

Multispin Axis Structures for Antiferromagnets*

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(Received April 9, 1958)

Neutron diffraction intensities have been computed for antiferromagnetic spin arrangements in the rock-salt-type structure. If the spin directions in the unit cell occur at relative angles other than 0° or 180° , the neutron scattering from powder specimens does not lead to a unique solution of the spin arrangement. A unique solution can be obtained from neutron scattering by a single-domain crystal. Neutron diffraction from crystals of nickel oxide shows that in all crystals examined, either the magnetic moments were parallel to more than one direction in the crystal, or antiferromagnetic domains were present. The results can be quantitatively accounted for by assuming the crystal consisted of domains with a common magnetic axis.

THE application of neutron diffraction methods now makes it possible to arrive at descriptions of the detailed arrangement of atomic moments in magnetic solids. Below a critical ordering temperature, there may arise a three-dimensional periodic arrangement of moments which superimposes a characteristic magnetic structure upon the original crystal structure. In a recent paper¹ the results of a neutron diffraction investigation by powder methods of the antiferromagnetic ordering in MnO, FeO, CoO, and NiO were reported. The interpretation of the neutron diffraction patterns was based on the assumption that within a single magnetic unit cell the atomic moments were parallel or antiparallel to a single magnetic axis. It was concluded that the structures of all the monoxides were based on ferromagnetic sheets of moments parallel to (111) planes, with the direction of magnetization reversed on adjacent sheets. The most probable axis of magnetization for FeO was along the [111] direction perpendicular to the ferromagnetic sheet, whereas for MnO, and NiO the most probable direction lay within the ferromagnetic sheet. The observation of diffuse neutron scattering left some uncertainty regarding the precise direction of the magnetic axes, and consequently there was the possibility of a tilt of the moment direction out of the (111) plane toward the [001] direction, particularly in the case of CoO.

A crystallographic deformation occurs at the same temperature as the magnetic ordering. In the paramagnetic state, the oxides are cubic; upon passing into the antiferromagnetic state, MnO and NiO become rhombohedral with $\alpha > 60^\circ$, FeO rhombohedral with $\alpha < 60^\circ$, and CoO tetragonal with $c/a < 1$.^{2,3} The arrangement of moments in MnO, NiO, and FeO is consistent with the crystal deformation in the sense that the unique crystal axis is perpendicular to the ferromagnetically coupled sheets. This simple correlation is absent for CoO. Since Mn^{+2} is in an *S* state and the orbital moment of Ni^{+2} is quenched by the crystalline field, dipole-dipole interactions favor the moments

lying within (111) planes⁴ in agreement with the neutron diffraction results. The orbital contributions to the moment of Co^{+2} is appreciable, however, and from recent calculations, Kanamori⁵ concludes that the magnetic axis should be nearly parallel to the tetragonal [001] axis. On the other hand, calculations by Loeb and Goodenough⁶ show that minimum dipole energies may also be obtained from more complex types of spin configurations in which the atomic spins form angles other than 0° or 180° with each other.

In the previous work it was pointed out that although a set of solutions could be deduced which was consistent with data limited to neutron diffraction from powder specimens, these solutions were not unique since they depended on certain basic assumptions which limited the range of possible structures. It is the purpose of this paper to explore the consequence of removing the restriction that there is a single magnetic axis in a domain of an antiferromagnet and consequently to generalize the problem to include the multimagnetic-axis structures. As a result of this generalization, it is found that a variety of multiaxis arrangements are consistent with data obtainable from powder specimens. Further calculations showed that neutron diffraction from a single crystal which consists of a single antiferromagnetic domain could be used to differentiate between the alternative arrangements. Nickel oxide was chosen as a suitable material to investigate, and neutron scattering experiments were undertaken in order to ascertain the angular distribution of spin directions within the magnetic unit cell.

NEUTRON DIFFRACTION POWDER PATTERNS FROM MULTIAXIS STRUCTURES

The theory of the scattering of neutrons by atomic moments has been given by Halpern and Johnson.⁷ In their analysis of the coherent diffraction pattern produced by scattering from an ordered arrangement of

* Neutron diffraction experiments were made at the Brookhaven National Laboratory Reactor, Upton, New York.

¹ W. L. Roth, *Phys. Rev.* **110**, 1333 (1958).

² H. P. Rooksby, *Acta Cryst.* **1**, 226 (1948).

³ N. C. Tombs and H. P. Rooksby, *Nature* **165**, 442 (1950).

⁴ S. I. Kaplan, *J. Chem. Phys.* **22**, 1709 (1954).

⁵ J. Kanamori, *Progr. Theoret. Phys. (Japan)* **17**, 177 (1957); **17**, 223 (1957).

⁶ A. L. Loeb and J. B. Goodenough, Conference on Magnetism and Magnetic Materials, Boston, Massachusetts, October 16-18, 1956 (unpublished).

⁷ O. Halpern and M. H. Johnson, *Phys. Rev.* **55**, 898 (1939).

moments, the magnetic moments were assumed parallel or antiparallel. An extension of the original analysis required to compute the scattering from moments making arbitrary angles with each other in a rocksalt-type structure is given in the appendix.

A general formulation for the description of the possible magnetic structures in the rocksalt-like oxides is shown in Fig. 1. The atomic spins are arrayed in four antiferromagnetic substructures Mjj' ($j=1, 2, 3, 4$) such that if the spin direction of atom j is $\mathbf{S}_j = [u_j v_j w_j]$, the spin on atom j' is reversed and $\mathbf{S}_{j'} = -\mathbf{S}_j = [\bar{u}_j \bar{v}_j \bar{w}_j]$. In the general case, it is assumed there is no relationship between the magnetization directions of the substructures, and hence to uniquely define the spin structure in an unit cell (or a single domain) it is necessary to prescribe the four spin vectors \mathbf{S}_j .

The magnetic scattering from a representative number of multi-axis structures has been computed.

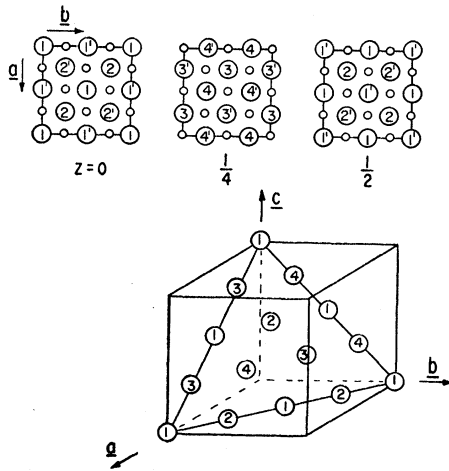


FIG. 1. Magnetic substructures in rocksalt-type crystals. The small circles represent oxygen and an antiferromagnetic substructure is designated by the cations MM' .

