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A NEUTRON DIFFRACTION STUDY
OF COBALTOUS 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
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(Calcutta University)

The Ohio State University
1965

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PLEASE NOTE:
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CHAPTER I

INTRODUCTION

The scattering of neutrons by magnetic atoms, especially the coherent scattering by the ordered magnetic atoms, provides a very effective method of studying magnetic structure on an atomic scale. The scattering is due to the interaction of the neutron magnetic moment with the magnetic moment resulting from all the unpaired electrons in an atom (as in a transition series element). The scattered intensity depends on the spin quantum number of the scattering atom, a magnetic form factor arising out of the spatial distribution of unpaired electrons and also, in the case of coherent scattering, on the magnetization vector and magnetic lattice or sublattice structure. The information obtained by neutron diffraction on any or all of these may serve as the basis for a theoretical understanding and interpretation of magnetic phenomena such as ferromagnetism or antiferromagnetism. In this work, the properties of cobaltous oxide in its antiferromagnetic state have been studied by neutron diffraction with special emphasis on the magnetic form factor.
An antiferromagnetic substance is characterized by an antiparallel ordering of its atomic spins below a transition temperature, called the Neél temperature. In the simplest case, the atoms may be considered to lie on two sublattices whose spins are oppositely directed. The percentage saturation of the alignment of these spins is temperature dependent, and above Neél temperature this magnetic correlation is lost and the substance exhibits paramagnetism. At the Neél point the substance will usually show crystal lattice distortion, a specific heat anomaly, a susceptibility anomaly and other evidences of magnetic transition. Some of these anomalies have been observed as early as 1914.\textsuperscript{1,2} But the concept of antiferromagnetism was first proposed by Neél in 1932.\textsuperscript{3}

Theories on antiferromagnetism in transition element oxides account for the antiparallel alignment as being due to an indirect exchange interaction\textsuperscript{4,5,6} occurring between the two magnetic ions via an intervening oxygen ion. The electrons participating in the interaction are the magnetic electrons; that is, the unpaired electrons of the unfilled 3d shell. The distribution of these electrons in the crystal may provide important evidence as to the nature of the antiferromagnetic bond.

This distribution can be obtained experimentally through the determination of the magnetic form factor by neutron diffraction.
techniques. The spatial extension of the magnetic electron as a
distribution has dimensions comparable to the wavelength of thermal
neutrons and, as such, introduces an interference effect on the
diffracted neutron beam. Like the equivalent x-ray diffraction case
(except that only the magnetic electrons are involved here), the
scattered wave is built up from the contributions of the different
parts of the electron cloud--the contributions being in the same phase
in the forward direction and getting rapidly out of phase with increasing
scattering angle. The effect is a decrease of intensity with increasing
scattering angle. This is described by a magnetic form factor
(following the analogy of atomic form factor in x-ray) term in the
scattered intensity expression. The magnetic form factor is a function
of the magnetic electron density distribution, scattering angle (2θ),
and neutron wavelength (λ).

Reported in the following is an experiment in which the
integrated intensities of Bragg peaks for a single crystal of cobaltous
oxide are determined, and these data are utilized to find the magnetic
form factor of Co^{2+} as a function of the neutron scattering vector, 4π
sin θ/λ . These are compared with some recent calculations of the
form factor of Co^{2+}. 
CHAPTER II

EXPERIMENTAL ARRANGEMENT

II. 1. Neutron Source

The neutron source was the Battelle Research Reactor at West Jefferson, Ohio, which is a swimming pool type reactor, operating at a power of 2 megawatts and producing a thermal neutron flux of about $2 \times 10^{13}$ n/cm$^2$/sec in the reactor core. The beam tube from the core has its first 8 inches filled with graphite to reduce the fast neutron component of the flux. The beam is monochromatized by transmission reflection through a lead crystal suspended in crystal holder fitting inside a stainless steel tube loaded with shielding material. Details of beam port and external shielding for minimizing the background are described in the Master's thesis of R. E. Malenfant at The Ohio State University (1960).

II. 2. The Diffractometer

The diffractometer consisted of a crystal table and counter arm mounted for double axle rotation about a common vertical axis (Figure 1). Each of these motions is effected by rotating one of two
Figure 1

Photograph of the Diffraction Apparatus
360-tooth 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 two independent motors coupled to the worms through separate stepping motors. For a scan the table angle is set at \((\theta_B - \theta)\) and the counter angle at \(2(\theta_B - \theta)\), and the angular relation between the crystal planes and the counter is preserved throughout the scan.

II. 3. The Counters

The diffraction counter (Figure 1) was cylindrical, two inches in diameter and 10 inches long. This was filled with BF\(_3\) gas (96 percent B\(^{10}\)) at a pressure of 60 cm. and had more than 80 percent efficiency for thermal neutrons passing parallel to the axis. The counter shield consisted of borated paraffin in a box 13" x 13" x 20" long. A monitor counter 1 inch in diameter, with BF\(_3\) gas (11 percent B\(^{10}\)) at 20 cm. of Hg pressure and with an efficiency of 1-2 percent, was placed perpendicular to the incident neutron beam. The monitor readings served as the scale factor for comparing the intensity scans on different time spans.

The counters were basically alpha proportional counters, detecting the 2.3 mev alpha particles emitted by the high cross-section \((n,\alpha)\) reaction of B\(^{10}\).
II. 4. The Electronic Circuit

The signal from each counter passes through a cathode follower located at the base of the counters. The output from the monitor counter cathode follower goes directly to the monitor amplifier and that from the diffraction counter cathode follower goes by a two-stage preamplifier to a linear amplifier. The outputs of the two amplifiers go to the respective scalers. These different operations are coordinated by a diffractometer control panel—it starts, stops and resets the scaler, activates the printer, and starts and stops the motor drive which rotates the crystal table and the diffraction counter, all in desired sequence. This is accomplished by opening and closing the circuits through the use of a number of relays. The operation of the control system can be manual or automatic.

II. 5. Crystal Mount

The crystal was mounted on a thermoelectric cooler (see later) by means of two crossed spring aluminum clamps. The cooler itself was mounted on a G.E. Crystal Orienter (Figure 2) fixed to a cast aluminum holder so that the G.E. Orienter could have an oscillatory motion by means of a cam arrangement. The aluminum holder was rigidly fixed to the diffractometer table (Figure 3).
Figure 2

The crystal, the cooler and the crystal orienter are shown. The cooler is coaxial with the $\phi$-rotation dial which has a $360^\circ$ rotational motion. The $\gamma$ rotation is that associated with the large arc of the orienter and is shown here in its $0^\circ$ position.
Figure 3

Cast aluminum holder for the G.E. Orienter, rigidly fixed to the diffractometer table. Aluminum cap to the cooler in position.
The orien ter (Figure 2) has two rotational motions, a $\phi$ rotation of $360^\circ$ about the cooler axis and a $\gamma$ rotation of $90^\circ$ which puts the $\phi$-rotation axis at some angle relative to the horizontal plane. The $\phi$ and $\gamma$ rotations are used to bring any desired reflection into the zero-layer reciprocal lattice position with the scattering vector coincident with the horizontal axis of the orien ter. When this is done the oscillation of the entire orien ter about the horizontal axis keeps the required plane always vertical, but coincident reflections are arbitrarily rotated (see later).

At the beginning of an experiment, the centering of the crystal with respect to the neutron beam collimator axis was observed by a cathetometer. Then the crystal was centered within practicable limits to the axis of $\phi$-rotation by adjusting the aluminum clamps. The c-axis of the crystal was made coincident with this axis by noting the Bragg angle for (004) reflection at $\phi = 0^\circ$, $90^\circ$, $180^\circ$ and $270^\circ$, and adjusting the crystal until $\Delta \Theta$ for $\Delta \phi = \pi$ came within a practicable minimum ($\Delta \Theta = \pm 1.15^\circ$). Finally, a $\{111\}$ peak was studied to find the true zero for $\phi$.

II. 6. The Cooler

The cooler used was a commercial thermoelectric 2-stage cascade cooler manufactured by Jepson Company, Chicago, Illinois (Figure 2). This was made up from semiconducting couples, arranged
electrically in series. The couples consist of two kinds of bismuth telluride alloy—p-type and n-type. When current flows through the device so that electrons in the n-type material and holes in the p-type material both flow away from the same junction, energy is carried away from the junction in both materials and it is cooled. Several stages of units like this may be put in cascade, a large stage used as a heat sink to a smaller stage, to achieve lower temperature. The one used in the experiment had two stages. The minimum temperature attainable in vacuum (produced by covering the cooler by an aluminum cap (Figure 3) and evacuating) was $-62^\circ C$. With the modification of the tip to hold crystal clamp, the lowest attainable temperature was $-45^\circ C$. Figure 4 shows the current-temperature characteristics of the cooler.

A diode-rectifier bridge was used to supply current to the cooler. The ripples on the d.c. produced small fluctuations in temperatures ($\pm 0.25^\circ C$). But a study of the temperature variation of intensities showed that the corresponding error was well below the overall experimental error limit. The temperature was measured by a copper-constantan thermocouple, and the record of the temperature during the scan was observed with a recording potentiometer (Figure 5).

A vacuum cryostat was used to obtain very low temperature diffraction data. Before assembling the cryostat for an experiment
Figure 4

The current-temperature characteristics of the cooler.

The parameters in mm of Hg are the pressures inside the aluminum cap.
Figure 5

A typical temperature record during a scan.
the crystal holder with the crystal in position was mounted on the inner shield of the cryostat and the crystal was aligned with respect to the rotation axis of the crystal holder. The crystal and shield were then mounted on the cryostat.
CHAPTER III

NEUTRON DIFFRACTION FROM COBALTOUS OXIDE: THEORY

III. 1. Nuclear and Magnetic Scattering

In the case of neutron scattering, the main scattering interaction from most atoms is through the nucleus. The interaction with the nucleus involves specific nuclear forces not well understood, and so the nuclear scattering amplitude must be measured for each isotope. However, within a factor of two or three most nuclei have almost equal scattering amplitudes. Nuclear scattering is generally isotropic because of the high localization of the nuclear matter with respect to the neutron wavelength. Consequently, the nuclear form factor for neutron scattering is a straight line.

There is a direct neutron-electron interaction, but this is negligibly small compared with interactions of the neutron and atomic magnetic moments. In case of iron group elements, the magnetic moment is mostly due to spins, the orbital current is wholly or almost wholly quenched. According to Halpern and Johnson,
the differential scattering cross-section of an atom for such a case will be

\[ d = \left[ b^2 + p^2 q^2 \right] d\alpha \quad \ldots \ldots \ldots (1) \]

if the incident neutron beam is unpolarized. Here \( b \) is the nuclear scattering amplitude; \( q \) is a geometric factor to describe the coherent scattering from a system of aligned magnetic moments in a crystal lattice--\( q \) is defined by the vector

\[ q = \hat{\epsilon} (\hat{\epsilon} \cdot \hat{K}) - \hat{K} \quad \ldots \ldots \ldots (2) \]

where \( \hat{K} \) is a unit vector in the direction of the atomic magnetic moment and \( \hat{\epsilon} \) is the unit scattering vector. \( p \) is the coherent magnetic scattering amplitude, defined by the equation

\[ p = \frac{e^2 \gamma}{mc^2} f S_{\text{eff}} \quad \ldots \ldots \ldots (3) \]

where \( \gamma \) is the neutron magnetic moment in nuclear magnetons, \( e \) and \( m \) are the electron charge and mass, \( c \) the velocity of light. \( S_{\text{eff}} \) is the effective electron spin of the atom, \( f \) is the relative magnetic form factor defined by the equation

\[ f = \left\langle B \left| \sum_{1} \exp \left( i(k - k') \cdot r_l \right) \frac{S_l \cdot S}{S(S+1)} \right| B \right\rangle \quad (4) \]
where \( \mathcal{B} \) is the totality of atomic quantum numbers except the spin quantum number, \( k \) and \( k' \), incident and diffracted neutron propagation vector, \( \mathbf{S}_1 \), the spin of the \( l \)-th electron, \( \mathbf{S} \) the neutron spin, and \( \mathbf{r}_1 \) the position vector of the \( l \)-th electron.

