domain which contributes to that reflection since only one domain contributes to a given magnetic reflection. A determination of the fractional domain volumes, \( \pi_1, \pi_2, \pi_3, \) and \( \pi_4 \), can be made by measuring the intensities of \((hkl), (\bar{h}k\bar{l}), (h\bar{k}l), \) and \((h\bar{k}\bar{l})\), correcting these intensities for absorption, and taking the corrected intensities as proportional to the fractional volume. The most accurate measurement made for the above terms was the data from the \{111\} reflections. These data yield the volumes \( \pi_1 = 0.41, \pi_2 = 0.33, \pi_3 = 0.13, \pi_4 = 0.13 \). The magnetic reflections reported in this chapter and used to derive the magnetic scattering cross section of the nickel ion are those arising from the largest domain volume, \( \pi_1 = 0.41 \). This domain will be referred to as the \( \{111\} \) domain and the selection rules for the Miller indices are those given in Equation 14.

The results of the \( \{111\} \) domain magnetic intensity measurements are summarized in Table 4. The absorption correction employed, the observed absolute scattering cross
### TABLE 3
CONSTANTS FOR THE NiO CRYSTAL

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Adopted Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant, $a_0$</td>
<td>$4.1745 \text{ Å (1)}$</td>
</tr>
<tr>
<td>Coherent scattering amplitude of nickel, $b_n$</td>
<td>$1.03 \times 10^{-12} \text{ cm (2)}$</td>
</tr>
<tr>
<td>Coherent scattering amplitude of oxygen, $b_o$</td>
<td>$0.58 \times 10^{-12} \text{ cm (2)}$</td>
</tr>
<tr>
<td>Spontaneous sub-lattice magnetization at 298°C, $M$</td>
<td>$0.90$</td>
</tr>
<tr>
<td>Neutron wavelength,</td>
<td>$1.112 \pm 0.002 \text{ Å}$</td>
</tr>
<tr>
<td>Linear absorption coefficient, $\mu_0$</td>
<td>$0.70 \pm 0.01 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>Nickel thermal vibration parameter, $B_n$</td>
<td>$0.5 \pm 0.1 \times 10^{-16} \text{ cm}^2$</td>
</tr>
<tr>
<td>Oxygen thermal vibration parameter, $B_o$</td>
<td>$0.8 \pm 0.1 \times 10^{-16} \text{ cm}^2$</td>
</tr>
<tr>
<td>Secondary extinction coefficient, $g$</td>
<td>$159 \pm 15$</td>
</tr>
<tr>
<td>Instrumental constant, $C$</td>
<td>$1.31 \pm 0.07 \times 10^6 \text{ neutron-cm/64}^2 \text{ monitor}$</td>
</tr>
</tbody>
</table>


(2) C. G. Shull and E. O. Wollan, Phys. Rev. 81, 527 (1951).
<table>
<thead>
<tr>
<th>hkl(1)</th>
<th>P (relative)</th>
<th>A</th>
<th>(p)^2 x10^-24cm^2</th>
<th>f (relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>1040</td>
<td>.75</td>
<td>.1739</td>
<td>17.9 ± .15</td>
</tr>
<tr>
<td>311</td>
<td>205</td>
<td>.65</td>
<td>.1491</td>
<td>16.6 ± .20</td>
</tr>
<tr>
<td>133</td>
<td>190</td>
<td>.68</td>
<td>.1250</td>
<td>15.2 ± .10</td>
</tr>
<tr>
<td>511</td>
<td>117</td>
<td>.65</td>
<td>.0770</td>
<td>11.9 ± .10</td>
</tr>
<tr>
<td>333</td>
<td>140</td>
<td>.76</td>
<td>.0714</td>
<td>11.5 ± .20</td>
</tr>
<tr>
<td>153</td>
<td>51</td>
<td>.64</td>
<td>.0657</td>
<td>11.0 ± .20</td>
</tr>
<tr>
<td>351*</td>
<td>74</td>
<td>.80</td>
<td>.0760</td>
<td>11.8 ± .10</td>
</tr>
<tr>
<td>533</td>
<td>51</td>
<td>.81</td>
<td>.0624</td>
<td>10.7 ± .10</td>
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<tr>
<td>711</td>
<td>32</td>
<td>.65</td>
<td>.0450</td>
<td>9.1 ± .20</td>
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<tr>
<td>155</td>
<td>47</td>
<td>.77</td>
<td>.0369</td>
<td>8.2 ± .10</td>
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<tr>
<td>355</td>
<td>20</td>
<td>.69</td>
<td>.0266</td>
<td>7.0 ± .20</td>
</tr>
<tr>
<td>731*</td>
<td>28</td>
<td>.74</td>
<td>.0304</td>
<td>7.5 ± .20</td>
</tr>
<tr>
<td>137*</td>
<td>32</td>
<td>.76</td>
<td>.0336</td>
<td>7.9 ± .20</td>
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<tr>
<td>733</td>
<td>24</td>
<td>.81</td>
<td>.0206</td>
<td>6.1 ± .10</td>
</tr>
<tr>
<td>555</td>
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<td>.70</td>
<td>.0140</td>
<td>4.6 ± .25</td>
</tr>
<tr>
<td>175</td>
<td>12</td>
<td>.85</td>
<td>.0163</td>
<td>5.5 ± .4</td>
</tr>
<tr>
<td>571</td>
<td>12</td>
<td>.82</td>
<td>.0190</td>
<td>5.9 ± .2</td>
</tr>
<tr>
<td>911</td>
<td>22</td>
<td>.90</td>
<td>.0233</td>
<td>6.6 ± .2</td>
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### TABLE 4—Continued