Since complete single-crystal data are not available, no attempt was made to analyze all of the possible configurations of the four independent spin vectors, and arrangements were chosen largely for symmetry considerations. Drawings of the spin configurations are shown in Figs. 2 and 3, and the intensities calculated for the first two powder diffraction peaks $\{111\}$ and $\{113\}$ are tabulated in Table I.⁸ The scattering is given in units of $F^2/64p^2$ and to compare with experiment the appropriate magnetic scattering amplitudes and angular factors must be applied, and corrections made for absorption, extinction, and thermal motion.

The first six models are the single magnetic axis structures considered in detail in a previous paper. The magnetic scattering agrees with intensities computed for the structures: $\text{MnO}-A_{(111)}$, $\text{NiO}-A_{(111)}$,

⁸ For $A_{(111)}$ the specific direction $[\bar{1}10]$ is chosen, but identical results obtain for any other direction in the (111) plane.

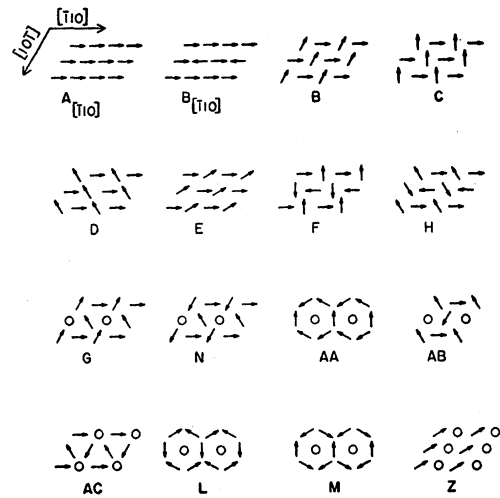


FIG. 2. Multispin axis structures. The distribution of spins within the (111) plane is shown. The structures are described in detail in Table I.

$\text{CoO}-A_{[11\bar{1}]}$, or $A_{[111]}$, and $\text{FeO}-A_{[111]}$. $A_{[100]}$ and $B_{[UVW]}$ are the structures proposed by Shull, Strauser, and Wollan⁹ and Li,¹⁰ respectively. (The powder intensities from Arrangement B are invariant with $[UVW]$.) Because of uncertainties introduced by the diffuse scattering and the dependence of the absolute values on the magnetic scattering amplitudes and form factors, the unitary intensities for MnO , NiO , and CoO are not known precisely, but it appears safe to conclude that for MnO and NiO , $\sum (F^2/64p^2)$ for $\{111\}$ is within the range 26–32, and that 49 to 57 represents the possible excursion of values $\{113\}$. For CoO , the value for $\{111\}$ may be as small as 22, and for FeO , it is less than 2.

In the group of structures $B-E$ there are two axes of magnetization but all the moments are confined to the

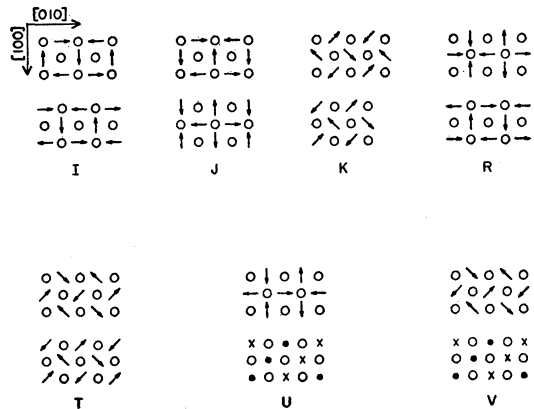


FIG. 3. Multispin axis structures. The distribution of spins in adjacent (001) planes is shown. Open circles are oxygen; \bullet and \times designate spins pointing up and down into the paper.

⁹ Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).
¹⁰ Y. Y. Li, Phys. Rev. **100**, 627 (1955).

TABLE I. Powder pattern intensities from multispin axis structures.

Model	S_1	S_2	S_3	S_4	$\Sigma(F_{\text{mag}}^2/64\rho^2)$	
					{111}	{113}
$A_{(111)}$	$\bar{1}10$	$\bar{1}10$	$\bar{1}10$	$\bar{1}10$	32	49.5
$A_{[11\bar{1}]}$	$1\bar{1}\bar{1}$	$1\bar{1}\bar{1}$	$1\bar{1}\bar{1}$	$1\bar{1}\bar{1}$	28.4	54.3
$A_{[\bar{1}\bar{1}7]}$	$\bar{1}\bar{1}\bar{7}$	$\bar{1}\bar{1}\bar{7}$	$\bar{1}\bar{1}\bar{7}$	$\bar{1}\bar{1}\bar{7}$	26.8	56.5
$A_{[100]}$	100	100	100	100	21.3	64
$B_{[UVW]}$	UVW	UVW	$\bar{U}\bar{V}\bar{W}$	UVW	21.3	64
$A_{[111]}$	111	111	111	111	0	93
B	$\bar{1}10$	$\bar{1}01$	$\bar{1}01$	$\bar{1}10$	32	49.5
C	$\bar{1}10$	$\bar{1}\bar{1}2$	$\bar{1}\bar{1}2$	$\bar{1}10$	30.9	50.9
D	$\bar{1}10$	$0\bar{1}1$	$0\bar{1}1$	$\bar{1}10$	26.7	56.7
E	$\bar{1}10$	$\bar{2}11$	$\bar{2}11$	$\bar{1}10$	32	49.5
F	$\bar{1}10$	$\bar{1}\bar{1}2$	$1\bar{1}0$	$1\bar{1}2$	24	60.4
H	$\bar{1}10$	$0\bar{1}1$	$1\bar{1}0$	$0\bar{1}\bar{1}$	21.3	64
G	$\bar{1}10$	101	$0\bar{1}1$	111	29.3	53.1
N	$\bar{1}10$	$10\bar{1}$	$0\bar{1}\bar{1}$	111	18.7	67.6
AA	$2\bar{1}\bar{1}$	121	$\bar{1}\bar{1}2$	111	28.3	54.6
AB	$\bar{1}10$	$0\bar{1}\bar{1}$	$10\bar{1}$	111	6.7	83.8
AC	111	$\bar{1}10$	$10\bar{1}$	$0\bar{1}\bar{1}$	29.3	53.1
L	$\bar{1}\bar{1}1$	$\bar{1}\bar{1}\bar{1}$	$1\bar{1}\bar{1}$	111	0	93.1
M	$\bar{1}\bar{1}1$	$\bar{1}\bar{1}\bar{1}$	$1\bar{1}\bar{1}$	$\bar{1}\bar{1}\bar{1}$	21.3	64
Z	111	$\bar{1}\bar{1}1$	111	$\bar{1}\bar{1}1$	14.2	73.7
I	010	$\bar{1}00$	$\bar{1}00$	010	32	49.5
J	010	100	010	100	10.7	78.5
K	$\bar{1}10$	$\bar{1}\bar{1}0$	110	$\bar{1}\bar{1}0$	21.3	64
R	100	010	100	$0\bar{1}0$	21.3	64
T	110	$\bar{1}\bar{1}0$	110	$\bar{1}\bar{1}0$	21.3	64
U	100	$0\bar{1}0$	001	001	26.7	56.7
V	110	$\bar{1}\bar{1}0$	001	001	13.8	74.2

(111) plane. F and H also are based on two magnetic axes, but the moments are arranged to form small "closure loops" in the (111) plane. From powder data alone, structures B and E are indistinguishable from $A_{(111)}$, and within the limits of experimental error, C and D are acceptable.