For a spherically symmetric charge distribution, equation (4) becomes

\[
 f(k) = \int_{0}^{\infty} U(r') \frac{\sin Kr'}{Kr'} \, dr' \quad \ldots \ldots \quad (5)
\]

where \( U(r') \) is the radial distribution of electron number density, \( r' \) the radial distance from the nucleus, and \( K \) is equal to \( 4\pi \sin \theta /\lambda \), \( \lambda \) the neutron wavelength. The form factor, as shown in equation (5), is maximum for forward scattering \((\theta = 0)\) where it has a value equal to unity. For a more general case, where

\[
 \gamma_i = \left[ \frac{R_i(r)}{r} \right] \bigotimes_{l_i}^{m_i} (\cos \theta) \, \hat{\phi} \, m_i (\phi) \text{ and } K = k - k'
\]

is parallel to the atomic z-axis, the form factor for the \( i \)-th electron is given by

\[
 f_{ii} = \sum_n i^n (2n + 1) \, C^n (l_i m_i ; l_i m_i) \, <J_n> \quad \ldots \ldots \quad (6)
\]

where \( C^n(l_i m_i ; l_i m_i) \) are the integrals of the products of the three associated Legendre functions, and
\[ \langle J_n \rangle = \int_{-\infty}^{\infty} R_1^2 J_n (Kr) \, dr \quad \ldots \ldots \quad (7) \]

where \( J_n (Kr) \) are the spherical Bessel functions. \( \langle J_n \rangle \) is of course the \( f(k) \) in equation (5). For \( K \) having an arbitrary direction, the form factors in the new case are related to the form factors (6) by

\[ f'_{ii} = \sum_{ii} g_{ii} (\rho) \, f_{ii} \quad \ldots \ldots \quad (8) \]

where \( \rho \) is the angle between \( K \) and the \( z \)-axis of the atom.\(^{12} \)

The 3d-electron distribution of the \( M^{++} \) ions in the oxides of the iron group elements are 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.\(^ {13} \) Watson and Freeman\(^ {14} \) have calculated by modification of equation (8) the form factors of the \( M^{++} \) ions based on a free ion Hartree-Fock wave function taking into consideration the \( e_g \) and \( t_{2g} \) symmetry required by the crystalline field. Their form factor for any reflection \( (h \, k \, l) \) can be written as

\[ f = f + f_{AS} \quad \ldots \ldots \ldots \quad (9) \]

with

\[ f_{AS} = x f_e + (1 - x) f_t \quad \ldots \ldots \ldots \quad (10) \]
where \( f \) is the average or spherically symmetric form factor given by equation (5), \( f_{\text{AS}} \) is the correction applied to \( f \) due to the anisotropy of the magnetic electron distribution in the crystal, and the \( f_e \) and \( f_t \) terms are the asymmetric form factors for the unpaired electrons of the type \( e_g \) (\( \chi = 1 \)) or for type \( t_{2g} \) (\( \chi = 0 \)) respectively. If the unpaired electron density of the ion is a mixture of \( e_g \) and \( t_{2g} \) electrons, \( \chi \) 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

\[
f_e = -A(\rho, \vartheta) \, J_4 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (11)
\]

\[
f_t = \frac{3}{2} A(\rho, \vartheta) \, J_4 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (12)
\]

with

\[
A(\rho, \vartheta) = \frac{1}{8} \left( 35 \cos^4 \rho - 30 \cos^2 \rho + 3 + \frac{5}{8} \sin^4 \rho \, \cos 4\vartheta \right). \ldots (13)
\]

where \( \vartheta \) is the azimuthal angle of the scattering vector. In terms of the Miller indices \( h \, k \, l \),

\[
A(\rho, \vartheta) = \frac{h^4 + k^4 + l^4 - 3 (h^2k^2 + k^2l^2 + l^2h^2)}{(h^2 + k^2 + l^2)^2} \quad \ldots (14)
\]

The factor \( \langle J_4 \rangle \) in equations (11) and (12) is a special case of equation (7) and is tabulated in the Reference 14.
III. 2. Mosaic Crystal

The transition from the case of scattering of neutrons by a single atom to that of scattering by a lattice of atoms is treated in various publications; \(^{15, 16, 17, 18}\) it is parallel to the treatment given in textbooks on x-ray diffraction. \(^{19, 20}\)

The important quantity for scattering from an antiferromagnetic lattice is the effective intensity structure factor for the unit cell, defined as

\[
F_{hkl}^2 = \left| \sum b_r \exp(2\pi i(\bar{h}x/a_0 + \bar{k}y/b_0 + \bar{l}z/c_0)) \right|^2 e^{-2W} \ldots (15)
\]

where

\[
b_r^2 = b^2 + 2bpq \cdot \lambda + p^2q^2 \ldots \ldots \ldots (16)
\]

where \(\lambda\) is a unit vector in the direction of polarization of the incident neutron beam. For an unpolarized beam average \(\bar{q} \cdot \lambda = 0\) and \(F_{hkl}^2\) can be separated into

\[
F_{\text{nucl}}^2 = \left| \sum b \exp(2\pi i(\bar{h}x/a_0 + \bar{k}y/b_0 + \bar{l}z/c_0)) \right|^2 e^{-2W} \ldots (17)
\]

and

\[
F_{\text{mag}}^2 = \left| \sum pq \exp(2\pi i(\bar{h}x/a_0 + \bar{k}y/b_0 + \bar{l}z/c_0)) \right|^2 e^{-2W} \ldots (18)
\]
where \( b, p \) and \( q \) are the same quantities used in equation (1),
h, k, and \( l \) are the Miller indices for the reflection plane, \( a_0, b_0 \)
and \( c_0 \) are the crystal lattice constants. The sum is over the atoms in
the unit cell.

The exponential term \( e^{-W} \) is the Debye-Waller correction
for the effect of thermal vibration and is, for a monatomic cubic
crystal, \(^{16}\)

\[
W = B \left( \frac{\sin \theta}{\lambda} \right)^2 \quad \cdots \cdots \cdot (19)
\]

\[
B = \frac{6h^2}{MK\theta} \left( \frac{\phi(x)}{x} + \frac{1}{4} \right) \quad \cdots \cdots \cdot (20)
\]

where \( h \) is Planck's constant, \( K \) the Boltzmann constant, \( M \) 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

\[
\phi(x) = \frac{1}{x} \int_0^\infty \frac{\xi \, d\xi}{e^{\frac{\xi}{x} - 1}} \quad \cdots \cdots \cdot (21)
\]

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 these treatments fail, and the practice is to fit the
data by a suitable choice of $B$ of equation (19) for each atom.

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 are
additive.

For such a crystal the integrated power or the integrated
reflection, which is proportional to the area under a diffraction peak
plot of scattered intensity versus scattering angle (29), can be
expressed as

$$ P = I_0 Q V A \text{ (n/sec)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (22) $$

where $I_0$ is the power incident upon the crystal, $V$ is the volume of
the crystal, $A$ is the absorption and extinction correction term, and

$$ Q = \frac{\lambda^3 N c^2}{\sin 2\theta} (F_{\text{nucl}}^2 + F_{\text{mag}}^2) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (23) $$
with $N$ the number of unit cells per cm$^3$, $\lambda$ the neutron wavelength, 
$\theta$, the Bragg angle, and $F_{\text{nucl}}^2$ and $F_{\text{mag}}^2$ given by equations (17) and (18) respectively.

**III. 3. Structure and Structure Factor of CoO**

As equations (17), (18), (22) and (23) show, a knowledge of the structure of CoO is necessary for determination of the structure factors and vice versa. Complimentary evidences have been acquired in the last two decades leading to the understanding of the structure of CoO to a great extent.

The crystalline structure of CoO above its Néel temperature of $\approx 278^0K^{21,22,23}$ is face centered cubic (NaCl). At the Neel temperature it undergoes a sharp change from cubic to tetragonal symmetry,$^{24,25}$ and then the a/c ratio gradually increases with decreasing temperature.

The first measurement of the magnetic structure was obtained by Shull$^{25}$ from a powder sample, and showed that the magnetic unit cell dimension must be double that of the chemical unit cell. In the pseudocubic magnetic unit cell the 32 atomic moments are distributed among 8 magnetic sublattices paired to generate 4 antiferromagnetic submotifs. The magnetic structure problem is then to discover the structure of each submotif and the relationship of the submotifs to each other.
The simplest assumptions are that (1) the direction of the alternate spin of each submotif is antiparallel and (2) there is a single magnetic axis in the unit cell.

There are only two ways in which the four magnetic submotifs may be correlated in a single magnetic axis structure. We call the two models, A and B (Figure 6). The model A is characterized by the fact that the crystallographically unique (111) planes are ferromagnetic sheets and the alternate (111) planes have parallel and antiparallel arrangements of their spins.

For both models,

\[ F_{\text{nucl}} = 32 (b_c e^{-W_c} + b_o e^{-W_o}) \text{, for } h, k, l, \text{ all even and } h + k + l = 4n \]

\[ = 32 (b_c e^{-W_c} - b_o e^{-W_o}) \text{, for } h, k, l, \text{ all even and } h + k + l = 4n + 2 \]

\[ = 0 \text{, for all other cases} \]

The subscripts c and o refer to the cobalt and oxygen atoms, and n is a positive or negative integer or zero.

For Model A:

\[ F_{\text{mag}} = 32 pq e^{-W_c} \text{, for } h, k, l, \text{ all odd and } h-k, k-l \]

\[ 1-h = 4n, \text{ with } n \text{ a positive or negative integer or zero.} \]

\[ = 0 \text{, otherwise} \ldots \ldots (25) \]
Figure 6

Correlation of magnetic sublattices. These are the two possible correlations subject to the restriction that there is a single magnetic axis within the cell. The full circles represent the Co$^{++}$ ion with spin up and the open circles those with spin down. The diagonal sheet in model A contain only ions with spin up, but that in model B has both kinds of ions.
For Model B:

\[ F_{\text{mag}} = 16pq\epsilon \omega_{C}, \text{if } h, k, l \text{ are all odd} \]

\[ = 0, \text{ otherwise} \quad \ldots \ldots \quad (26) \]

It is evident that in a single crystal of this type, the nuclear and magnetic scattering are completely resolved.