<table>
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<tr>
<th>hkl(1)</th>
<th>P (relative)</th>
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<th>$(p)^2 \times 10^{-24}$ cm²</th>
<th>f (relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>931*</td>
<td>15</td>
<td>.84</td>
<td>.0228</td>
<td>6.5 ± .2</td>
</tr>
<tr>
<td>193*</td>
<td>11</td>
<td>.82</td>
<td>.0174</td>
<td>5.6 ± .3</td>
</tr>
<tr>
<td>933</td>
<td>8</td>
<td>.80</td>
<td>.0152</td>
<td>5.3 ± .3</td>
</tr>
<tr>
<td>755</td>
<td>6</td>
<td>.70</td>
<td>.0130</td>
<td>4.9 ± .3</td>
</tr>
<tr>
<td>177</td>
<td>5.5</td>
<td>.83</td>
<td>.0065</td>
<td>3.5 ± .2</td>
</tr>
<tr>
<td>377</td>
<td>2.5</td>
<td>.82</td>
<td>.0026</td>
<td>2.2 ± .3</td>
</tr>
<tr>
<td>1111</td>
<td>7.1</td>
<td>.65</td>
<td>.0150</td>
<td>5.3 ± .2</td>
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<tr>
<td>577</td>
<td>1.8</td>
<td>.80</td>
<td>.0030</td>
<td>2.4 ± .3</td>
</tr>
<tr>
<td>1131</td>
<td>6.4</td>
<td>.78</td>
<td>.0098</td>
<td>4.3 ± .3</td>
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<td>1133</td>
<td>9.2</td>
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<td>4.8 ± .2</td>
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<td>&lt;2.0</td>
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<tr>
<td>1311</td>
<td>8.3</td>
<td>.65</td>
<td>.0152</td>
<td>5.3 ± .3</td>
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<tr>
<td>399</td>
<td>&lt;1.0</td>
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<td>&lt;.0001</td>
<td>&lt;1.5</td>
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<tr>
<td>1333</td>
<td>10</td>
<td>.71</td>
<td>.0212</td>
<td>6.2 ± .5</td>
</tr>
</tbody>
</table>

(1) Indices marked with an asterisk denote that the data is an average of the (hkl) and (hk) reflections. The h index is to be taken as the first two digits for hkl's of four digits.
section, \( p^2 \), and the resulting relative form factor value, \( f \), are given for each reflection. An absolute determination of \( f \) is not possible since the magnetic scattering amplitude for zero scattering angle is not known, \textit{a priori}. The indicated error of the \( f \) values are those resulting from the statistical uncertainty of the measurements except in the cases of (111) and (311) in which there is an additional error due to extinction correction.