The next group of structures are based on four axes of magnetization. Of these arrangements, AB and AC have true rhombohedral symmetry, but only G , AA , and AC are in satisfactory agreement with the powder diffraction data from MnO and NiO.

The final group of structures L , M , Z are based on magnetization directions parallel to $[111]$ directions. Model L is a multiaxis model, with rhombohedral symmetry, and it agrees with the neutron diffraction data obtained from FeO equally as well as the single-axis structure $A_{[111]}$.

The arrangements discussed thus far reflect in some degree the rhombohedral symmetry observed by x-rays for MnO and NiO in the antiferromagnetic state. The next group were chosen to conform with the tetragonal symmetry of CoO. Because of uncertainties in the Co^{+2} form factor, all structures except J and V are in possible concordance with the powder diffraction data. Drawings representing these tetragonal configurations are given in Fig. 3; to demonstrate the relationship to the tetragonal axis, two adjacent atomic layers parallel to (001) are shown.

NEUTRON DIFFRACTION FROM CRYSTALS OF NiO

From the brief survey in Table I it is clear that there are many antiferromagnetic structures which are consistent with the neutron diffraction data from powders of MnO, FeO, NiO, and CoO. Single-crystal intensities for several of these models have been computed and the intensities for the individual (111) reflections are tabulated in Table II. For comparison purposes, the single-crystal predictions for the single magnetic axis structures are included. It is clear that in principle the problem of discriminating between the alternative spin arrangements can be solved by measuring the neutron scattering from a single domain-single crystal since the distribution of intensity throughout the magnetic reciprocal lattice is quite different for the various models.

Nickel oxide was selected for study because large single crystals¹¹ were available and as a consequence of the high Néel temperature (250°C) the antiferromagnet is nearly magnetically ordered at room temperature. Crystals were cleaved from a boule supplied

TABLE II. Single crystal intensities from multispin axis structures.

Model	$F^2/64\rho^2$				
	(111)	$(\bar{1}\bar{1}1)$	$(1\bar{1}\bar{1})$	$(11\bar{1})$	{111}
$A_{(111)}$	16	0	0	0	32.0
$A_{[100]}$	10.7	0	0	0	21.3
$B_{[UVW]}$	2.66	2.66	2.66	2.66	21.3
$A_{[111]}$	14.2	0	0	0	28.4
B	12	4	0	0	32.0
C	8	7.5	0	0	30.9
D	4	9.3	0	0	26.7
E	14.9	1.0	0	0	32.0
G	4	4.9	0.9	4.9	29.3
AA	4	4.6	0.9	4.6	28.3
AC	0	4.9	4.9	4.9	29.3
I	8	8	0	0	32.0
U	4.7	2	2	4.7	26.7

by the Linde Air Products Company. X-ray and chemical analysis confirmed the fact that the cleaved sections were good single crystal NiO. The crystals, which ranged in size from $2 \times 2 \times 2$ mm³ to thin sections $2 \times 3 \times 0.05$ mm³, were mounted on vanadium supports in a conventional x-ray goniometer head. Integrated intensities were obtained both by rocking the crystal through the reflecting range and by traversing radially through the reciprocal lattice point.

The reflections could be indexed on the basis of a cubic unit cell with $a_0 = 8.35$ Å. The all even (hkl) are the result of nuclear scattering, and the magnetic scattering is concentrated in those reflections where h, k, l are all odd. A section of the reciprocal lattice is plotted in Fig. 4 where the nuclear reciprocal lattice is shown with solid lines and the magnetic reciprocal lattice is dotted. The points correspond to the re-

¹¹ The term "crystal" as used in this paper refers to that morphological entity which may include antiferromagnetic domains or twins.

flections expected for a single-domain crystal with a $A_{[UVW]}$ structure. The nuclear peaks occur at the expected positions and the magnetic reflections fall upon a grid with $\frac{1}{2}$ the spacing observed for the nuclear data. This is direct experimental confirmation for the double unit cell deduced for nickel oxide from the powder data.

When the neutron scattering from different crystals was compared, it was found that although the nuclear intensities were relatively consistent and reproducible, the distribution of intensities in the magnetic reciprocal lattice was highly variable. Some observations illustrating the variability in magnetic scattering is given in Table III, which tabulates the ratio of intensities at (111) and $(\bar{1}\bar{1})$. The magnetic scattering also could be altered by heating the crystal to a temperature above

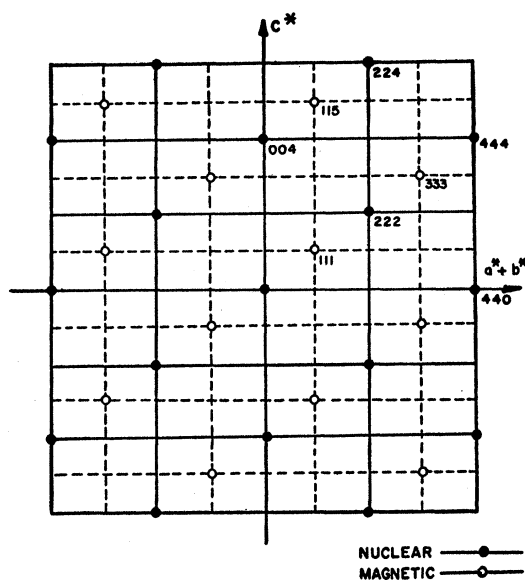


FIG. 4. Magnetic and nuclear reciprocal lattice for nickel oxide. Open circles designate reflections permitted for single domain of $A_{[UVW]}$ structure.

the antiferromagnetic Curie temperature, cooling and remeasuring at room temperature. These results demonstrated that in the different crystals of nickel oxide the magnetic structure was variable. Since identical intensities were not obtained for the various {111} reflections, it follows that the magnetic texture was not randomly distributed with respect to the crystal axes—i.e., there was a magnetic texture which was coarse grained. However, since the half-widths of the magnetic peaks were less than $0^{\circ}21'$, the resolution of the neutron spectrometer, there is a triply periodic distribution of magnetic moments extending for distances of 1000 Å or more. Consequently, there were antiferromagnetic domains within the crystals, and the domain dimensions were in the range 0.1 to 100 μ .

The results from polydomain crystals confirm the magnetic supercell inferred from the powder data and

TABLE III. Magnetic scattering from cleaved crystals of NiO.

Crystal	Neutron intensity (111)	Neutron intensity ($\bar{1}\bar{1}$)	Ratio (111)/($\bar{1}\bar{1}$)
I	15 100	nil	> 10
II	4840	559	8.7
II ^a	1743	1310	1.3
IV	2680	969	2.8

^a After heating to 300°C.

directly demonstrate the relationship between the magnetic and nuclear reciprocal lattices. However, the magnetic scattering from a polydomain single crystal cannot be used to determine the detailed magnetic structure, since it is a consequence of both the distribution of magnetic moments within the unit cell and the distribution of domains within the crystal.