III. 4. Effect of Domain Structure

The diffraction experiments done so far with Co0 were with powder specimens. In powder diffraction it is not possible to decide between the models A and B. This is evident from the diversity of the models suggested to explain earlier powder data. These results are summarized below, where the Miller indices in the bracket describe the spin direction.

<table>
<thead>
<tr>
<th>Shull et al.</th>
<th>Li</th>
<th>Roth</th>
<th>Kanamori</th>
<th>Nagamaiya and Motizuki</th>
</tr>
</thead>
<tbody>
<tr>
<td>or A [001]</td>
<td>or A [111]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>or C [100]</td>
<td>[010]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Over the above these, Roth showed that a number of multispin axis structures give results consistent with existing data. The problem of discriminating between the alternative spin arrangements can be solved by measuring the neutron scattering from a single domain single axis single crystal, since the distribution of intensity throughout the magnetic reciprocal lattice is quite different for various models.

The practical problem is that it is very difficult to grow single domain single crystals and for a multidomain crystal it is difficult to distinguish between a magnetic structure in which the magnetic moment directions are multiple within a unit cell and the one in which the multiple directions are produced by a domain structure. So long as theories and techniques in this area are not suitably developed, we have to assume a polydomain single magnetic axis structure, because it is simpler and usually crystals are polydomain. The information obtained from such a crystal is, however, more significant than that from powder specimen.

An antiferromagnetic domain may be defined as a region in a crystal in which the antiferromagnetic pattern of magnetic moments is triply periodic throughout the volume. For model B, antiferromagnetic domains result if there is a rotation of the direction of moments. This kind of domains we call S-domains. In model A, antiferromagnetic domains result either if there is a rotation of the
direction of moments within the ferromagnetic sheet (S-domain) or if there is a change in the crystallographic orientation of the ferromagnetic sheets (which we call T-domains). So, if for a specimen, it could be ascertained whether only S-domains exist or both S- and T-domains simultaneously exist, this would be decisive evidence for a choice between models A and B. This point will be elaborated further during the analysis of the experimental data.

Once the nature (S- or T-) and types of the domains are determined, their effect on the intensity is taken care of by the modification of the terms Ω and V in equation (22). For S-domains, the quantity Ω is modified by changing the term q in equations (25) and (26) to \( \sum_i W_i q_i \), where \( q_i \) is the q-value for the i-th type of S-domain and \( W_i \) is the weight factor for volume of that type of domain, and the sum is over all the types of S-domain. For T-domains, the volume V is replaced by \( \pi_i V \), where \( \pi_i \) is the fractional volume of the type of T-domain which is effective in the particular reflection.

III. 5. Effects of Absorption and Extinction

In the absence of other attenuating effects, the effect of true absorption or the attenuation of the incident beam due to capture of neutrons by nuclei is introduced by the absorption correction term A
in equation (11), where \( A \) is given by

\[
A = \frac{1}{V} \int_{V} \exp\left(-\mu t\right) \, dv
\]  

(27)

where \( \mu \) is the linear absorption coefficient, and \( t \) is the total
absorption path for the neutrons arriving at \( dv \) and exiting thence
to the counter. But in addition to this linear absorption, there are
two other processes\(^{18,19}\) which decrease the diffracted beam
intensity. For a crystal of thickness considerably greater than 1000 A°,
the incident beam will be appreciably attenuated as a result of the process
of reflection by successive planes. This attenuation as compared with
the ideal uniform bathing of the whole crystal is called the primary
extinction. Usually a mosaic crystal can be considered to be ideally
imperfect; that is, the mosaic blocks are sufficiently small for only
a negligible amount of primary extinction to take place within them.
Another ground for neglecting the primary extinction is Hamilton's
proof\(^{29}\) that the primary extinction correction is least when the
reflection is purely nuclear or purely magnetic, which is true for the
present case.

The individual mosaic blocks reflect at slightly different angles
and the radiations reflected from them are not coherent. But at any
particular angular setting of the crystal the beam will eventually
reach mosaic blocks identical in orientation with the ones through which the beam traveled at the surface, and there will be attenuation by coherent scattering. This attenuation due to passing of the beam through different mosaic blocks at the same orientation is called the secondary extinction. The secondary extinction factor $E_S$ is defined as the ratio of the ideal intensity to the intensity under secondary extinction.

A numerical integration method was adopted to determine the combined effect of secondary extinction and absorption for individual Bragg reflections, and the correction factor so obtained, which was equivalent to the simultaneous use of $A$ of equation (27) and $E_S$ above, was utilized for the factor $A$ of equation (22).
CHAPTER IV

ANALYSIS OF EXPERIMENTAL DATA

IV. 1. The Crystal

The CoO crystal used for this study was kindly supplied by Dr. Y. Nakagumi of Tochigi Chemical Industrial Company, Osaka, Japan, who grew the crystal by a flame fusion method described in the literature.\(^1\)

As necessitated by the boundary conditions of the numerical integration method for absorption and extinction corrections, attempts were made to make the crystal spherical. Dummy experiments with methods used for making crystals spherical\(^2, 3\) suggested that there was a finite possibility of the crystal breaking up along a cleavage plane. So the crystal was cut and polished to an approximate cube, 6.01 mm x 6.03 mm x 6.06 mm in size, with crystallographic directions shown in Figure 7. The correction factors were applied with the assumption of the crystal as a pseudosphere, and then certain empirical corrections from the symmetry of the specimen were introduced to come as close to the reality as practicable.
Figure 7

The dimensions of the Co0 crystals and the normals to the crystal faces are shown with respect to the crystallographic axes.
IV. 2. Measurement of Integrated Power

In the following, reference to the integrated reflection of

(h k l) will be used to denote the experimental value obtained from

\[ P = \sum_{i=1}^{n} C(\theta_i) - \sum_{i=1}^{n} B_i(\theta_i) \] ........................(28)

where \( C(\theta_i) \) is the counting rate in units of neutrons per \( 1.7 \times 10^5 \) monitor counts observed at a crystal setting \( \theta_i \), which falls within the diffraction peak, \( n \) is the total number of such observations equally spaced in \( \theta \) (with the usual interval of \( 0.1^\circ \)), and \( B_i(\theta_i) \) is the background counting rate in units of \( 1.7 \times 10^5 \) neutrons in monitor at \( \theta_i \). The background count was usually obtained by dephasing the counter and the crystal. The monitor counts were variously preselected depending on the expected power of the peaks, increasing with decreasing power for better statistics, and finally all the data were scaled to monitor count \( 1.7 \times 10^5 \). The time interval for \( 1.7 \times 10^5 \) monitor count was between 75 and 80 sec. during the entire period of the experiment.

That the integrated power of the peaks obtained with different monitor counts compared correctly is evidenced from the equality of the integrated powers of the same (004)-peak obtained with different monitor counts, when scaled to the monitor count \( 1.7 \times 10^5 \). This is shown in Table 1.
### TABLE 1

LINEARITY OF INTEGRATED POWER AS A FUNCTION OF MONITOR COUNT

<table>
<thead>
<tr>
<th>h k l</th>
<th>Monitor Count</th>
<th>Integrated Power</th>
<th>Integrated Power Scaled to Monitor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.7 x 10^5</td>
</tr>
<tr>
<td>004</td>
<td>1 x 10^4</td>
<td>1 5 9 1 6</td>
<td>2 7 0 5 7 2</td>
</tr>
<tr>
<td></td>
<td>5 x 10^4</td>
<td>7 9 4 6 6</td>
<td>2 7 0 1 8 1</td>
</tr>
<tr>
<td></td>
<td>1.5 x 10^5</td>
<td>2 3 8 8 5 9</td>
<td>2 7 0 7 0 7</td>
</tr>
<tr>
<td></td>
<td>1.7 x 10^5</td>
<td>2 7 1 1 9 1</td>
<td>2 7 1 1 9 1</td>
</tr>
<tr>
<td></td>
<td>2.1 x 10^5</td>
<td>3 3 4 7 7 8</td>
<td>2 7 1 0 1 1</td>
</tr>
<tr>
<td></td>
<td>6.8 x 10^5</td>
<td>1 0 8 3 8 3 6</td>
<td>2 7 0 9 5 9</td>
</tr>
</tbody>
</table>

### IV. 3. Deviation from Monochromaticity of Incident Beam

The wavelength of the incident beam was determined from a preliminary experiment to be $\lambda = .9587 \pm .0084 \text{ A}^\circ$. However, there was a small component with half the wavelength of the main beam. The effect of this was to augment the integrated power of a Bragg peak (h k l) by the superposition of a small Bragg peak (2h 2k 2l) due to wavelength $\lambda/2$. The amount of this second order effect was found, by comparing the integrated powers of the two nuclear peaks.
(022) and (044), to be .3 percent, and each $(h \ k \ l)$ peak power was corrected by this factor of the intensity of the $(2h, 2k, 2l)$ peak.

IV. 4. The Coincident Reflection

It sometimes occurs, when scanning over a Bragg reflection, that the crystal is so oriented that conditions for a second or a number of other reflections are simultaneously satisfied. The presence of these coincident reflections modifies the power of the primary reflection.

The simplest case, when there is only one secondary reflection, is illustrated in Figure 8. Point 0 is the center of the Ewald sphere of reflection which passes through three reciprocal lattice points, $A$, $B$, and $C$. Unit vectors $\mathbf{S}_A$, $\mathbf{S}_B$ and $\mathbf{S}_C$ give the directions of the incident, primary and secondary beams respectively. If we designate the reflection processes by two subscripts, describing the direction of the incident and the reflected beam, the reciprocal lattice vector $\mathbf{V}_{BC}$ is associated with a reflection from the directions $\mathbf{S}_B$ to the direction $\mathbf{S}_C$. Now, each of the beams can be reflected into each of the other two directions, so that when three lattice points are on the sphere, there are six reflection processes to be taken into account.

Of these, the reflection $A \rightarrow C$ removes power from the incident beam, thereby decreasing the power available for transfer
Figure 8

The Ewald sphere and the coincident reflection representation in the reciprocal lattice space.
Sphere of reflection
in the $A \rightarrow B$ reflection; the process $B \rightarrow C$ directly removes the power from the primary reflected beam. These are the so-called "aufhellung" processes. These are opposed by the process $A \rightarrow C \rightarrow B$ which adds power to the primary beam. This increase in power of the primary reflection is called the "umweganregung" process. These effects, long known in x-ray diffraction studies, have recently been reported for energy-dependent neutron reflectivity experiments as well as for monochromatic neutron reflection experiments.

The problem of coincident reflection has hitherto been handled in two ways. Attempts have been made to index the coincident reflections with the corresponding angles of rotation from the primary peak around the diffraction vector and choose an orientation of the crystal to avoid the coincident reflection. Method of calculations for "umweganregung" peaks has been determined—but only for cases satisfying certain simplifying conditions. A computer program to determine whether major "aufhellung" reflections are present when an intensity measurement is made is available; but this holds true only for an idealized geometry. Improving the quality of the beam (and thus reducing the intensity) to approximate this geometry would render the observation of weak magnetic reflections impossible. In many cases the problem is made very complicated by the presence of
too many coincident peaks, leaving very little suitable orientation of the crystal (especially for comparatively broad peaks). Cole, Chambers and Dunn have found as many as 17 "umweganregung" peaks within every 30° of rotation of the crystal around the scattering vector.