The relative form factor values are plotted against \( \sin \theta / \lambda \) in Figure 19. For the purpose of comparison a smooth curve based on a free ion Hartree-Fock calculation for the spin magnetic 3d electron form factor\(^{32} \) is also shown. The intercept at \( \sin \theta / \lambda \) is adjusted to fit the experimental points for small values of \( \sin \theta / \lambda \), and an arbitrary expansion of 1.25 is applied to the \( \sin \theta / \lambda \) values of the free ion calculation in order to give a more reasonable representation to the data at large \( \sin \theta / \lambda \). It is clear that the experimental points cannot be fitted with a monotonic isotropic form factor function. The anisotropic magnetic scattering will now be related to a nonspherical electron distribution about the \( \text{Ni}^{++} \) ion.
Figure 19

Magnetic Form Factor
FORM FACTOR (ARBITRARY UNITS)
CHAPTER V

INTERPRETATION OF DATA

It can be shown (cf. Appendix I) that the measured form factor of an (hkl) reflection is related to the projection of the ion's electron density onto the [hkl] direction by

\[ f(k) = \int_{-\infty}^{\infty} L(z) \sin(kz) \, dz, \tag{21} \]

where \( k = \frac{4\pi \sin \theta}{\lambda} \), \( z \) is an axis parallel to [hkl] and through the lattice site of the ion, and \( L(z) \) is the electron density projected onto the \( z \) axis. Thus, for a given value of \( k \), or \( \sin \theta / \lambda \), the form factors, \( f_1(k) \) and \( f_2(k) \), observed for the reflections, \((h_1k_1l_1)\) and \((h_2k_2l_2)\), occurring at the same scattering angle will be different if \( L(z_1) \) and \( L(z_2) \) are different. If \( L(z_1) \) falls off faster with increasing \( z \) than does \( L(z_2) \), \( L(z_1) \) will have higher values in the neighborhood of \( z = 0 \), and thus \( f_1(k) > f_2(k) \) by Equation 21. If \( f_1(k) \) is determined for several values of \( k \), corresponding to measurements of the \((nh_1,nk_1,nl_1)\) reflections, the resulting form factor curve
will lie above the \( f_2(k) \) curve determined from the 
\((n h_2, n k_2, n l_2)\) reflections. Both form factors will approach
the same values for small \( \sin \theta / \lambda \) values.

The experimental values of the \( \text{Ni}^{++} \) form factor
displayed in Figure 19 show that for given \( \sin \theta / \lambda \), the
\((h h h)\) reflections have the smallest \( f \)-values and that
reflections with normals close to a cube axis (e.g., \((711)\),
\((11,1,1)\) and \((13,1,1)\)) yield the highest form factor values.
These observations lead to the conclusion that the projected
electron density, \( L(z) \), is most condensed along the cube
axes and most extended along the body diagonals. This does
not mean, however, that the 3d orbitals of the nickel ion
are directed along the four \( \{111\} \) axes but on the contrary
that the extension of electron density is along the \( \{100\} 
\) or cube axes. This can be ascertained by noting the
properties of the function \( L(0) = \left( \frac{1}{\pi} \right) \int_{-\infty}^{\infty} f(k) \, dk \), which
is maximum for the reflections with the highest form factor
curve. If the extension of electron density were along the
\( \{111\} \) axes, \( L(0) \) would be nearly the same for the \( (h h h) \) and
the \( (h 0 0) \) reflections and greatest for the \( (h h 0) \), whereas
for a density extension along the \( \{100\} \) axes, \( L(0) \) is
greatest for the \( (h 0 0) \), least for the \( (h h h) \) and intermediate
for the \( (h h 0) \) planes as is the actual case. It is thus
concluded that the extension of magnetic electron density
is greatest along the directions of the cube axes. The
interpretation of this observation in terms of current theories of crystalline field and molecular orbitals is of immediate interest.