MAGNETIC SCATTERING FROM ANNEALED NiO CRYSTAL

Since it was recognized that, in order to distinguish between the single and multi-axis hypotheses, neutron scattering from a crystal made up of a single magnetic domain would be necessary, considerable work was carried out on the properties of antiferromagnetic domains in NiO. Thin sections approximately 30 μ thick were prepared and studied with transmitted polarized light. Twinned structures and photoelastic patterns were observed, and by associating the crystallographic rhombohedral deformation with the magnetic ordering, the optically distinguishable structures may be related to antiferromagnetic domains. Experiments demonstrated that large untwinned regions could be grown in thin sections by annealing the crystals at 1500°C for one hour. In Fig. 5 is shown a photomicrograph of an annealed NiO thin section. The section is observed in transmission between crossed polarizers and the optic axes of the domains determined by standard optical techniques. Referring to Fig. 1, the optic axis in each domain is taken parallel to [111]. In order to obtain magnetic scattering of reasonable magnitude, a crystal several mm³ in volume is desirable, but it is not possible to pass sufficient light through such a crystal to establish the absence of twins. Conse-

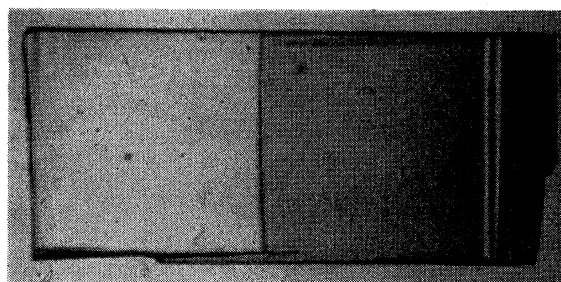


FIG. 5. Photomicrograph of nickel oxide thin section. The specimen is about $1 \times 2 \times 0.03$ mm and in this case the domains are crystallographic twins.

TABLE IV. Neutron intensities from NiO crystal annealed at 1500°C.

hkl	Intensity		hkl	Intensity		
	Observed	Calculated ^a		Observed	Calculated ^a	
111	396	458	333	60	38	
$\bar{1}\bar{1}\bar{1}$	452		$\bar{3}\bar{3}\bar{3}$	57		
11 $\bar{1}$	790	915	33 $\bar{3}$	112	76	
$\bar{1}\bar{1}1$	692		$\bar{3}\bar{3}3$	105		
113	208	287	115	53	38	
$\bar{1}\bar{1}\bar{3}$	202		$\bar{1}\bar{1}\bar{5}$	53		
11 $\bar{3}$	105	144	11 $\bar{5}$	116	76	
$\bar{1}\bar{1}3$	92		$\bar{1}\bar{1}5$	98		
222	1382	1480	440	5570	5260	
$\bar{2}\bar{2}\bar{2}$	1435		440	4810		
22 $\bar{2}$	1470		226	772		
$\bar{2}\bar{2}2$	1440		22 $\bar{6}$	800		
004	6690	6860	226	790	780	
00 $\bar{4}$	6960		$\bar{2}\bar{2}\bar{6}$	716		
331	130		444	4730		
$\bar{3}\bar{3}\bar{1}$	120	140	444	4720	4580	
33 $\bar{1}$	73		44 $\bar{4}$	4890		
$\bar{3}\bar{3}1$	66		444	4200		

^a Calculated for $A_{[110]}$ structure, assuming the antiferromagnetic domain composition $\frac{1}{3}A, \frac{2}{3}B$.

quently, "massive" crystals several mm³ in volume were annealed and the magnetic scattering measured to see whether the results were consistent with those expected for a single domain.

Secondary extinction is particularly large for the scattering of neutrons from single crystals. Extinction usually is minimized by utilizing as imperfect a crystal as possible—either by selecting a crystal with a large mosaic spread or purposely creating imperfections by deformation. In the present instance, the method used to produce single-domain crystals results in the formation of extremely perfect crystals and consequently extinction effects are large. To simplify the extinction corrections, an approximately spherical crystal was produced by cleaving a cube and polishing {111} faces on the corners to produce a cubo-octahedron. The crystal then was heated in air to 1500°C for one hour. X-ray Laue photographs indicated the surface to be single-crystalline and highly perfect.

The annealed NiO crystal was mounted to rotate about a [110] direction and a set of intensities in the hkl zone of the reciprocal lattice was obtained (Fig. 4). The integrated intensities are tabulated in Table IV and from the spread of values for centrosymmetric reflections of the same form, the average appears to be reliable within a few percent. In the absence of extinction, the nuclear intensities should be proportional to $Q_{(hkl)}$:

$$Q_{hkl} = \frac{\lambda^3 N^2}{\sin 2\theta} F_{hkl}^2,$$

where λ is the neutron wavelength, N the number of

unit cells per unit volume, 2θ the scattering angle, F_{hkl} the structure factor. Nuclear intensities were computed by basing all values on the magnetic unit cell and taking for the nuclear scattering amplitudes 1.03×10^{-12} cm for nickel and 0.58×10^{-12} for oxygen, and correcting the intensities for thermal vibration by the factor $\exp[-2B(\sin\theta/\lambda)^2]$, with $2B = 1 \times 10^{-16}$. The calculated versus observed nuclear intensities are plotted in Fig. 6, which demonstrates the tremendous effect of extinction on the stronger nuclear peaks. For small values of Q , the assumption that the intensity is proportional to Q is valid, and the scattering may be placed on an absolute basis,

$$I_{\text{calc}} = 0.995 \times 10^3 Q \exp(-\sin^2\theta); \quad Q \lesssim 10^{-3}.$$

This result may now be applied to the magnetic scattering. Assuming a spin-only moment for Ni²⁺ in NiO, the magnetic scattering amplitude is $p = 0.53 \times 10^{-12} f$, where f is the magnetic form factor. Expressing Q in terms of $(F^2/64p^2)$, normalizing with respect to the nuclear scattering at small Q , and correcting for lack of magnetic saturation at room temperature by the factor $I_{298}/I_0 = 0.74$, one obtains for the magnetic scattering:

$$I_{\text{calc}} = 0.0463 \frac{F^2}{64p^2 \sin 2\theta} \frac{f^2}{\left[\exp - 2B \left(\frac{\sin\theta}{\lambda} \right)^2 \right]}.$$

From the distribution of intensity in the magnetic reciprocal lattice, it is immediately obvious that the crystal is not a single domain of the $A_{(111)}$ structure. It is possible, however, to account for the observed magnetic scattering on the basis of the $A_{(111)}$ structure by regarding the crystal as built up from two kinds of antiferromagnetic domains. The domain texture is