The second way of handling the coincident reflection problem is to determine theoretically the intensity effect in a given primary reflection due to one or more secondary reflections. Here again the solutions have been obtained for special cases. The theories assume a flat plate sample, and have solutions for low secondary extinction and low absorption limits.

In view of these difficulties, a practical method was devised to meet the problem. A plot of the intensity of a Bragg peak against the angle of rotation, say θ, of the crystal around the scattering vector, would show a uniform background level, broken by peaks and troughs. The background level represents the true peak, the peaks being the "umweganregung" peaks and the troughs corresponding to the "aufhellung" processes. Compared with the height of the "background," the peaks and troughs are small in size. If, during an intensity measurement, the crystal rotates about the scattering vector, and sweeps several times over the entire range of θ, the effects of all the peaks and all the troughs will tend to cancel each
other, and the average intensity will come very close to the true intensity. For cases where there are few coincident peaks or where the "umweganregung" peaks are more or less equal to the "aufhellung" troughs in number and intensity, this averaging process will yield extremely good results. For a crystal with high symmetry, the rotation would have to cover only one symmetry cycle.

The validity of this averaging by rotation was put to test in an initial experiment with the CoO oxide crystal. The crystal was mounted to rotate about the c-axis. For the (004) peak this was the φ-rotation (Chapter III. 5). A sequence of integrated intensities was obtained for the (004) peak, φ = 343° to φ = 90° in 1° steps. These integrated intensities are plotted in Figure 9. The dip in intensity around φ = 45° is caused by the gradual increase of the effective absorption path length from φ = 0° to φ = 45° and then the gradual decrease of it. The small scale fluctuations are due to statistics as well as coincident reflections. In some cases the two causes overlap.

In the next step, the crystal was tuned at φ = 12° for (004) peak, and during the scanning it was oscillated around the scattering vector with an amplitude ± 28° and a frequency of 6 oscillations per minute. The integrated peak power compared with the average of peak powers obtained from the points in Figure 9 in the range φ = 12° ± 28°, as follows:
Figure 9

The integrated intensities of the (004) peak as a function of $\phi$ with the oscillator off.
INTEGRATED INTENSITY (NEUTRONS / 1.0 x 10^6 MONITOR / 0.1°)

(004) PEAK
Hence, the effect of the rotation or oscillation of the crystal about the scattering vector at each $\theta$-position of the crystal within a Bragg peak is to average over the peaks and troughs of the power versus $\varphi$ graph for the Bragg peak power at that $\theta$-position. Following the argument of the previous paragraph, this again closely approximates true peak power.

For close existence of peaks and troughs in the power versus $\varphi$ graph, the amplitude of oscillation is not important either for the averaging process or for getting the true peak power. This will be evident from Table 2. The equality of the powers in the same row but different columns shows the truth of the statement for the averaging process, and the equality of the powers in the same column confirms the method of getting the true power. The small dispersion in the same column is ascribed to absorption and that between the two columns to the non-uniformity of oscillation.

During the measurement of magnetic scattering, the crystal was oscillated about the scattering vector with a suitable amplitude (usually $16^\circ$) to correct for the coincidence reflection effect during each scan of the Bragg peaks. To achieve this, a special cast
TABLE 2

OSCILLATION AMPLITUDE EFFECT DATA

(Peak 004; Rest Position, $\phi = 12^\circ$;
Monitor Count, $1.7 \times 10^5$)

<table>
<thead>
<tr>
<th>Amplitude of Oscillation</th>
<th>Integrated Power With Oscillation During Scanning</th>
<th>Average Power of $\phi$ = Constant Peaks over Oscillation Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.5^\circ$</td>
<td>293310</td>
<td>289390</td>
</tr>
<tr>
<td>$12^\circ$</td>
<td>292493</td>
<td>288490</td>
</tr>
<tr>
<td>$16^\circ$</td>
<td>291610</td>
<td>287164</td>
</tr>
<tr>
<td>$20^\circ$</td>
<td>291941</td>
<td>286600</td>
</tr>
<tr>
<td>$24^\circ$</td>
<td>291833</td>
<td>285889</td>
</tr>
<tr>
<td>$28^\circ$</td>
<td>289632</td>
<td>285056</td>
</tr>
</tbody>
</table>
aluminum mount was built, as mentioned in Section III. 5. The G.E. Orienter was attached to a steel plate, which could rotate about a horizontal axis on a tapered roller bearing system fixed rigidly to the cast aluminum mount. A horizontal aluminum plate connected to the steel plate had, at its rear, a driving motor whose axis was connected to a cam system (Figure 3). When the motor was on, the steel and aluminum plates would oscillate due to the cam arrangement, with axis of the oscillatory arc horizontal. The amplitude of oscillation could be adjusted by the position of the cam screw. Before the scan of a Bragg peak, the Bragg plane was brought to a vertical position by $\phi$ and $\gamma$ rotations of the crystal in the G. E. Orienter. Thus, the scattering vector was brought along the rotation axis of the system. Then the oscillation serves as a sweep over the $\omega$-angles, and the corresponding power was the true peak power.

IV. 5. Absorption and Extinction Correction

The numerical integration method for the absorption and secondary extinction correction was adopted from Hamilton's treatment\textsuperscript{30} for a generalized surface. A Cartesian system is defined with an axis $n$ parallel to the incident beam and an axis $m$ parallel to the diffracted beam (the angle between them being $2\theta$, the scattering angle). Zachariassen's power equation\textsuperscript{42} is generalized and written
as a difference equation in this coordinate system:

\[ P_H(n,m) = P_H(n,m-1) \left[ 1 + \tau \Delta m \right] + P_O(n,m-1) \sigma \Delta m \]

\[ P_O(n,m) = P_O(n-1,m) \left[ 1 + \tau \Delta m \right] + P_H(n-1,m) \sigma \Delta m \]  \hspace{1cm} (29)

where \( P_H \) and \( P_O \) are the values of the power arriving at the parallelogram denoted by the point \((n,m)\) on a grid of mesh size \( \Delta n \times \Delta m \), \( \mu \) the linear coefficient of true absorption, \( \sigma = Q W(\theta) \), \( W(\theta) \) given in equation (32), \( Q = \frac{\lambda^2 N c^2 F^2}{\sin 2\theta} \), \( \tau = - (\mu + \sigma) \). Starting from the points of the grid near the incident boundary, the above equations are used in a machine program to determine the values of \( P_H \) and \( P_O \) at all points of the grid. If the values of \( P_H \) at the first points of the grid outside the exit boundary are denoted by \( P_H(a), P_H(b), \ldots P_H(k) \), the integrated intensity becomes

\[ R^0 = \int_{-\infty}^{+\infty} \frac{R(\Delta \theta)}{\Delta \theta} \Delta \theta / \int_{-\infty}^{+\infty} W(\Delta \theta) \, d(\Delta \theta) \] \hspace{1cm} (30)

where

\[ R(\Delta \theta) = \left[ \frac{P_H(a) + P_H(k)}{2} + \sum_{i=1}^{k-1} P_H(i) \right] \Delta n \sin 2\theta \] \hspace{1cm} (31)

For an ideally imperfect crystal it is generally assumed that \( W(\Delta \theta) \) is a Gaussian distribution function with standard deviation \( \eta \), termed the mosaic spread parameter. However, for convenience
a simpler form was adopted:

\[
W(\Delta \theta) = \frac{1}{2} r^3 \eta, \text{ if } |\Delta \theta| \leq \eta \sqrt{3} \tag{32}
\]

\[
= 0, \text{ if } |\Delta \theta| > \eta \sqrt{3}
\]

For such a distribution function, the integrated intensity is given simply by

\[
R^\theta = 2\eta \int 3 \left[ R(\Delta \theta) \right]_{\Delta \theta=0} \tag{33}
\]

\(R^\theta \Delta m\) gives the intensity over a disc of thickness \(\Delta m\).

Assuming the crystal as a pseudosphere the total intensity is

\[
I^\theta = \sum_r R^\theta (r) \Delta m \tag{34}
\]

The secondary extinction correction factor \(E_S\) is then given by

\[
E_S = \frac{I^\theta}{QVA} \tag{35}
\]

where \(Q, V,\) and \(A\) are defined in equation (22).

The detailed program to carry through these steps is given in Appendix A. Since a theoretical treatment for proper mesh size is extremely unwieldy and was not available in this particular case, an empirical estimation was decided, as is customary in such cases.
Initially, the value of $\eta$ was found out by selecting from a series of approximate $\eta$'s the one which gave the absorption factors for which the ratios of the integrated powers of the peaks (044), (444), and (222) agreed with the ratios of the experimental integrated power of the same peaks. $\eta$ found out this way was equal to 5 minutes. Then this $\eta$ was used back in the program with the $\eta$-generating section deleted to find out the extinction-absorption factor $E_\Sigma A_{\mu} = A$ for the different magnetic peaks. These factors are given in column 3 of Table 9.

A small empirical correction for deviation from sphericity was applied from the consideration of symmetry. The variation of integrated power of the (004) peak in Figure 9 shows that the effective absorption path length is a continuous, periodic function of $\phi$, at $\psi = 0$. It was also found that the integrated powers of the peaks in the same zone, which have same $\psi$ but different $\phi$'s symmetrically oriented about $\phi = 0^\circ$, or equivalent $\phi = 90^\circ$, $180^\circ$ and $270^\circ$, are equal. The peaks belonging to the same zone in Table 9 are to be noticed. This equality was found to be valid for all the zones studied. Conforming to the domain structure of CoO (see IV. 8) this could only be explained by assuming that the effective absorption path length has the same periodicity with respect to $\phi$ as evidenced in Figure 9. The possibility of a mirror image of the function about the horizontal axis is ruled
out by the fact that this would require the effective absorption path length to be equal at all \( \phi \)'s for \( \gamma = 45^\circ \), which is not supported by measurements from the crystal in that orientation. However, the effective path length as a function of \( \phi \) is not expected to be exactly the same as at \( \gamma = 0 \). The function at \( \gamma = 0 \) could only serve as a first approximation for correction at other \( \phi \)'s. A comparison of the powers of the (151) set and (115) set shows that there is a variation of effective absorption path length with \( \gamma \) also. But it was difficult to find even an approximate correction for that.

**IV. 6. Effect of Temperature: The Debye-Waller Correction**

The thermal vibration factor in the temperature correction term is usually determined from diffracted intensities of a single peak measured at two temperatures. If \( I_1 \) and \( I_2 \) denote the integrated power of a nuclear peak at temperatures \( T_1^\circ \) and \( T_2^\circ K \), the ratio of \( I_1 \) and \( I_2 \) is given by

\[
\frac{I_1}{I_2} = \left( \frac{b_c e^{-BcD} \pm b_0 e^{-B_0D}}{b_c e^{-rBcD} \pm b_0 e^{-rB_0D}} \right)^2
\]

where

\[
D = \left( \frac{\sin \theta}{\lambda} \right)^2
\]
and $B_c$, $B_o$, and $rB_c$, $rB_o$ are the thermal vibration factors for the cobalt 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. Any set of three intensity ratios will determine the parameters $r$, $B_c$ and $B_o$.