The electronic structure of free Ni\(^{++}\) in its ground state consists of an argon core plus 8-3d electrons and can be described as a \(^3P_4\) state \((S = 1, L = 3, J = 4)\). In the NiO crystal the Ni\(^{++}\) ion will be situated in an electric field which arises in the most part from the six nearest neighbor O\(^-\) ions. It has been shown that the spatial degeneracy of the orbital angular momentum of the ground state will be removed in this case by a crystalline Stark effect.\(^{33}\) The orbital motion is said to be quenched, i.e., the eigenvalues of the components of the angular momentum operators \(L_x\), \(L_y\), and \(L_z\), are zero. If this is the case, and the energy of the first excited orbital state is very large, the atomic magnetic moment of the Ni\(^{++}\) will result from the spin magnetic moment of the ion, and the neutron magnetic scattering amplitude will depend on the spin quantum number, \(S = 1\). If this value of \(S\) is substituted into the expression for the scattering amplitude, \(p\), given by Equation 4 and evaluated at \(\sin \theta/\lambda = 0\), i.e., \(f = 1\), the result, \(p_0 = 0.54 \times 10^{-12}\) cm\(^-1\), is obtained. Since \(f(k) = p(k)/p_0\), the individual form factor values could be evaluated from the measured absolute values of \(p\). For \(S = 1\), this results in unusually small values
of \( f \) near \( \sin \theta / \lambda = 0 \) (\( f(0.104) \approx 0.78 \)), and it is not possible to fit the low-angle data with a form factor curve similar in shape to the free ion curve shown in Figure 19. A value of \( S_{\text{eff}} \approx 0.8 \) is necessary if the low angle data is to be fitted with a reasonable curve. The implications of this will be discussed after consideration of the form factor asymmetry and expansion.

The 3d electron distribution of the Ni\(^{++} \) ion is modified from the free ion case by the crystalline field which splits the 3d shell into triply degenerate \( t_{2g} \) orbitals and doubly degenerate \( e_g \) orbitals.\(^{34,35} \) The \( t_{2g} \) orbitals have \( xy, xz, \) and \( yz \) symmetry (where \( x, y, \) and \( z \) refer to the cubic axes of the crystal) and the \( e_g \) orbitals have \( 3z^2-r^2 \) and \( x^2-y^2 \) symmetry. This means that the \( t_{2g} \) orbitals are directed along \( \{ hh0 \} \) axes and that the \( e_g \) orbitals are directed along \( \{ h00 \} \) axes. Thus the asymmetries which appear in the measured form factor will depend on which orbitals the magnetic electrons occupy. As was shown in the beginning of this chapter the form factor indicates that the \( \{ h00 \} \) are directions of maximum spin density extension. This means that more unpaired electron density is associated with the \( e_g \) orbitals and that the \( t_{2g} \) orbitals are more nearly filled with paired spins and must therefore have lower energy.

Watson and Freeman\(^{32} \) have recently calculated the form factor of Ni\(^{++} \) based on a free ion Hartree-Fock wave
function\textsuperscript{36} taking into consideration the $e_g$ and $t_{2g}$ symmetry required by the crystalline field. Their form factor for any reflection (hkl) can be expressed as

$$f = f + f_{AS},$$

(22)

with

$$f_{AS} = xf_e(h,k,l) + (1-x)f_t(h,k,l),$$

(23)

where $f$ is the average or spherically symmetric form factor, $f_{AS}$ is the correction applied to $f$ due to the anisotropy of the magnetic electron distribution in the crystal, and the $f_e(h,k,l)$ and $f_t(h,k,l)$ terms are the asymmetric form factors for unpaired electrons of type $e_g$ ($x = 1$), or for type $t_{2g}$ ($x = 0$), respectively. If the unpaired electron density of the ion is a mixture of $e_g$ and $t_{2g}$ electrons, $x$ will have a value between 1 and 0 equal to the fractional occupation of the $e_g$ orbitals. The functional variation of the asymmetric terms is given by

$$f_e(h,k,l) = -A(h,k,l) \langle j_4 \rangle,$$

$$f_t(h,k,l) = (3/2) A(h,k,l) \langle j_4 \rangle,$$

with

$$A(h,k,l) = \frac{h^4 + k^4 + l^4 - 3(h^2 k^2 + h^2 l^2 + k^2 l^2)}{(h^2 + k^2 + l^2)^2}.$$
for a cubic lattice. The factor $\langle j_\psi \rangle$ is an integral whose value is a function of $\sin \theta / \lambda$ and the radial wave function and is tabulated together with $\overline{F}$ in Reference 32. The $\langle j_\psi \rangle$ factor is zero at $\sin \theta / \lambda = 0$ and, for Ni$^{++}$, increases to a maximum of 0.091 at $\sin \theta / \lambda = 0.8$ and is equal in magnitude to $\overline{F}$ at $\sin \theta / \lambda = 0.65$. The $A(h,k,l)$ factor has values between $-2/3$ for (hhh) and 1.0 for (h00) and seldom has values smaller in absolute value than 0.2 for the reflections considered here. As can be seen from the above the $f_{AS}$ may be rewritten as

$$f_{AS} = [(3 - 5x) A(h,k,l) \langle j_\psi \rangle ]/2,$$

from which it is evident that the asymmetries cancel out for $x = 0.6$ and deviations from an isotropic form factor are more pronounced the further $x$ is from the value of 0.6.