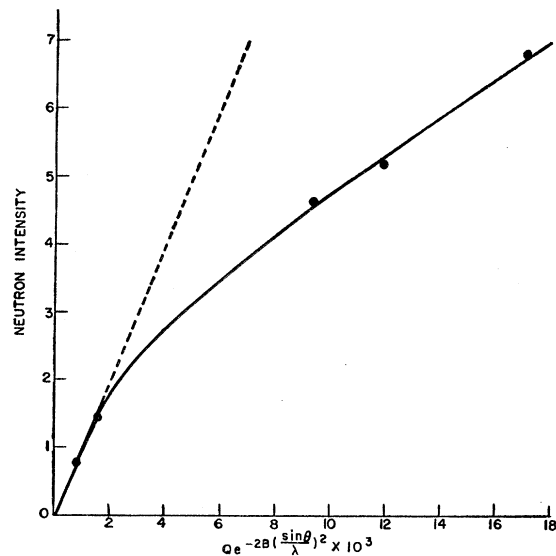


FIG. 6. Nuclear scattering from single crystal of NiO. The departure from the dotted curve is due to extinction.

shown in Fig. 7, where A and B represent the two types of domain. In domain A , the magnetic moments lie in the (111) planes and are directed along the specific directions $[\bar{1}10]$ and $[1\bar{1}0]$ in alternate sheets. One ferromagnetic sheet is shown and the magnetization direction is $[\bar{1}10]$. In the adjacent domain the direction of magnetization is unaltered, but the ferromagnetic sheet is rotated to become parallel to the $(1\bar{1}\bar{1})$ plane of the original domain. The extension of the original ferromagnetic sheet in domain A becomes an antiferromagnetic sheet in domain B , but the spin directions in the two domains remain parallel. Assuming the domain composition was approximately $\frac{1}{3}A$, $\frac{2}{3}B$, neutron intensities were calculated and the results are tabulated in Table IV. Since the data were normalized with respect to the nuclear scattering, the magnetic intensities are on an absolute scale, and considering the uncertainties introduced by the effects of extinction, the agreement is satisfactory. The distribution of intensities among reflections of the same form is quite good, although the observed magnetic scattering does not decrease with $\sin\theta/\lambda$ as rapidly as computed. This suggests that the Ni^{+2} magnetic form factor curve may decrease less rapidly with $\sin\theta/\lambda$ than was assumed on the basis of the Mn^{+2} form factor.¹²

MAGNETIC SCATTERING FROM UNTWINNED NiO CRYSTALS

The preceding analysis points up the difficulty of distinguishing between a magnetic structure in which the magnetic moment directions are multiple within a unit cell and one in which the multiple directions are produced by a domain texture. Thin section studies had demonstrated the feasibility of growing untwinned single crystals so an attempt was made to measure the magnetic scattering from untwinned crystals despite their small size. Two sections approximately $2 \times 3 \times 0.08$ mm³ were polished with faces parallel to (110) . This was the maximum thickness which was sufficiently transparent for optical study of internal texture. The sections were annealed at 1500°C, but a completely untwinned individual was not obtained. It was possible, however, to shield portions of the crystals behind sections of cadmium which absorbed the thermal neutrons completely, so that scattering could be obtained from volumes which microscopically appeared

TABLE V. Neutron scattering from untwinned portions of single crystals of NiO.

	Magnetic				Nuclear			
	(111) ($\bar{1}\bar{1}\bar{1}$)	($1\bar{1}\bar{1}$) ($\bar{1}\bar{1}1$)	($1\bar{1}1$) ($\bar{1}\bar{1}\bar{1}$)	($1\bar{1}\bar{1}$) ($\bar{1}\bar{1}1$)	(222) ($\bar{2}\bar{2}\bar{2}$)	($2\bar{2}\bar{2}$) ($\bar{2}\bar{2}2$)	($2\bar{2}2$) ($\bar{2}\bar{2}\bar{2}$)	($2\bar{2}2$) ($\bar{2}\bar{2}2$)
Crystal A	0	0	714	356	756	684	686	718
	0	0	803	310	648	762
Crystal B	0	0	442	748	786	856	705	852
	0	0	464	856	785	876	732	752

¹² L. M. Corliss and J. M. Hastings (private communication).

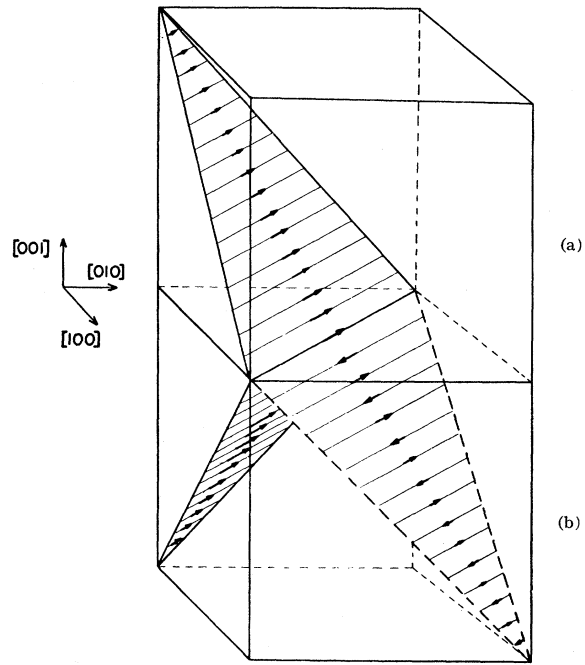


FIG. 7. Antiferromagnetic domain configuration in annealed crystal of nickel oxide. A (111) plane is shown and the spin directions in adjacent planes are reversed.

to be single domain. Unfortunately, the untwinned single-crystal volume was only about 0.10 mm³ and the diffracted intensities were quite small. The section was mounted to rotate about a face diagonal arbitrarily defined to be $[\bar{1}10]$, oriented by means of the nuclear reflections, and the set of magnetic reflections (111) , $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$ measured. The section then was remounted to rotate about $[110]$, reoriented, and the remaining members of the form $(\bar{1}11)$, $(1\bar{1}\bar{1})$, $(1\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$ measured.

The integrated intensities obtained from the two crystals are summarized in Table V. The agreement of the nuclear reflections indicates the intensities are reliable to approximately 15%. Of the eight $\{111\}$ magnetic reflections, four were absent ($<3\sigma$) and the remaining four reflections occurred in pairs in which the ratio of intensities was approximately 2:1. The similarity of these results with those obtained from the annealed "massive" NiO crystal suggest that the data obtained from the latter is also characteristic of an untwinned crystal.

The distribution in reciprocal space of the magnetic scattering from the untwinned sections of nickel-oxide crystal is not consistent with that expected from a single-domain crystal of the $A_{[UVW]}$ structure. If the optical evidence for the absence of twins were accepted, and if the assumption of a single magnetic spin direction in a single domain were retained, it would be necessary to modify the notion of a relationship between the magnetic structure and the crystalline deformation.