Measurements for CoO were made at $77^\circ$K and $297^\circ$K using the cryostat referred to in Chapter II. The nuclear peaks studied were $(222)$, $(444)$ and $(666)$. The experiment revealed a broadening in size and shifting in position of the peaks at $77^\circ$K relative to their respective size and position at $297^\circ$K. This was expected because of the usual tetragonal distortion of CoO lattice with decreasing temperatures. This phenomenon had been studied in detail with the $(111)$ peak. The half-width of the peak, which is a measure of its sharpness, was determined at various temperatures and was plotted against temperature (Figure 10). The graph shows that the line-width increases with the decrease of temperature—almost linearly in the initial stage and asymptotically to a saturation value at very low temperatures. This corresponds to the gradual increase in tetragonal distortion of the lattice with decreasing temperature. Using experimental values of the lattice parameters of CoO at $20^\circ$C and $-180^\circ$C, the change in the half-width of the peak between these two temperatures has been
Figure 10

Study of crystal distortion effect. The half-width of (111) peak versus temperature curve.
calculated to be $0.28^\circ$ which agrees quite well with the value $0.30^\circ$ obtained from the graph.

The $(666)$ peak at $77^\circ K$ (crystal in the cryostat) showed evidence of coincident reflections and hence its intensity value was not dependable. Since the direct determination of $r$, $B_c$ and $B_o$ with only the help of intensities of $(222)$ and $(444)$ was impossible, use was made of the B value of Ni (which is next to Co in periodic table) and $B_o$ in NiO as first approximations to $B_c$ and $B_o$ respectively. These values ($B_c = 0.5 \times 10^{-16} \text{ cm}^2$, $B_o = 0.6 \times 10^{-16} \text{ cm}^2$ and $r = 0.46$), when used in equation (36), gave $(I_1/I_2)^{1/2}$ within 1 percent of the experimental values for $(222)$ and $(444)$ and hence were considered quite suitable for the present purpose.

**IV. 7. Temperature Dependence of Spontaneous Magnetization:**

*The Néel Point*

The integrated power of the $\bar{1}11$ peak was plotted after Debye-Waller correction, as a function of temperature in $^\circ K$ and extrapolated to $0^\circ K$ to obtain $I_0$. Then $I/I_0$ was calculated and plotted again as a function of temperature in $^\circ K$ (Figure 11). This graph was compared with $B_{3/2}^2$ vs. $T$ graph, where $B_{3/2}$ is the Brillouin function$^{45}$ with $S = 3/2$. The agreement is not satisfactory. This may be partially understood by the fact that in CoO the orbital momentum is only partially quenched by the crystalline electric field. The spin value, $S = 3/2$,
Figure 11

$I/I_o$ for the ($\overline{111}$) peak as a function of temperature, compared with $B_{3/2}^2$ and $B_{1/2}^2$ as functions of temperature.
corresponds to the 'spin only' case, i.e., when the orbital momentum is completely quenched.

Abragam and Pryce\(^46\) have shown that the partially quenched orbital angular momentum of Co\(^{++}\) ion in a combined cubic and tetragonal electric field may be described by a pseudo-angular momentum \(L = 1\) belonging to a degenerate ground state. However, spin-orbit interaction and exchange interaction perturbation remove all the degeneracy except Kramers' degeneracy. The lowest state corresponds to \(J = \frac{1}{2}, M = \frac{1}{2}\) and may be written in the form

\[
\left| \frac{1}{2} \right> = a \left| \frac{3}{2}, -1 \right> + b \left| \frac{1}{2}, 0 \right> + c \left| -\frac{1}{2}, 1 \right> \ldots (38)
\]

where \(\left| \frac{3}{2}, -1 \right>\) means wavefunction of the state \(S_z = \frac{3}{2}, l_z = -1\.

Hence the 'effective spin' of the ground state may be considered as \(\frac{1}{2}\), and temperature variation of the spontaneous magnetization may be expected to follow a variation as \(B_{1/2}^2\). The \(B_{1/2}^2\) vs. temperature graph was also plotted in Figure 11. It is seen that the situation improves somewhat, but still remains unsatisfactory.

This suggests that the simple theories\(^47,48\) of spontaneous magnetization based on direct exchange are not adequate, and need modification by the inclusion of other effects, e.g., superexchange.

Table 3 shows the integrated power of \((111)\) peak at different temperatures as well as fractional intensities at these temperatures after Debye-Waller correction.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>77.3</td>
<td>173,902</td>
<td>1</td>
<td>265.4</td>
<td>78,009</td>
<td>.448</td>
</tr>
<tr>
<td>233.1</td>
<td>119,828</td>
<td>.689</td>
<td>269.4</td>
<td>70,133</td>
<td>.403</td>
</tr>
<tr>
<td>235.9</td>
<td>119,269</td>
<td>.685</td>
<td>273.3</td>
<td>62,565</td>
<td>.360</td>
</tr>
<tr>
<td>236.5</td>
<td>117,618</td>
<td>.676</td>
<td>278.4</td>
<td>50,909</td>
<td>.293</td>
</tr>
<tr>
<td>237.4</td>
<td>117,293</td>
<td>.674</td>
<td>279.5</td>
<td>48,866</td>
<td>.281</td>
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<tr>
<td>237.9</td>
<td>116,418</td>
<td>.669</td>
<td>284.8</td>
<td>34,712</td>
<td>.199</td>
</tr>
<tr>
<td>239.4</td>
<td>114,739</td>
<td>.659</td>
<td>288.2</td>
<td>23,871</td>
<td>.137</td>
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<tr>
<td>240.4</td>
<td>113,872</td>
<td>.654</td>
<td>290.4</td>
<td>16,128</td>
<td>.094</td>
</tr>
<tr>
<td>242.3</td>
<td>111,117</td>
<td>.639</td>
<td>291.7</td>
<td>9,128</td>
<td>.052</td>
</tr>
<tr>
<td>243.8</td>
<td>109,496</td>
<td>.629</td>
<td>293.4</td>
<td>6,680</td>
<td>.038</td>
</tr>
<tr>
<td>246.4</td>
<td>106,427</td>
<td>.612</td>
<td>295</td>
<td>4,269</td>
<td>.024</td>
</tr>
<tr>
<td>248.2</td>
<td>104,112</td>
<td>.598</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>251.7</td>
<td>99,663</td>
<td>.573</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>253.7</td>
<td>96,902</td>
<td>.557</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>256.1</td>
<td>91,511</td>
<td>.526</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>260.5</td>
<td>85,502</td>
<td>.491</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The experimental graph in Figure 11 was extrapolated to 
$I/I_0 = 0$ value, the intercept in the abscissa $T^0$ was $295^0 + 1^0$K. This is the magnetic transition temperature, or the Néel point.

Table 4 compares the $T_N$ of CoO obtained by the present method with $T_N$'s determined by other methods.

**TABLE 4**

**COMPARISON OF THE NÉEL POINT OF CoO OBTAINED BY DIFFERENT METHODS**

<table>
<thead>
<tr>
<th>Author</th>
<th>Method</th>
<th>Transition Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La Blanchatais$^{49}$</td>
<td>Susceptibility</td>
<td>292.2$^0$</td>
</tr>
<tr>
<td>Foex$^{50}$</td>
<td>Dilatation</td>
<td>292.2$^0$</td>
</tr>
<tr>
<td>Street &amp; Lewis$^{51}$</td>
<td>Young's Modulus</td>
<td>289.2$^0$</td>
</tr>
<tr>
<td>Fine$^{52}$</td>
<td>Young's Modulus</td>
<td>271$^0$</td>
</tr>
<tr>
<td>Trombe$^{53}$</td>
<td>Susceptibility</td>
<td>292$^0$</td>
</tr>
<tr>
<td>Greenwald$^{54}$</td>
<td>X-Rays</td>
<td>278$^0$-284$^0$</td>
</tr>
<tr>
<td>Bizette &amp; Assayag$^{55}$</td>
<td>Specific Heat</td>
<td>289.7$^0$</td>
</tr>
<tr>
<td>Present Work</td>
<td>Neutron Diffn.</td>
<td>295$^0 + 1^0$</td>
</tr>
</tbody>
</table>
IV. 8. Domain Structure of CoO: Submotif Relation:
Spin Direction

As discussed in article II. 4. CoO domain structure may be of the following kinds: for model B, only S-domains, and for model A, S- and T-domains. The most important interaction in CoO determining the spin-direction is the magnetostrictive interaction in the cubic field. The spin direction for minimum energy for this phenomenon is $[001]$, and the energy is minimized by a tetragonal contraction. In going from cubic to tetragonal symmetry, any of the axes $x$, $y$, $z$ have equal probability as the axis of contraction. By applying external influences along different axes, the weight of the probabilities along the axes may be altered. This process of change of symmetry gives rise to twinning, which may be considered as a special case of growth twinning. We may call it spin-twinning and refer to the corresponding domains as spin domains or S-domains.

There are three types of S-domains specified by the axes of contraction $[100]$, $[010]$ and $[001]$. The domains and their mirror planes may be described as follows:

<table>
<thead>
<tr>
<th>Domains</th>
<th>$S_{II} - S_{II}$</th>
<th>$S_{II} - S_{III}$</th>
<th>$S_{III} - S_{III}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin Axes</td>
<td>$[100], [010]$</td>
<td>$[100], [001]$</td>
<td>$[010], [001]$</td>
</tr>
<tr>
<td>Mirrors</td>
<td>$\bar{1}10$</td>
<td>$\bar{1}01$</td>
<td>$0\bar{1}1$</td>
</tr>
</tbody>
</table>

23, 24
In the case of NiO, the most important interaction determining the spin direction is the dipole-dipole interaction. The dipolar energy is minimized by a configuration in which the spins lie in (111) ferromagnetic sheets, with alternate sheets having opposite spin direction. The antiferromagnetic deformation is rhombohedral, with contraction along one of the $\langle 111 \rangle$ axes. Because this contraction may occur along any of the four equivalent directions in the parent cubic crystal, crystallographic twinning takes place, giving rise to what is called T-domains. There are four types of T-domains corresponding to the four contraction axes:\(^{56}\) $T_I - [111]$, $T_{II} - [\bar{1}11]$, $T_{III} - [\bar{1}1\bar{1}]$ and $T_{IV} - [1\bar{1}1]$. In $T_{II}$, $T_{III}$ and $T_{IV}$, the ferromagnetic sheet gets rotated from $(111)$ to $(\bar{1}11)$, $(\bar{1}1\bar{1})$ and $(1\bar{1}1)$ respectively.

In CoO, the dipolar interaction is very small compared to the magnetostrictive interaction and may be considered as a small perturbation to the Hamiltonian inclusive of the magnetostrictive term. In model B, this only tilts the spin-axis by $\pm 2^\circ$ from $[001]$ -direction.$^{57}$ In model A, a process similar to that in NiO will occur, but only as a second order effect. Hence in model A, there will be four T-domains along with the S-domains, but the fractional volumes of $T_I$, $T_{II}$, $T_{III}$ and $T_{IV}$ will be random.

The most general expression for modified $q^2$ in equations (25) and (26) is $\sum_\rho \alpha^\rho q^{2\rho}$, where $\alpha = 1$ to 4 corresponding to the four
T-domains and $\beta = 1$ to $3$ corresponding to the three $S$-domains.