For a fixed crystallographic direction the magnitude of the asymmetric term in the form factor increases with increasing $\sin \theta / \lambda$ and may be positive or negative depending upon the sign of $A(h,k,l)$. Thus the greatest deviations in the form factor will be observed for high angle reflections where the $\overline{F}$ has fallen off to a value comparable with the asymmetric term. Before proceeding further with the analysis of the form factor asymmetries, the effects of spin polarization and orbital angular momentum states will be considered.
As was mentioned previously with regard to Figure 19, the symmetric free ion form factor falls off much too rapidly with increasing sin $\theta / \lambda$ and a reasonable fit to the data requires a 25 per cent expansion of the sin $\theta / \lambda$ scale. This is equivalent to compressing the charge density of the ion by 20 per cent. A recent investigation has been made of the spin density contraction effects which could be expected when the Ni$^{++}$ ion is placed in a NiO crystal (i.e., the crystal field potential is introduced into the hamiltonian). This calculation shows that the Ni$^{++}$ energy is lowered by an expansion of the $t_{2g}$ orbits and a contraction of the $e_g$ orbits. This results in a slightly expanded average form factor, $\bar{f}$, for $e_g$ electrons. The effects of spin polarization are also treated in this calculation.

This effect is the result of the electron exchange interaction which occurs in an ion between electrons of the same spin. Within the argon core the electrons with positive spins interact with an attractive exchange force. This enhances the density of positive spins in the central region of electron distribution leaving a net negative spin density in the regions close to the nucleus and at large radii. The total spin in the argon core is of course zero; but at nonzero scattering angles gives a positive contribution to the magnetic scattering with a form factor expanded with respect to $\bar{f}$ of the free ion. There is also
a spin polarization of the same character for the 3d electrons. Watson and Freeman assume the $t_{2g}$ states to be of lower energy, and find that the distribution of positive spins in the $t_{2g}$ states are also contracted relative to the free ion case. The two electrons in the $e_g$ orbits are also contracted by the electron exchange. Thus all of the spin polarization effects effectively expand the form factor. Combining the effects of the crystalline field and spin polarization gives a form factor which is expanded from that of the free ion form factor by approximately 4 per cent (6 per cent at $\sin \theta / \lambda = 0.2$ and 3.5 per cent at $\sin \theta / \lambda = 0.6$).

Lov$^3$ has made paramagnetic resonance measurements of MgO doped with nickel. He finds there is an orbital contribution to the magnetic moment of Ni$^{++}$ in NiO as evidenced by the measured spectroscopic splitting factor, $g$, of 2.225. Resonance experiments on other divalent nickel compounds$^4$ with similar internal crystal fields also exhibit $g$-values of that order, between 2.2 and 2.3. Thus the magnetic moment of the ion contains an orbital contribution and one might expect the magnetic scattering to be greater than the spin only value and described by a $S_{\text{eff}} = 1.1$. As shown later, however, the value $S_{\text{eff}} = 0.83$ is more appropriate. The orbital moment produces an effective expansion of the form factor since the orbital magnetic moment produces a maximum magnetic field (and
hence neutron scattering) around \( r = 0 \). This expansion of the form factor has been treated by Blume.\(^{41}\) The results of this calculation for the symmetric form factor may be written as

\[
\overline{f} = (1/1 + a) (\overline{f}_S + a \overline{f}_{or}),
\]

where \( \overline{f}_S \) and \( \overline{f}_{or} \) are the symmetric form factors of the spin and orbital moments respectively and \( a = -(4 \lambda / \Delta) \), where \( \lambda \) is the spin-orbit coupling coefficient and \( \Delta \) is the energy separation of the Ni\(^{++} \) ground state and the first excited state. The asymmetric term becomes

\[
f_A = (1/1 + a) (f_{AS}),
\]

where \( f_{AS} \) is defined here as the asymmetric spin form factor given by Equation 23. There are orbital terms which are added to \( f_{AS} \) but are smaller by a factor of 100 than \( f_{AS} \) and completely negligible for Ni\(^{++} \). The total form factor is then

\[
f = \overline{f} + f_A.
\]