In the $A_{(111)}$ structure, the distribution of magnetic scattering among the eight $\{111\}$ reflections is independent of the direction of the atomic spins within the ferromagnetic sheet, and consequently antiferromagnetic domains which differ only by the rotation of the axes of magnetization within the (111) plane cannot explain the observed intensity distribution. To account for the results on the basis of the single axis $A_{[UVW]}$ structure, it is necessary that there be a change in crystallographic orientation of the ferromagnetically coupled sheet of atomic spins. Accordingly, either hypothesis that the deformation is a consequence of exchange-striction or magnetostriction requires the existence of twins in the volume of crystal observed by the neutrons.

Since the neutron scattering is not consistent with a single domain-single magnetic axis configuration, the magnetic structure is based on a multispin arrangement, such as B , or alternatively domains of the $A_{(111)}$ structure were present even though they were not detected by the optical observations. The absence of optically detectable domains can be explained by assuming that either the domains were present in thin lamellae parallel to the section face so that the light passed successively through them, or that the domain dimensions were comparable to the wavelength of light and consequently could not be resolved.

PERIODICITY OF MAGNETIC SCATTERING SYSTEM

In all crystals of nickel oxide studied to date, the atomic spins have been parallel and antiparallel to more than one direction in the crystal. Consequently, it is pertinent to inquire about the nature of the short-range and long-range correlations between moments. Some information of this type was obtained by observing the shapes of the magnetic diffraction peaks, and the manner with which they varied with temperature.

The half-width of the (111) magnetic peak was measured at room temperature and at temperature close to the antiferromagnetic Néel temperature (Fig. 8). The half-width of the magnetic peak was $0^{\circ}29'$, equal within experimental error to the resolving power of the slit system and approximately the same as that observed for the nuclear (222) peak. Any diffraction broadening due to interruptions of the long-range correlation of moments is less than $0^{\circ}06'$, and the minimum domain size may be estimated from the usual line-broadening equation,

$$t \gtrsim \frac{\lambda}{B \cos \theta} \sim \frac{1}{0.001} = 1000 \text{ \AA.}$$

When nickel oxide is heated to a temperature close to 250°C , the long-range moment correlation disappears and the coherent magnetic scattering decreases abruptly. The dashed curve in Fig. 8 shows that when

the long-range magnetic order had decreased to the extent that the coherent Bragg scattering was 1% of the room temperature value, the half-width of the magnetic peak appeared to be slightly increased, of the order of $0^{\circ}48'$ compared to $0^{\circ}29'$ previously. A simple interpretation of the line widths in terms of a "magnetic particle size" suggests there are regions of magnetic order extending for 100–200 Å even when 99% of the long-range correlation has disappeared. The analogy of a magnetic particle size is undoubtedly an oversimplification; the magnetic peak at 262°C is noticeably asymmetric, and the shift in peak position from $12^{\circ}10'$ at 25°C to $12^{\circ}00'$ at 262°C is too large to be accounted for purely by thermal expansion. The asymmetric shape and peak shift suggest that the breakdown of magnetic order might be profitably analyzed by methods similar to those used by Warren and co-workers in their studies of work hardening and the faulting in carbon black.

A search was made in the vicinity of (111) at 260°C for diffuse magnetic scattering¹³ which would be indicative of short-range correlations of moments still being present although the long-range order had disappeared. The lengths of the vertical bars in Fig. 8 are proportional to the statistical uncertainty in the measurements. Within experimental error, no diffuse scattering could be detected; estimating from the counting statistics a diffuse intensity 0.2% of the peak

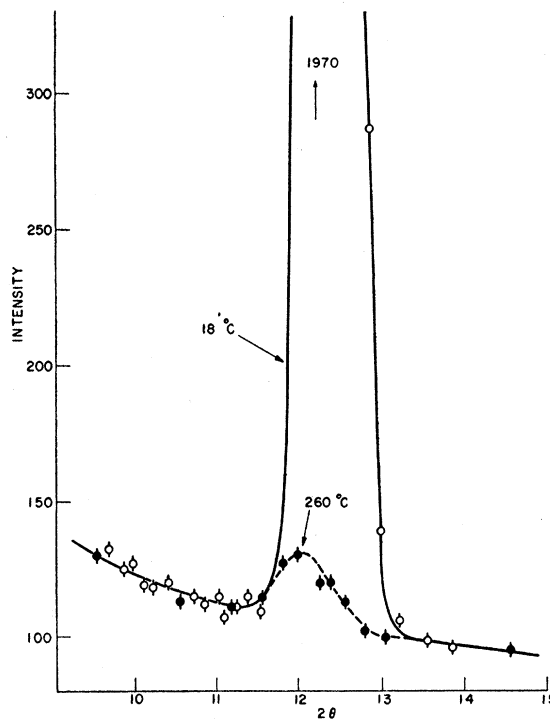


Fig. 8. Magnetic scattering from nickel oxide crystal at room temperature and near the Néel temperature.

¹³ A. W. McReynolds and T. Riste, Phys. Rev. **95**, 1161 (1954).

intensity or 4% of the background would have been observed.

The magnetic structure in an annealed crystal appears to be at least a quasi-equilibrium configuration in the sense that the structure may be regenerated after being heated into the paramagnetic state by cooling to the antiferromagnetic state. The peak intensity above background of the (111) reflection measured as a function of increasing and decreasing temperature is shown in Fig. 9. The coherent magnetic scattering disappears at 533°K, in reasonable agreement with the Néel temperature obtained from magnetic measurements. The temperature dependence of the magnetic scattering has been compared with that calculated by normalizing at 300°K and assuming a Brillouin dependence of the moment with $J=1$ and $T_c=533^\circ\text{K}$.

DISCUSSION

The series MnO, FeO, CoO, and NiO crystallize in similar rocksalt-like structures and the regular increase of the antiferromagnetic Curie temperature with increasing atomic number indicates that the exchange energy increases monotonically with the filling of the 3*d* shell. There are widely differing crystalline anisotropies in the antiferromagnetic state, and a variety of explanations have been offered for the relationship between the crystal deformation and the atomic spin structure. Greenwald and Smart¹⁴ have discussed the

deformations as a consequence of the dependence of exchange energies on interatomic distances, and alternatively Li¹⁰ has attributed the deformation to anisotropy magnetostriction. Estimates of the anisotropy energies of FeO and CoO by Kanamori⁵ suggest that orbital multipole interactions are the principal source of magnetic anisotropy in the deformation-free state of the crystals, but that the crystal deformation is a consequence of magnetostriction arising from crystalline field interactions.

The interactions in MnO and NiO are most susceptible to theoretical treatment since spin-orbit interactions may be neglected. For a system of dipoles in the cubic rocksalt structure, Kaplan⁴ found the minimum energy configuration an array of parallel dipoles in a {111} plane, but did not identify any optimum direction within the plane. Loeb and Goodenough,⁶ on the other hand, conclude that there is an optimum orientation of the dipoles within the {111} plane along a $\langle 110 \rangle$ direction. This is consistent with the present interpretation of the neutron scattering from NiO crystals, where it was found that the moment directions were $[\bar{1}10]$ and $[1\bar{1}0]$ predicated on the assumption that the crystal was composed of domains of single-spin axis structure.