This necessitates the experimental determination of twelve unknown coefficients $C^\alpha_\rho$.

To determine the coefficients $C^\alpha_\rho$ we write the equations (22), (23), (25) and (26) in the form

$$\frac{P \sin 2 \theta}{32^2 \times I_0 V A \lambda^3 N_c^2 p^2 e^{-2W}} = \text{Constant} \times P = P_c = \sum C^\alpha_\rho q^2_\rho \quad \ldots (39)$$

For model $B$ and $hhl$ peaks, this divides the twelve equations in three sets having four equivalent equations. Their forms are

$$P_c (hhl) = C_1 \frac{1^2 + h^2}{2h^2 + 1^2} + C_2 \frac{h^2 + 1^2}{2h^2 + 1^2} + C_3 \frac{2h^2}{2h^2 + 1^2} \quad \ldots (40)$$

and the other two sets obtained by the permutation of the indices.

The equations for model $A$ are also simplified because of the fact that the condition $h-k, k-1, 1-h = 4n$ in equation (25) in the domain with $(111)$ as the ferromagnetic sheet and its modified form in the other domains allow only certain specific peaks in each domain to have non-zero intensities. Hence the equation for $(hkl)$ have only
terms with $C^1_\beta$ coefficients, that for $(h \ k \ l)$ only those with $C^2_\beta$ coefficients and so on. The equations for model A and $(h \ h \ l)$ peaks are

$$P_c(h \ h \ l) = C^1_1 \frac{1^2 + h^2}{2h^2 + 1} + C^1_2 \frac{h^2 + 1^2}{2h^2 + 12} + C^1_3 \frac{2h^2}{2h^2 + 12} \ldots \ldots (41)$$

which with the other two permutations form the set for $T_\mathbb{I}$-domains.

The other three sets (for $T_\mathbb{II}$, $T_\mathbb{III}$ and $T_\mathbb{IV}$ domains) are obtained by replacing the superscript 1 by 2, 3 and 4 respectively.

Twelve $(\bar{1}1\bar{3})$ peak intensities were measured for complete solution of equations (40) and (41). The results are shown in Table 5.

### Table 5

**INTEGRATED POWERS OF $\{11\bar{3}\}$ PEAKS**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Temp. $^\circ$C</th>
<th>Integrated Power (Arbitrary Unit)</th>
<th>Peak</th>
<th>Temp. $^\circ$C</th>
<th>Integrated Power (Arbitrary Unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>311</td>
<td>-39.2</td>
<td>28,303</td>
<td>131</td>
<td>-39.4</td>
<td>27,502</td>
</tr>
<tr>
<td>311</td>
<td>-39.3</td>
<td>27,138</td>
<td>131</td>
<td>-39.2</td>
<td>27,422</td>
</tr>
<tr>
<td>311</td>
<td>-39.3</td>
<td>27,682</td>
<td>113</td>
<td>-39.2</td>
<td>23,666</td>
</tr>
<tr>
<td>311</td>
<td>-39.3</td>
<td>27,027</td>
<td>113</td>
<td>-39.4</td>
<td>23,166</td>
</tr>
<tr>
<td>131</td>
<td>-39.3</td>
<td>28,186</td>
<td>113</td>
<td>-39.4</td>
<td>23,382</td>
</tr>
<tr>
<td>131</td>
<td>-39.2</td>
<td>27,370</td>
<td>113</td>
<td>-39</td>
<td>23,486</td>
</tr>
</tbody>
</table>
The above values lead to the following solutions for \( C^\rho \)'s:

for model B, \( C_1 = C_2 = .29, C_3 = .42 \)

for model A, \( C_1^1 = C_2^1 = C_2^2 = C_2^3 = C_1^4 = C_2^4 = .29 \)

\[ C_3^1 = C_3^2 = C_3^3 = C_3^4 = .42 \]

The results clearly indicate the existence of two equal S-domains and a third S-domain of somewhat greater volume. They also suggest that if T-domains exist, they all are of equal volume. The latter result is surprising because the T-domains was expected to be random on account of the smallness of the dipolar interaction.

To probe this issue further, the \( \{111\} \) set was investigated. For model B, the four peaks in this set will have equal integrated intensities irrespective of the distribution of volume over the three S-domains. But, for the model A, the integrated intensity of each of these peaks will be proportional to the fractional volume of a particular type of T-domain. Table 6 shows the results of the measurements on the \( \{111\} \) peaks.

The equality of the integrated intensities will also lead us to the unreasonable conclusion of the equality of all the T-domain volumes in an A-model structure.

As a final check, the measurements of \( \{111\} \) and \( \{113\} \) sets were repeated after the temperature cycling of the crystal through
the Néel point in a condition free of external field effects. It was argued that the approximate equality of the $S$-domains will continue because of the nonexistence of the external field, but the $T$-domains, if they exist, will change in volume distribution according to the thermal inhomogeneity during each cooling process.

The observed intensity patterns of both the \{111\} and \{113\} sets remained unchanged by thermal cycling. The repeated equality of the $T$-domain results led to the conclusion that the model B describes the submotif relation in Co0.

A $\phi$-correction (see IV. 5) on the \{113\} brought the integrated intensities of the $(h\,h\,l)$ peaks to 91 percent of the integrated

---

TABLE 6

INTEGRATED POWERS OF \{111\} PEAKS

<table>
<thead>
<tr>
<th>Peak</th>
<th>Temperature °C</th>
<th>Integrated Power (Arbitrary Unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>-40.5</td>
<td>123792</td>
</tr>
<tr>
<td>111</td>
<td>-40.5</td>
<td>120859</td>
</tr>
<tr>
<td>111</td>
<td>-40.5</td>
<td>120462</td>
</tr>
<tr>
<td>111</td>
<td>-40.5</td>
<td>120694</td>
</tr>
</tbody>
</table>
intensities of the (1 h h) and (h 1 h) peaks and hence the fractional volume distribution of the domains to $C_1 = C_2 = .31$ and $C_3 = .38$. These were the values of $C$ used in the calculation of the form factor. The $q^2 = \sum C^2 \rho^2$ values for different peaks are shown in Table 9.

The above calculations were based on the assumption that the directions of the spin were along the crystal axes or very close to them as suggested by Kanamori. Roth assigned the direction [111] for the spin in CoO from his powder diffraction experiment. The results of Table 6 favor a [001] spin alignment assignment. With the spin directions along [111] there would not be equality of these [111] peaks even in the ideal case of all the domains in the model A being equal; they would break up, into two sets of one and three, the intensity of the latter set being only 70 percent of the intensity of the former. But Table 6 shows that the deviation at the worst is only three percent; hence the conclusion that the spin directions are along [100] [010] and [001] within a few percents, leading to Kanamori's assignment [001] [010] [100] $\pm 2^\circ$.

IV. 9. Determination of the Instrumental Constant

The integrated intensity $P$ in equation (22) can be evaluated for magnetic reflections, except for the $p^2$ term occurring in
Q (equations (23) and (26)), provided the incident intensity $I_0$ is known. A determination of $I_0$ 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.

Since $V$ in equation (23) is constant for our experiment, it would be convenient to define an instrumental constant $C = I_0V = P_0/QA$, for a diffraction peak of observed integrated intensity $P_0$. The nuclear peaks studied for the determination of $C$, were three nuclear sum reflections, (004), (044) and (444), and two nuclear difference peaks (222) and (666). The extinction-absorption factors $A$ were calculated using the mosaic spread parameter $\eta = 5$ minutes (see III. 5). The value of the instrumental constant arrived at was

$$C = 1.97 \pm 0.09 \times 10^8 \text{ neutron-cm}/1.7 \times 10^5 \text{ monitor}.$$ 

This corresponds to $I_0 = 2.6 \times 10^4 \text{ neutrons/cm}^2/\text{sec}$ which compares well with the other estimations made in this laboratory.

The validity of this value of $C$ can be demonstrated by calculating the crystal structure factors for the various nuclear peaks using $C$ and the experimental integrated intensities, and comparing them with theoretically determined structure factors, as shown in Table 7.
### TABLE 7

**COMPARISON OF EXPERIMENTAL AND THEORETICAL STRUCTURE FACTORS, $F_{\text{nuc}}^2$**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Integrated Intensity (Neutrons/1.7 x 10^5 Monitor/0.1°)</th>
<th>$F_{\text{nuc}}^2$ (10^{-24} cm^2)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.97 x 10^8</td>
<td>222 61761 .54 94.49 100.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>004</td>
<td>278817 .45 643.76 647.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>004</td>
<td>208447 .45 597.24 598.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>444</td>
<td>172304 .48 557.66 553.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>666</td>
<td>14894 .56 53.62 49.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**IV. 10. Constants for the CoO Crystal**

Pertinent diffraction data for the CoO crystal and the constants of the diffractometer are collected in the following table (Table 8).

**IV. 11. Magnetic Intensity Data**

Figure 12 shows a typical diffraction pattern of CoO. As mentioned earlier, the peaks are either purely nuclear or purely magnetic. The Miller indices of nuclear peaks are all even, and those of the magnetic peaks all odd.
TABLE 8
CONSTANTS FOR THE CoO CRYSTAL

<table>
<thead>
<tr>
<th>Quality</th>
<th>Adopted Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant (a_{\text{O}}), at 20°C</td>
<td>4.2495 Å^59</td>
</tr>
<tr>
<td>Lattice Constants, at -180°C (a_{\text{O}})</td>
<td>4.2552 Å^59</td>
</tr>
<tr>
<td></td>
<td>4.2058 Å^59</td>
</tr>
<tr>
<td>Coherent Scattering Amplitude of Cobalt, (b_{\text{C}})</td>
<td>.25 \times 10^{-12} cm^60</td>
</tr>
<tr>
<td>Coherent Scattering Amplitude of Oxygen, (b_{\text{O}})</td>
<td>.577 \times 10^{-12} cm^60</td>
</tr>
<tr>
<td>Neutron Wavelength</td>
<td>.9587 \pm .0084 Å^60</td>
</tr>
<tr>
<td>Linear Absorption Coefficient,</td>
<td>1.04 cm(^{-1})</td>
</tr>
<tr>
<td>Cobalt Thermal Vibration Parameter, (B_{\text{C}})</td>
<td>.5 \times 10^{-16} cm^2</td>
</tr>
<tr>
<td>Oxygen Thermal Vibration Parameter, (B_{\text{O}})</td>
<td>.6 \times 10^{-16} cm^2</td>
</tr>
<tr>
<td>Mosaic Spread Parameter,</td>
<td>5 minutes of angle</td>
</tr>
<tr>
<td>Instrumental Constant, (C)</td>
<td>1.97 \pm .09 \times 10^8 Neutrons- Cm/1.7 \times 10^5 Monitor</td>
</tr>
</tbody>
</table>

75
Figure 12

A typical neutron diffraction pattern of CoO.
DIFFRACTED INTENSITY (NEUTRONS / I \cdot 10^8 MONITOR)

COUNTER ANGLE - DEGREES

(222)
(333)
(444)
(555)
(666)
The lowest temperature attainable during the study of most of the magnetic peaks was between -36°C and -40°C. As is evident from Figure 11, the spontaneous sublattice magnetization at these temperatures is only partially saturated. Hence the integrated intensities of these peaks were corrected to the complete saturation value with the help of the curve in Figure 11.