Blume has given the parameters which allow \( \overline{f}_{or} \) to be evaluated for Ni\(^{++} \). Using Blume’s results with \( \Delta = 8500 \text{cm}^{-1}, \lambda = -325 \text{cm}^{-1} \) for the free ion, together
with the Watson and Freeman spin polarized, crystal field calculation gives a net value of $f$ for Ni$^{2+}$ in NiO as shown in Figure 20. The free ion form factor is also shown to demonstrate the magnitude of the expansion. The points plotted in Figure 20 represent the best effort to obtain a symmetric form factor by subtracting appropriate asymmetric terms (Equation 25) from the observed form factors. To arrive at the data presented in Figure 20 the following procedure was employed: (1) adjust each $f_{obs}$ by a constant so that the first three points (111, 311, 133) fit the theoretical curve (this amounts to letting the $S_{eff}$ value be an undetermined parameter), (2) subtract from the observed form factors the calculated $f_A$, (3) determine the proper scale factor for $\sin \theta / \lambda$ to bring the adjusted theoretical curve into agreement with the data, and (4) iterate the above steps until suitable agreement between the points and curve resulted. In the second step it was necessary to vary $x$, the fractional occupation of the eg orbits by unpaired electrons. In connection with this fitting process it is convenient to define a reliability index given by

$$R = \frac{\sum |f_{obs} - f_{calc}|}{\sum |f_{calc}|}.$$
Figure 20

The experimental data and various calculated form factor curves are shown. The experimental points are corrected for e.g., symmetry and adjusted in absolute value to correspond to $S_{\text{eff}} = 0.83$. 
The final values obtained were $x = 1.0$, scaling factor equal to 14.5 per cent, and $S_{\text{eff}} = 0.83$. These values give a $R = 0.06$. For $x = 0.0$, $R = 0.13$, and the value of $x = 1.0$ is based on the fact that any admixture of $t_{2g}$ electrons increases the value of $R$. The adjusted form factor curve scaled by 14.5 per cent in $\sin \theta / \lambda$ is shown in Figure 20, and the deduced points are obtained using $S_{\text{eff}} = 0.83$.

The above calculations have several limitations, some of them noted by the authors, which should be mentioned here. The wave functions used to evaluate the $\tilde{F}$ term are the free ion wave functions whereas the more recent wave functions for $\text{Ni}^{++}$ in NiO should be used. Also the $f_{AS}$ have only been evaluated for the free ion case. On the latter point it can be noted that an insignificant adjustment of $f_{AS}$ could be made by applying a 1-2 per cent expansion to the $\langle j_4 \rangle$ values of Watson and Freeman. This may be justified by the fact that the $e_g \tilde{F}$ is expanded by that amount. However, since the expansion of $\langle j_4 \rangle$ will not have a large effect on the conclusions to be made, and since no precise knowledge of the true $e_g$ expansion is available, the $\langle j_4 \rangle$ factor was not adjusted in any way. A more serious limitation of the theoretical work is in the $\text{Ni}^{++}$ in NiO calculation in which an approximate point charge description of the crystalline field is used. The authors also point out that it is doubtful if
refinements in the crystalline field model would lead to better wave functions since attempts to improve calculations of crystalline field strengths have led to poor results\(^4\) and indicate that the crystalline field model of a localized ion is inadequate. Thus the spin polarized, crystal field calculation is not expected to predict the experimental situation for crystalline Ni\(^{++}\) but to give an idea of the effects to be expected.

Other neutron diffraction measurements of Ni\(^{++}\) form factors\(^4\) and the nickel metal form factor\(^4\) are in approximate agreement with this form factor expansion. The results of Alperin\(^4\) which can be directly compared to the present work yield a smaller expansion of 10 per cent compared to the 14.5 per cent found here.