Loeb and Goodenough have given expressions for the dipole-dipole energy of multispin axis structures in a rocksalt-like structure, and Keffer and O'Sullivan¹⁵ have shown that there is an identical functional dependence of the dipolar interaction energy and the intensities of powder neutron diffraction peaks on the parameters which describe the orientation of the magnetic substructures. Consequently, all structures which are compatible with the neutron data from powders for the $A_{(111)}$ structure similarly are compatible with the requirement of minimum dipole-dipole energy. Conversely, the requirement that a spin system possess minimum dipolar anisotropy provides no basis for discriminating between single or multiple spin axis structures.

The calculations presented here show that neutron diffraction patterns from powders of MnO, NiO, CoO, and FeO provide an unequivocal assignment of the location and direction of the atomic spins only if it is known that the moments are parallel to a single crystallographic axis. Alternatively, many multispin axis structures are compatible with the powder data. Although in principle the alternatives can be distinguished by single-crystal neutron diffraction, the problem is complicated by the presence of antiferromagnetic domains. The present results of neutron scattering from crystals of nickel oxide clearly show that in all crystals examined, either the ferromagnetic sheets or the atomic spins were parallel to more than one crystal direction. This can be interpreted on the basis of either (a) a polydomain-single magnetic axis

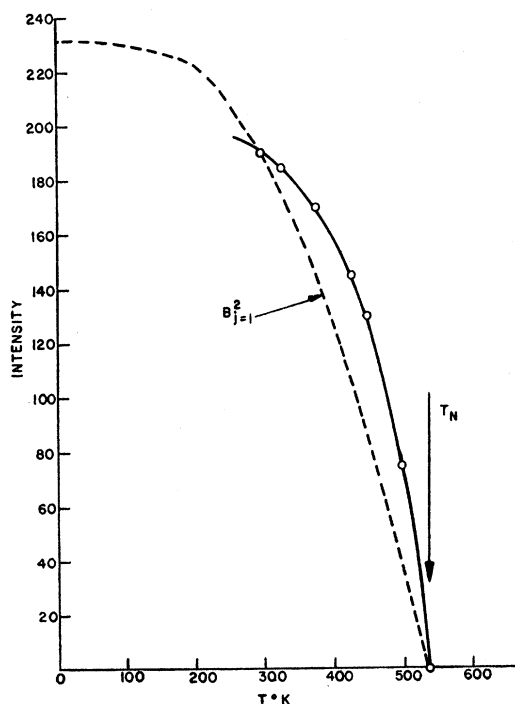


FIG. 9. Magnetic scattering from (111) planes in nickel oxide as function of temperature.

¹⁴ S. Greenwald and J. S. Smart, Phys. Rev. 82, 113 (1951).

¹⁵ F. Keffer and W. O. Sullivan, Phys. Rev. 108, 637 (1957).

crystal, or (b) a single domain-multimagnetic axis crystal.

From dipolar anisotropy considerations, structure *AC* (corresponding to Fig. 3 of Loeb and Goodenough) is an attractive solution for the spin arrangements in rhombohedral MnO and NiO. Unfortunately, the NiO single-crystal data eliminate this attractive model, although conceivably it still may be appropriate for MnO. Structures such as *I* are attractive spin arrangements for CoO since the x-ray observations indicate the crystal symmetry is tetragonal below the Néel temperature. However, because of the large crystal anisotropy (the crystal is deformed 1.2% at 77°K) it is doubtful that simple dipolar interactions predominate, and the most recent powder neutron diffraction data indicate the magnetic axis to be approximately $[11\bar{7}]$, a compromise between the dipolar forces tending to orient the spins within the (111) plane, and the crystal field interaction favoring a direction parallel to the tetragonal axis.

The alternative spin arrangements (a) single axis-multidomain and (b) multiaxis-single domain differ basically in regard to the extent of the long-range correlation between nonparallel spins. If the predominant correlation is the short-range ordering of parallel spins, the single magnetic axis solution $A_{[UVW]}$ is obtained. This solution has the virtue of simplicity and leads to the conclusion that the spin arrangement in the entire group of rocksalt-like oxides is the same, and that the direction of magnetization depends upon the coupling between the spins and the crystalline fields. Thus for MnO and NiO, the interaction is predominantly dipolar and the spins lie in (111) sheets. In FeO the crystalline field anisotropy predominates and the moments are parallel to $[11\bar{1}]$, whereas in CoO the compromise between crystalline field and dipolar anisotropies tip the magnetic axis approximately 12° away from the tetragonal axis toward the (111) plane. These conclusions are consistent with the neutron scattering from crystals of NiO if it is assumed that in nearly perfect, annealed crystals, antiferromagnetic domains are present for which there is a common direction of magnetization. This signifies the presence of twins, and of the four possible spin axes, only those exist which conserve the direction of magnetization through the twin boundary.

Although the alternative multispin axis arrangements cannot be eliminated, it should be recalled that one of the principal reasons for introducing these complicating considerations was to eliminate the discrepancy that the crystal symmetry of the monoxides in the antiferromagnetic state appeared to be different when observed by neutrons and x-rays. The present data clearly show that the antiferromagnetic spin arrangement in NiO does not have threefold symmetry; the true symmetry of NiO must be less than rhombohedral and the distortion apparently is so small

that it has not been detected by x-ray methods. For the $A_{[110]}$ structure, in nickel oxide a magnetostrictive distortion of the order of 10^{-5} perpendicular to the $[111]$ direction would appear reasonable, significantly smaller than the 10^{-3} contraction which has already been observed parallel to $[111]$.

No information of this type is currently available on the other antiferromagnetic oxides. It would be desirable to obtain three-dimensional single-crystal neutron diffraction data from NiO and the other antiferromagnets, but it would appear wise first to develop methods which give assurance that the crystals contain a single antiferromagnetic domain. Among the interesting possibilities for investigating domain texture is the study of the effect of thermal, stress, and magnetic annealing by both neutron scattering and magnetic torque measurements. However, it appears possible to account for the experimental observations presently available on nickel oxide by the single magnetic axis structure which leads to the conclusion that the interaction between magnetic moments on both nearest and next nearest neighboring nickel ions is parallel and antiparallel.