The results of the magnetic intensity measurements are summarized in Table 9. The extinction-absorption correction was employed, and then by the application of the equations (23), (26) and (3), the quantity \( fS_{\text{eff}} \) was calculated, where \( S_{\text{eff}} \) is the effective spin of the atom and \( f \) is the relative magnetic form factor defined and discussed in III. 1.

The \( fS_{\text{eff}} \) values are plotted against \( \sin \theta / \lambda \) in Figure 13. For the purpose of comparison a smooth curve based on a free ion Hartree-Fock calculation for the spin magnetic 3d electron form factor\(^{61} \) is also drawn. An arbitrary expansion of 12% 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 \( \sin \theta / \lambda \). The intercept of the free ion curve, which fits the data for peaks at low \( \sin \theta / \lambda \) quite well at \( \sin \theta / \lambda = 0 \) is 1.93. The expanded curve also has the same intercept value. By definition, this is the value of \( S_{\text{eff}} \), because \( f(0) = 1 \). This value of \( S_{\text{eff}} \) agrees very well with Roth's\(^{62} \) value, \( S_{\text{eff}} = 1.90 \), obtained with a powder sample.
TABLE 9
MAGNETIC INTENSITY DATA

<table>
<thead>
<tr>
<th>h k l</th>
<th>$P_0$, Integrated Intensity In Neutrons/1.7 x 10^5 Monitor/0.1°, at -40°C</th>
<th>A, Absorption-Extinction Correction Factor</th>
<th>$q^2$</th>
<th>$fS_{eff}$</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>121194</td>
<td>.486</td>
<td>.67</td>
<td>1.76</td>
<td>.91±.02</td>
</tr>
<tr>
<td>311</td>
<td>28509</td>
<td>.538</td>
<td>.68</td>
<td>1.11</td>
<td>.58±.01</td>
</tr>
<tr>
<td>313</td>
<td>19794</td>
<td>.553</td>
<td>.66</td>
<td>1.06</td>
<td>.55±.01</td>
</tr>
<tr>
<td>333</td>
<td>19228</td>
<td>.553</td>
<td>.66</td>
<td>1.05</td>
<td>.54±.01</td>
</tr>
<tr>
<td>333</td>
<td>15390</td>
<td>.560</td>
<td>.67</td>
<td>1.01</td>
<td>.52±.01</td>
</tr>
<tr>
<td>333</td>
<td>15052</td>
<td>.560</td>
<td>.67</td>
<td>1.00</td>
<td>.52±.01</td>
</tr>
<tr>
<td>151</td>
<td>15181</td>
<td>.560</td>
<td>.69</td>
<td>0.99</td>
<td>.51±.01</td>
</tr>
<tr>
<td>151</td>
<td>15268</td>
<td>.560</td>
<td>.69</td>
<td>0.99</td>
<td>.51±.01</td>
</tr>
<tr>
<td>515</td>
<td>4685</td>
<td>.567</td>
<td>.66</td>
<td>0.65</td>
<td>.34±.01</td>
</tr>
<tr>
<td>515</td>
<td>4619</td>
<td>.567</td>
<td>.66</td>
<td>0.65</td>
<td>.34±.01</td>
</tr>
<tr>
<td>117</td>
<td>4316</td>
<td>.567</td>
<td>.63</td>
<td>0.64</td>
<td>.33±.01</td>
</tr>
<tr>
<td>733</td>
<td>2971</td>
<td>.569</td>
<td>.68</td>
<td>0.54</td>
<td>.28±.01</td>
</tr>
</tbody>
</table>
TABLE 9--Continued

<table>
<thead>
<tr>
<th>h k l</th>
<th>P, Integrated Intensity in Neutrons/1.7 x 10^5 Monitor/0.1°, at -40°C</th>
<th>A, Absorption-Extinction Correction Factor</th>
<th>q^2</th>
<th>f_{s_{\text{eff}}}</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>2936</td>
<td>.569</td>
<td>.68</td>
<td>0.54</td>
<td>.28±.01</td>
</tr>
<tr>
<td>555</td>
<td>1768</td>
<td>.570</td>
<td>.67</td>
<td>0.44</td>
<td>.23±.01</td>
</tr>
<tr>
<td>119</td>
<td>1588</td>
<td>.571</td>
<td>.63</td>
<td>0.43</td>
<td>.23±.01</td>
</tr>
<tr>
<td>737</td>
<td>904</td>
<td>.571</td>
<td>.66</td>
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<td>.63</td>
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<tr>
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<td>.574</td>
<td>.68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1, 1, 15</td>
<td>119</td>
<td>.580</td>
<td>.62</td>
<td>0.13</td>
<td>.07±.06</td>
</tr>
</tbody>
</table>
Plot of $f_{\text{Seff}}$ values against $\sin \theta / \lambda$. 

Figure 13
Once $S_{\text{eff}}$ is known, the magnetic form factor, $f$, is known as a function of $\sin \theta / \lambda$. The $f(\frac{\sin \theta}{\lambda})$ values for different peaks are presented in the last column of Table 9. The indicated errors are those resulting from the statistical uncertainty of the measurements as well as from the errors in estimation of absorption-extinction correction.

It is to be noted in Figure 13 that the experimental points at the same abscissa are split apart for large values of $\sin \theta / \lambda$. Hence a monotonic isotropic form factor function cannot fit the experimental data. As discussed in Section III. 1, this suggests the existence of non-spherical charge distribution in Co$^{++}$ ion. However, this anisotropy effect is very small for small $\sin \theta / \lambda$ range and cannot explain the large deviation of the point for (311) peak. Its origin was sought in the argon-core spin polarized charge distribution.

These points are discussed in detail in the next chapter where the electron distribution in the Co$^{++}$ ion in Co0 is related quantitatively with the form factor data of Table 9.
CHAPTER V

INTERPRETATION OF DATA

The measured form factor of an \((h k l)\) reflection is related to the projection of the ionic electron density onto the \([h k l]\) direction by

\[
f(K) = \int_{-\infty}^{+\infty} L(z) \cos(Kz)dz
\]

where \(K = 4\pi \sin \theta / \lambda\), \(z\) is an axis parallel to \([h k l]\) and through the lattice site of the ion, and \(L(z)\) is the electron density projected onto the \(z\)-axis.\(^6^3\) 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 \((h_1 k_1 l_1)\) and \((h_2 k_2 l_2)\), 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 a higher value in the neighborhood of \(z = 0\), and thus \(f_1(K) > f_2(K)\) by equation (42). If \(f_1(K)\) is determined for several values of \(K\), corresponding to the measurements of the \((nh_1, nk_1, n l_1)\) reflections, the resulting form factor curve will lie above the \(f_2(K)\) curve determined from the \((nh_2, nk_2, n l_2)\) reflections.
Hence, if for an ion the projected electron density is most condensed along the cube axes and most extended along the body diagonals, the \((h \ h \ h)\) reflections will have the smallest \(f\)-values, and the reflections with normals close to a cube axes (e.g., 7, 1, 1; 11, 1, 1; 13, 1, 1, etc.) will yield the highest form factor values. If the extension of the electron density were greatest along the \(<111>\) axes, the \((h \ h \ h)\) reflections would have the largest \(f\)-values, and \((13, 1, 1)\) etc. would have the smallest. The experimental values of the \(\text{Co}^{++}\) ion form factor displayed in Figure 13 show that at the largest values of \(\sin \theta / \lambda\) the reflections with normals close to the cube axes have higher form factor values than the corresponding reflections with normals close to the \(<h \ h \ h>\) axes. This suggests greater condensation of magnetic electron density along the cube axes directions. But this splitting in \(f\)-values for a particular \(\sin \theta / \lambda\) converges rather rapidly with decreasing \(\sin \theta / \lambda\). Hence the consideration of the data over the entire range of \(\sin \theta / \lambda\) suggests the existence of a mixture of states, with the predominence of the state having the greatest magnetic electron density distribution along the directions of the cube axes.

The electronic structure of free \(\text{Co}^{++}\) ion in its ground state consists of an argon core plus seven 3d electrons and can be described as a \(^4F\,9/2\) state. In the \(\text{CoO}\) crystal, the \(\text{Co}^{++}\) ion will be situated in an electric field which arises in the most part from the six nearest
neighbor 0" ions. As discussed in section III. 1, the 3d electron
distribution of the Co\textsuperscript{++} 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. The \( t_{2g} \) orbitals have
\( xy, yz, zx \) 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 \( \langle h h o \rangle \) axes and the
\( e_g \) orbitals are directed along \( \langle h o o \rangle \) axes. Thus the asymmetries
which appear in the measured form factor will depend on the distribution
of the magnetic electrons, i.e., unpaired electrons, over these orbitals.
The conclusion of the last paragraph will then mean 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
the lower energy.

The next step was to determine quantitatively the distribution
of unpaired electrons over \( e_g \) and \( t_{2g} \), or, in other words, to determine
the value of \( x \) in equation (10). The \( A(p, \nu) \) for different \( \{ h k l \} \)
sets were calculated with the help of equation (14), \( \langle J_4 \rangle \) plotted
against \( \sin \theta/\lambda \) from the data in Reference 14, \( f_e \) and \( f_t \) calculated
from (11) and (12), and \( f_{AS} \) of equation (10) calculated for different
suitably chosen values of \( x \). For each value of \( x \) the \( \bar{f} \), the symmetric
magnetic form factor, was found out for all the peaks utilizing equation (9),
the table for $f_{AS}$ values and the values of $f$ from Table 9. The $f$ values were plotted against $\sin \theta/\lambda$ for each $x$ parameter value and compared with the free ion magnetic form factor monotonic graph (obtained from the data in Reference 14) or expansions thereof along $\sin \theta/\lambda$. The best agreement obtained was for the set with $x = 2/3$. Hence 33 percent of the unpaired electrons were in the $t_{2g}$ orbital and 67 percent in the $e_g$ orbital. The distribution of 3d-electrons of the Co$^{++}$ ion over the different orbitals in a crystal field is demonstrated diagrammatically in Figure 14.

The values $f$, the spherically symmetric magnetic form factor, for different peaks are listed in Table 10 along with the different quantities utilized to arrive at them as described in the last paragraph.

The values of $\tilde{f}$, the spherically symmetric magnetic form factor are displayed against $\sin \theta/\lambda$ in Figure 15. A comparison with the symmetric free-ion form factor shows that the free ion form factor falls off much too rapidly with increasing $\sin \theta/\lambda$. A reasonable fit to the data required a 12 percent expansion of the $\sin \theta/\lambda$ scale, which is equivalent to compression of the charge density by about 10 percent.