Some efforts have been made to account for the excess expansion of the experimental form factor. A Fourier inversion was made of a \((f_{obs} - f_{calc})\) curve. The resulting radial spin density curve had maxima positioned as in the spin-polarized argon core\(^3\) but the radial density was a factor of 10 larger than that of Watson and Freeman. Because of the relation of h.f.s. coupling to the argon core polarization, it seems unlikely that the neutron scattering anomaly results from an enhanced argon core polarization. Some modifications of the Watson and Freeman 3d spin distribution were also tried. In this case the
The tail of the distribution curve was terminated at various radial distances and the inversion of the renormalized distribution made. For a termination of the distribution curve at 0.75 Å (corresponding to a 20 per cent reduction of total charge), the resulting form factor curve represented the data fairly well out to \( \sin \theta /\lambda = 0.5 \) but then was too low for points beyond \( \sin \theta /\lambda > 0.5 \).

Moriya has shown that when the crystal field splitting of the spin levels of the nickel ion ground state becomes comparable to the exchange interaction a reduction in the expectation value of \( S_z \) is expected. According to Moriya the expectation value of the \( z \) component of spin may be expressed as

\[
\langle S_z \rangle \approx \left[ 1 - (D/2JZ)^2 \right]^{1/2},
\]

where \( D \) is the electric field splitting of the spin levels, \( J \) the exchange interval, and \( Z \) the number of nearest neighbors. The value of \( 2JZ = 400 \text{cm}^{-1} \) may be estimated from the Neel temperature as per Van Vleck. The largest observed \( D \) for Ni\(^{++}\) is about \( 4 \text{cm}^{-1} \) and therefore \( D/2JZ \) is 50 times smaller than the value required to give \( S_{\text{eff}} = 0.83 \). Thus no reduction of \( S_{\text{eff}} \) can be accounted for with the above mechanism.

The value of \( S_{\text{eff}} = 0.83 \) determined from the scattering data may be compared to other neutron diffraction
determinations for the Ni\(^{++}\) ion in KNiF\(_3\), \(S_{\text{eff}} = 0.91\)\(^4\) and in NiO, \(S_{\text{eff}} = 0.8\)\(^4\)\(^9\) and \(S_{\text{eff}} = 0.9\)\(^2\)\(^3\). These values are in disagreement with the \(S_{\text{eff}} = 1.11\) implied by the previously mentioned g-value measurements. This apparent disagreement between the results of the two types of measurements has not been reconciled or seriously considered. The usual interpretation of the resonance measurements is that

\[
g = 2.0023 - 8\frac{\lambda}{\Delta},
\]

(27)

where 2.0023 is the free spin value of \(g\) and the second term is the orbital contribution arising from the admixture of the first excited state to the ground state via the spin orbit coupling.\(^5\)\(^0\) With \(g = 2.225\) and \(\Delta = 8500\text{cm}^{-1}\) the resulting value of \(\lambda\) is -238\(\text{cm}^{-1}\) compared to the free ion value of -325\(\text{cm}^{-1}\). This reduction of the bound ion corresponds to an expansion of the free ion charge density in the crystal and thus places the g-value measurements in further disagreement with the form factor measurements which indicate a contraction in the charge distribution.

A different interpretation of experimental g-values obtained in several hydrated transition element salts has been made by Owen.\(^5\)\(^1\) He assumes that the \(\lambda\)-value of the metal ion in a crystal is unchanged from its free ion value.
By extending the molecular orbital theory developed by Van Vleck\textsuperscript{52} and Stevens\textsuperscript{53} Owen finds

\[ g = 2.0023 - \alpha^2(8\lambda/\Delta), \]  

(28)

where \( \alpha \) is the fraction of cation wave function which is admixed to the \( eg \) wave functions of the metal ion. The admixture parameter has the significance that the \( eg \) electrons are fractionally associated \( \alpha^2 \) with the metal ion and \( (1 - \alpha^2) \) with the various equivalent cations. The reduction of the second term in Equation 28 is then due to \( \alpha^2 < 1 \) rather than to a reduction in \( \lambda \) by the crystalline field. The expression for \( S_{\text{eff}} \) for neutron scattering may be written

\[ S_{\text{eff}} = S_0 \alpha^2 g/2. \]

In this case, \( S_0 = 1 \) (free ion spin), \( S_{\text{eff}} = 0.83 \), and \( g = 2.225 \), so \( \alpha^2 = 0.75 \). This compares very well with \( \alpha^2 = 0.76 \), derived from the experimental values of \( g \) and using the free ion \( \lambda \).