APPENDIX

The scattering of neutrons by a periodic arrangement of magnetic moments is shown in Fig. 10. The direction of the incident neutron is described by the unit vector \mathbf{k}_0 , the scattered neutron by \mathbf{k} , and λ is a unit vector describing the polarization state of the neutron. In a single magnetic axis system, the direction of atomic moments is parallel (or antiparallel) to a unit vector \mathbf{K} . The scattering vector \mathbf{e} is normal to the Bragg plane, and the scattering may be described in terms of a magnetic interaction vector \mathbf{q} which is defined by the equation

$$\mathbf{q} = \mathbf{e}(\mathbf{e} \cdot \mathbf{K}) - \mathbf{K}, \quad (1)$$

$$|\mathbf{q}|^2 = \sin^2 \alpha. \quad (2)$$

If the neutron beam is unpolarized, the magnetic and nuclear scattering are incoherent and the magnetic scattering is given by

$$q^2 \sum_{\nu\nu'} \rho_\nu \rho_{\nu'}^* e^{i(\mathbf{k}-\mathbf{k}_0) \cdot (\mathbf{r}_\nu - \mathbf{r}_{\nu'})}, \quad (3)$$

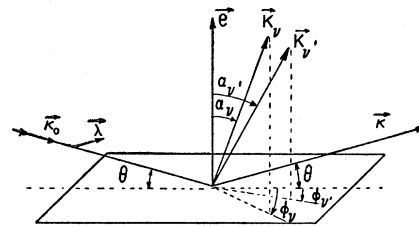


FIG. 10. Neutron scattering from multimagnetic axis system. \mathbf{k}_0 and \mathbf{k} are unit vectors proportional to the incident and scattered neutron, λ is the polarization state of the neutron, \mathbf{e} the scattering vector, θ the Bragg angle, and \mathbf{K}_ν is a unit vector defining the magnetic moment of the ν th atom.

where p is the magnetic scattering amplitude and \mathbf{r} is the position vector of the ν th atom. If the atomic moment is due only to electron spin (either because the atom is in an S state or because the orbital moment is quenched by the crystalline field), the magnetic scattering amplitude is given by

$$p = (e^2\gamma/mc^2)Sf = 0.539 \times 10^{-12} Sf \text{ cm}, \quad (4)$$

where S is the spin quantum number and f is the magnetic form factor.

To describe the scattering from a system in which the atomic moments make arbitrary angles with each other, in addition to α , the azimuthal angle ϕ is required to uniquely describe the moment. The magnetic scattering of an unpolarized beam is given by the equation:

$$\sum_{\nu\nu'} p_\nu p_{\nu'}^* e^{i(\mathbf{k}-\mathbf{k}') \cdot (\mathbf{r}_\nu - \mathbf{r}_{\nu'})} \sin\alpha_\nu \sin\alpha_{\nu'} \cos(\phi_\nu - \phi_{\nu'}). \quad (5)$$

This is equivalent to the formulas given by Shull and Wollan.⁴ It easily is seen that for a system in which all the moments are parallel (ferromagnetic case) or antiparallel (single-axis antiferromagnetic case):

$$\phi_\nu - \phi_{\nu'} = 0 \text{ or } \pi, \quad (6)$$

and Eq. (5) reduces to Eq. (3).

For convenience in specific structure calculations, it is useful to define the magnetic structure factor F_{mag} :

$$F_{\text{mag}} = \sum_\nu p_\nu e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_\nu} \sin\alpha_\nu e^{i\phi_\nu}. \quad (7)$$

It is easily shown that Eq. (5) is obtained by forming the complex conjugate,

$$F_{\text{mag}}^* = \sum_\nu p_\nu^* e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_\nu} \sin\alpha_\nu e^{-i\phi_\nu}, \quad (8)$$

and consequently

$$I_{\text{mag}} = K(\theta, \mu, T) |FF^*|. \quad (9)$$

The proportionality constant K depends on the experimental arrangement, scattering angle θ , absorption factor μ , and temperature factor T .

The magnetic scattering from MnO, FeO, CoO, and NiO can be indexed on the basis of a magnetic unit cell where $a_{(\text{magnetic})} = 2a_{(\text{nuclear})}$. Only those magnetic reflections with hkl all odd are observed. The magnetic structure is built up from eight magnetic substructures, M_j , generated by atomic moments with position coordinates $x_j y_j z_j$:

M_j	$x_j y_j z_j$		
1	fc+0	0	0
1'	$+\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
2	$+\frac{1}{4}$	$\frac{3}{4}$	0
2'	$+\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
3	$+\frac{3}{4}$	0	$\frac{1}{4}$
3'	$+\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$
4	$+\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$
4'	+0	$\frac{3}{4}$	$\frac{3}{4}$

The face-centering fc requires that moments with identical configuration are located at

$$(000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}) + x_j y_j z_j. \quad (10)$$

The magnetic substructures are associated in pairs $M_j M_{j'}$, and as a consequence of the exchange interaction, if the moment direction of an atom in substructure M_j is $\mathbf{S}_j = [U_j V_j W_j]$, then the corresponding direction $M_{j'}$ is $\mathbf{S}_{j'} = -\mathbf{S}_j = [-U_j -V_j -W_j]$. The pair $M_j M_{j'}$ is an antiferromagnetic substructure. These relations are shown in Fig. 3 where it may be seen that the magnetic structure is based on four antiferromagnetic substructures and that the (111) plane is populated by moments from each. The general problem is to discover the spin vectors $\mathbf{S}_1 \mathbf{S}_2 \mathbf{S}_3 \mathbf{S}_4$. For the special case $\mathbf{S}_1 = \pm \mathbf{S}_2 = \pm \mathbf{S}_3 = \pm \mathbf{S}_4$ there is a single magnetic axis and the problem is reduced to that treated previously.

For a structure containing only one kind of magnetic atom, substitution of the coordinates $x_j y_j z_j$ (10) into (7), gives for the generalized magnetic structure factor

$$F_{(hkl)} = 8p \{ \sin\alpha_1 e^{i\phi_1} + e^{2\pi i(h-k)/4} \sin\alpha_2 e^{i\phi_2} + e^{2\pi i(3h+1)/4} \sin\alpha_3 e^{i\phi_3} + e^{2\pi i(2h+k+1)/4} \sin\alpha_4 e^{i\phi_4} \}. \quad (11)$$

Assuming the magnetic scattering amplitudes and form factors are known, the multiaxis problem contains eight independent parameters $\alpha_j \phi_j$. It is clear that in the absence of further information or limitations, neutron scattering from powders is unlikely to define an unique solution to the multiaxis structure.

ACKNOWLEDGMENTS

The author would like to thank Dr. S. Tamor for assistance in formulating the neutron scattering problem, to Dr. E. W. Hart for pointing out a matrix transformation method which greatly simplified the calculation of multispin structures, and to Dr. L. M. Corliss and Dr. J. M. Hastings for many critical discussions.

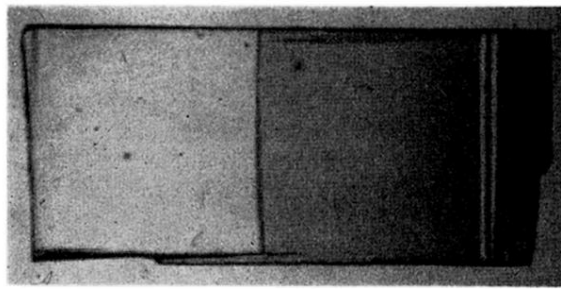


FIG. 5. Photomicrograph of nickel oxide thin section. The specimen is about $1 \times 2 \times 0.03$ mm and in this case the domains are crystallographic twins.