Watson and Freeman have investigated the spin density contraction effects in a Ni$^{++}$ ion when put in a cubic crystalline field. Extending their arguments to the case of the Co$^{++}$ ion in the crystalline
Figure 14

The distribution of the 3d-electrons of the Co$^{++}$ ion over the orbitals in an octahedral crystal field. The full circles represent an electron.
OCTAHEDRAL FIELD

Co^{2+}  3d^7

\[ 10200 \text{ cm}^{-1} \]

e_g

t_{2g}
<table>
<thead>
<tr>
<th>(h k l)</th>
<th>Sin θ/λ</th>
<th>A(p,j)</th>
<th>f_t</th>
<th>f_e</th>
<th>f_{AS} x = 2/3</th>
<th>f</th>
<th>Isotropic Magnetic Form Factor</th>
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<td>.50±.01</td>
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</tr>
<tr>
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<td>.305</td>
<td>+.64</td>
<td>-0.02</td>
<td>+0.03</td>
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<td>.28±.01</td>
<td></td>
</tr>
<tr>
<td>(h k l)</td>
<td>Sin θ/λ</td>
<td>$A(ρ, l)$</td>
<td>$f_t$</td>
<td>$f_e$</td>
<td>$f_{AS\ x = 2/3}$</td>
<td>$\bar{f}$</td>
<td></td>
</tr>
<tr>
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<td>---------</td>
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<td>+0.02</td>
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<td>+0.06</td>
<td>+.01</td>
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TABLE 10--Continued

Isotropic Magnetic Form Factor
Figure 15

Plot of the experimentally determined spherically symmetric magnetic form factor (represented as Form Factor) against Sin $\theta/\lambda$. For comparison, the form factor for the free Co$^{++}$ ion, the curve obtained by a 12 percent expansion along Sin $\theta/\lambda$ are plotted. Also included are the modified form factor curve obtained by including the effect of distribution A to the 12 percent expansion curve, and the curve obtained by including the effect of distribution B to the free ion form factor curve.
field, one reaches the conclusion that the cubic field expands theive $t_{2g}$ electrons and compresses the two $e_g$ electrons. This results
in a slightly expanded average form factor.

Freeman and Watson[^64] have also studied the effects of spin
polarization. A spin polarized calculation consists of letting the atomic
one electron wavefunctions of differing spin having different radial
dependence. Due to exchange terms, a Hartree-Fock many electron
function with a net spin will yield differences in radial functions for
electrons differing only in $m_s$ quantum numbers. Hence the spin
density of the neutron has to be written as

$$\rho_{\text{neutron}} = \frac{2}{3} \left[ U_{e_g \uparrow} \right]^2 + \frac{1}{3} \left\{ 3 \left[ U_{t_{2g} \uparrow} \right]^2 - 2 \left[ U_{t_{2g} \downarrow} \right]^2 \right\} + \sum_{\text{spin} \downarrow} \left[ U_{1(r)} \right]^2 - \sum_{\text{spin} \uparrow} \left[ U_{1(r)} \right]^2 \quad \ldots \ldots \ldots (43)$$

instead of just

$$\rho = \frac{1}{3} \left\{ 2 \left[ U_{e_g \uparrow} \right]^2 + \left[ U_{t_{2g} \uparrow} \right]^2 \right\} \quad \ldots \ldots \ldots (44)$$

The crystalline field enhances the spin polarization effect. In the argon
core this effect shows up as a net negative spin density in the regions
close to the nucleus and at large radii balanced by a positive spin density
distribution of equal magnitude in the central region. This leads to a
positive contribution to the magnetic scattering with a consequent
expansion of the form factor. As for the 3d electrons, the $\left[U_{t_{2g}^\uparrow}\right]^2$
are contracted relative to $\left[U_{t_{2g}^\downarrow}\right]^2$, and the two unpaired $e_g$ electrons
are also compressed, both leading to an expansion of the form factor.

Under the combined effect of the crystalline field and the spin
polarization, the form factor is expanded from its free ion value by
approximately 4 percent.

The expansion of the form factor is also partially accounted
for by the presence of the orbital magnetic moment producing a maximum
magnetic field and hence neutron scattering around $r = 0$. The non-
spherical asymmetric electric fields in a crystal may exert a 'quenching'
action on the orbital angular momenta of the iron group elements
'freezing' them on a position so that their effective value with respect
to an external field is zero. Depending on whether the quenching is
complete or partial the effective value of the total angular moment
of the ion may range from the spin only value to the free ion value.

The effective spin of Co$^{++}$ ion in CoO ($S_{\text{eff}} = 1.93$) derived in the last
chapter, as compared with the spin-only value 1.5 bears evidence to
the fact that the orbital angular momentum is only partially quenched
in this case. Blume has calculated the expansion of form factor in
Ni$^{++}$ due to a partially quenched orbital angular momentum. The study
will be more difficult for Co$^{++}$ because of its degenerate ground state.
However, his expansion value of 6 percent may be taken as an approximate value, and then this would closely account for the expansion of the free ion curve in Figure 15.

Efforts were made to account for the large deviation of the experimental point at Sin $\theta/\lambda = .19$ and the upward shift in the region about Sin $\theta/\lambda = .7$. A preliminary Fourier inversion of a $(f_{\text{obs}} - f_{\text{theot}})$ curve suggested the existence of a spin density at oxygen site, but the inherent difficulties due to termination error made such analyses difficult to interpret. The alternative method chosen was that of assuming different spin density distributions between $r = 0$ and $r = 4$ a.u., with zero integrated value. The distribution shown in Figure 16 having the shape of the large radius negative spin distribution of the argon-like core for spin polarized Ni$^{++}$ along with its antisymmetric distribution about $r = 2.0$ atomic units modified the 12 percent expanded form factor curve to a new curve (referred to as the curve for distribution A in Figure 15) which fitted all the experimental points satisfactorily. The spin density distribution A has its minimum at $r = 0.9$ atomic units and a maximum at $r = 3.08$ atomic units. The positions of the maximum and the minimum and the shape of the distribution curve would tend to lead to an inquiry for a link with argon-core spin polarization, but the fact that the amplitude of distribution A is 9 times that of Freeman-Watson distribution will discourage any such effort.
Figure 16

The plot of spin density distribution \( A \) against \( r \), the distance, from the center of the atom. \( \Delta \rho(r) \) is in electrons per 3d electron per atomic unit.
In an attempt to interpret the entire deviation of the experimentally observed magnetic form factors from the original unexpanded Watson-Freeman free ion form factor curve as direct Fourier transforms of a spin density distribution, a machine program was fed with different suitable spin density distributions and each output data set was algebraically added to the original Freeman-Watson curve to get different modified form factor graphs. These were compared to the experimental points. The curve which gave the closest agreement to data is represented in Figure 15 as the curve due to the spin density distribution B. This spin density distribution is shown in Figure 17. This distribution together with that calculated by Freeman and Watson for the Co$^{++}$ in the crystalline field account for the magnetic neutron scattering of CoO.

Finally, it may be remembered that there are certain limitations of the theory of the Co$^{++}$ ion in a crystalline field. There are the serious questions of (1) to what extent should one rely on the ionic model of a localized ion in an external 'crystalline' potential and in turn (2) how appropriate is the point charge potential. It is also doubtful if refinements in the crystalline field model would lead to better wavefunctions since attempts to improve calculations of crystalline field strengths have led to poor results. This suggests the necessity of including covalent terms for a still closer agreement between theory and experiment.
Figure 17

The plot of spin density distribution $B$ against $r$, the distance from the center of the atom. $\Delta \rho(r)$ is in electrons per 3d electron per atomic unit.
APPENDIX
APPENDIX I

709/7090 SCATRAN PROGRAM FOR THE DETERMINATION
OF THE ABSORPTION-EXTINCTION COEFFICIENTS

SOURCE LANGUAGE STATEMENTS:

1 DIMENSION (P(10201, KP), Q(10201, KP),
A(16), KU(16)) -
2 FLOATING (KU, MU) -
3 START READ INPUT, IF1, ((A(LA), KU(LA),
LA=0, 1, LA.LE. 10)) -
4 PO=1. -
5 MU=1.04 -
6 DELM=.0075 -
7 DO THROUGH (END), LA=0, 1, LA.LE. 10 -
8 SINT=SIN.(A(LA)) -
9 COST=COS.(A(LA)) -
10 SIN=SIN.(2*A(LA)) -
11 COS=COS.(2*A(LA)) -
12 DELMP=DELPM/SIN -
13 ETA=.00145 -
14 SIGMA=KU(LA)/(3.464*ETA) -
15 TAU=SIGMA+MU -
16 COFA=1. -DELM*TAU -
17 COFB=SIGMA*DELM -
18 F=0. -
19 DO THROUGH (ST9), K=0, 1, K. L. 50 -
20 IR=50.*((1. -(K/50.)*P.2).*P.0.5 -
21 IR2=2*IR -
22 KP=IR2+1 -
23 I=IR2*COS*COS -
24 J=IR2*SIN*SIN -
25 DO THROUGH (ST8), M=0, 1, M. LE. IR2 -
26 C=IR+(IR-M)*COS -
27 D=SIN*(M*(IR2-M)).P.0.5 -
28 NA=C-D -
29 NB=C+D -
30 N=0 -
31 ST2 TRANSFER (ST5) PROVIDED (N. GE. NA) -
32 ST3 P(M,N)=PO -
33 Q(M,N)=0. -
34 ST4 N=N+1 -
35 TRANSFER (ST2) -
36  ST5  TRANSFER (ST7) PROVIDED (N.E.NB) -

37  TRANSFER (ST6) PROVIDED (N.E.NA) -

38  \[ P(M,N) = P(M-1,N) \times COFA + Q(M-1,N) \times COFB - \]

39  \[ Q(M,N) = Q(M,N-1) \times COFA + P(M,N-1) \times COFB - \]

40  TRANSFER (ST4) -

41  ST6  TRANSFER (ST3) PROVIDED (M.LE.I) -

42  \[ P(M,N) = P(M-1,N) \times COFA + Q(M-1,N) \times COFB - \]

43  \[ Q(M,N) = 0. - \]

44  TRANSFER (ST4) -

45  ST7  TRANSFER (ST12) PROVIDED (M.G.J) -

46  \[ P(M,NB) = PO - \]

47  PROVIDED (M.E.0), \( Q(M,NB) = 0. - \)

48  PROVIDED (M.NE.0), \( Q(M,NB) = Q(M,NB-1) \times COFA + P(M,NB-1) \times COFB - \)

49  DO THROUGH (LOOP), \( L = 0, 1, NC. L \), IR2 -

50  NC=NB+L -

51  P(M,NC)=P(M,NB) -

52  LOOP \[ Q(M,NC) = Q(M,NB) - \]

53  ONE  PROVIDED (M.E.0. OR. M.E. IR2), \( Q(M,NB) = Q(M,NB) / 2.0 - \)

54  \( S = Q(M,NB) \times DELM \times DELM - \)

55  ST8  \( F = F + S - \)
CONTINUE-

WRITE OUTPUT, OF1, (A(LA), ETA, F)-

CONTINUE-

CALL SUBROUTINE ()=ENDJOB. ()-

P(M, NB)=P(M-1, NB)*COFA+Q(M-1, NB)
*COFB-

Q(M, NB)=Q(M, NB-1)*COFA+P(M, NB-1)
*COFB-

TRANSFER (ONE)-

(6F9.5) -

(1H, F10.4, 2E12.4)-

END PROGRAM (START)-
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51. R. Street and B. Lewis Nature 168 (1951) 1036.


54. S. Greenwald, Acta Cryst. 6 (1953) 396.


64. R. E. Watson and A. J. Freeman, Phys. Rev. 120 (1960) 1134.