It thus appears that Owen's covalent bonding treatment, which reconciles the free ion values of spin-orbit coupling with the measured \( g \)-values for magnetic energy level splitting, is confirmed by the neutron
scattering from NiO. It was therefore appropriate to use the free-ion value for \( \lambda \) in evaluating the orbital contribution to the form factor rather than the smaller value used by Blume.

Inasmuch as Watson and Freeman did not include any covalent terms in their wave functions in the crystalline field, the anomalous expansion of 14.5 per cent in the magnetic form factor is not altogether unexpected. On the contrary, the form factor expansion may be taken as additional evidence for the necessity of including covalent terms in the crystalline wave functions.
APPENDIX I

FORM FACTOR DEPENDENCE ON ELECTRON DENSITY

The general formula for the form factor of an atom may be expressed as

\[ f = \int \frac{U(x,y,z)e^{-i\mathbf{S} \cdot \mathbf{r}}}{V} \, dV, \quad (1) \]

in which \( \mathbf{S} = 2\pi/\lambda \), \( \mathbf{S} = \mathbf{s} - \mathbf{s}_0 \), with \( \mathbf{s}_0 \) and \( \mathbf{s} \) unit vectors in the direction of the incident and reflected beams, \( U(x,y,z) \) the density distribution of scattering matter, and \( \mathbf{r} \) the position vector to \( dV \) from the center of the atom. The volume integral includes all regions of non-zero \( U \). At the Bragg reflection position \( |\mathbf{S}| = 2 \sin \theta \) and the direction of \( \mathbf{S} \) is perpendicular to the reflecting plane. In this case

\[ \mathbf{S} \cdot \mathbf{r} = (2 \sin \theta) \, r \, \sin \beta, \]

where \( \beta \) is the angle between \( \mathbf{r} \) and \( \mathbf{S} \). Let \( z \) be an axis with origin at the center of the atom and parallel to \( \mathbf{S} \),
then \( r \sin \beta = z \) and

\[
f(k) = \int_{-X}^{X} \int_{-Y}^{Y} \int_{-Z}^{Z} U(x,y,z)e^{ikz} dx dy dz, \quad (2)
\]

with \( k = 4\pi \sin \theta / \lambda \). The right side of Equation 2 may now be reduced by performing the \( x \) and \( y \) integrations with the result

\[
f(k) = \int_{-Z}^{Z} L(z)e^{ikz} dz, \quad (3)
\]

in which \( L(z) \) is a function which describes the variation of the scattering density projected onto the \( z \) axis, i.e.,

\[
L(z) = \int_{-X}^{X} \int_{-Y}^{Y} U(x,y,z) dx dy.
\]

If the scattering density is symmetric with respect to the scattering plane, \( L(z) = L(-z) \), Equation 3 becomes

\[
f(k) = \int_{-\infty}^{\infty} L(z) \cos(kz) dz, \quad (4)
\]

in which the limits of integration have been set at \( \pm \infty \); this has no effect on the value of the integral. This equation defines the form factor of the reflections.
(nh,nk,nl) as a function of $\sin \theta / \lambda$ and in terms of the scattering density projected onto the z axis or [hkl] direction. Application of the Fourier Integral Theorem to Equation 4 gives

\[ L(z) = \frac{2}{\pi} \int_{0}^{\infty} f(k) \cos(kz) \, dk, \tag{5} \]

which relates the projected scattering density, L(z), to the experimental form factor function determined from a set of reflections (nh,nk,nl) which are perpendicular to the z axis.
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I, David Owen Murray, was born in Wellington, Ohio, October 20, 1932. I received my secondary-school education at Brighton, Ohio, and earned my Bachelor of Arts degree from Miami University in 1954. In 1954 I entered the graduate school of The Ohio State University, where I specialized in physics. While completing the requirements for the Doctor of Philosophy degree I held a teaching assistantship at the Department of Physics and Astronomy, a research assistantship under Professor R. A. Erickson, and was awarded a fellowship by Battelle Memorial Institute for the academic years of 1959-60 and 1960-61.