APPENDIX

Lindhard and Scharff applied Eq. (3) to the statistical Thomas-Fermi (TF) model of the atom. This leads directly to Bloch's relation $I=KZ$. It is of interest to consider $I(Z)$ for the Thomas-Fermi-Dirac (TFD) model, which includes the exchange interaction between electrons.[8] However, the TFD density distribution is not an explicit function of Z and hence not suited for the present purpose. A sufficiently accurate approximation is the TFX distribution, which follows from the TF distribution by a simple coordinate contraction $r_{\mathrm{TFX}}=\lambda^{-1}r_{\mathrm{TF}}$. The scaling parameter λ can be determined by the variational condition

$$\frac{\partial E}{\partial\lambda}=\frac{\partial}{\partial\lambda}[\lambda^2E_{\mathrm{kin}}+\lambda(E_{\mathrm{pot}}+E_{\mathrm{exch}})]=0.$$

Introducing the proper expressions[21] for the E in terms of the solution φ_0 of the TF equation $\varphi_0''=\varphi_0^{\frac{3}{2}}x^{-\frac{1}{2}}$, with $x=\mu^{-1}r$, one finds

$$\lambda_0=1+\left(\frac{\pi}{2}\right)^{\frac{1}{3}}\frac{\kappa_a'}{\kappa_k}\frac{\mu}{Z^{\frac{1}{3}}}\int_0^\infty\varphi_0^2dx\bigg/\int_0^\infty\varphi_0^{\frac{5}{2}}x^{-\frac{1}{2}}dx$$
$$=1+0.16Z^{-\frac{2}{3}}.$$

The coefficient 0.16 is a lower limit for the $Z^{-\frac{2}{3}}$ dependence of λ. Inserting $\rho_{\mathrm{TFX}}=(Z\lambda_0^3/4\pi\mu^3)(\varphi_0/x)^{\frac{3}{2}}$ in Eq. (3) yields

$$I_0=0.451\bar{\chi}_0\lambda_0^{\frac{3}{2}}Z\text{ ry}.$$

For the evaluation of the constant $\bar{\chi}_0$, one may use the fact that in the statistical model ω_0 and ω_p depend linearly on Z. If

$$\omega_0^2=-(e/mr)(dP/dr)$$

with

$$P=(Ze/r)-(1-1/Z)\int_0^\infty e\rho_{\mathrm{TF}}(\xi)|\xi-\mathbf{r}|^{-1}d^3\xi,$$

one finds for $Z\gg1$ and with the abbreviation

$$q_0=\varphi_0-x\varphi_0',$$

that

$$\ln\bar{\chi}_0\simeq\tfrac{1}{2}\int_0^\infty\varphi_0^{\frac{3}{2}}x^{\frac{1}{2}}dx\ln(1+q_0/x^{\frac{3}{2}}\varphi_0^{\frac{3}{2}})=\ln1.78.$$

Hence,

$$I_0=0.802\lambda_0^{\frac{3}{2}}Z\text{ ry}\simeq10.9(1+0.25Z^{-\frac{2}{3}})Z(\text{ev}).$$

In essence, this result confirms an earlier estimate by Jensen[22] for a highly simplified atomic model, and agrees with experimental observations.[8,23] It approaches Bloch's relation for large Z.

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[21] P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Wien, 1949). See pp. 390–392.

[22] H. Jensen, Z. Physik **106**, 620 (1937).

[23] W. Brandt (to be published).

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Crystal Structure and Ferrimagnetism in $NiMnO_3$ and $CoMnO_3$

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X-ray diffraction studies of individual crystals of $NiMnO_3$ and $CoMnO_3$ show that these compounds have the structure of ilmenite (space group $R\bar{3}$). The crystals have a plate-like crystal habit with the threefold symmetry axis perpendicular to the faces of the platelet. Positions of atoms within the unit cell have been determined by comparing calculated structure factors with those obtained from x-ray powder patterns. There are two Ni-O-Mn configurations that appear to be favorable to a magnetic superchange interaction, and these are sufficient to extend magnetic ordering in three dimensions.

I. INTRODUCTION

SUPEREXCHANGE interactions in rhombohedral sesquioxides with particular reference to Cr_2O_3, $\alpha-Fe_2O_3$ and their solid solutions have been discussed by Li.[1] The discussion can now be extended to include ferrimagnetism in the compounds $NiMnO_3$ and $CoMnO_3$ which have the same structure as the mineral ilmenite ($FeTiO_3$).[2–4] This ABX_3 structure is related to that of Cr_2O_3, where both A and B are Cr atoms. The metal atoms of ilmenites are arranged in alternate layers between oxygen layers and are ordered in the sequence *AB-BA-AB-BA* along the body diagonal of the rhombohedron.

The principal geometric parameters for qualitative understanding of superexchange interactions are the metal-to-oxygen distances and the metal-oxygen-metal angles. In order to consider such interactions in $NiMnO_3$ and $CoMnO_3$, the exact positions of the individual atoms must be determined. Proof of ordering of the metals into the *AB-BA-AB* sequence was obtained from x-ray diffraction studies of individual crystals. Positions of atoms within the unit cell were determined

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[1] Y. Y. Li, Phys. Rev. **102**, 1015 (1956).

[2] The synthesis and bulk magnetic properties of these compounds have been discussed by Swoboda, Vaughan, and Toole[3] and Bozorth and Walsh.[4]

[3] Swoboda, Vaughan, and Toole, J. Phys. Chem. Solids (to be published).

[4] R. M. Bozorth and D. E. Walsh, J. Phys. Chem. Solids (to be published).

from an analysis of the line intensities of x-ray powder patterns. From these data, metal-oxygen distances and metal-oxygen-metal angles were obtained.

II. X-RAY DIFFRACTION BY CRYSTALS

Small plate-like crystals of $NiMnO_3$ or $CoMnO_3$ are obtained from acidic aqueous media. The crystal platelets are hexagonal in shape, approximately 0.75 mm in diameter, and 10–50 microns thick. The threefold symmetry axis is perpendicular to the faces of the platelet. X-ray diffraction patterns of these crystals, obtained with a Buerger precession camera, were analyzed by use of a hexagonal system of reference.

Comparison of the upper level ($l\neq 0$) diffraction patterns of crystals of $NiMnO_3$ and $CoMnO_3$ shows clearly that the symmetry is rhombohedral. However, the first upper level photograph shows symmetry $3m$ and not the 3 symmetry present in the analogous pattern of an ilmenite single crystal. Cone-axis photographs, which reveal the symmetry of all upper levels, show that the only diffraction symmetry common to all levels is 3. It was therefore concluded that the symmetry $3m$ of the first upper level was caused by twinning normal to the threefold symmetry axis. A crystal containing a mixture of right- and left-handed threefold screw axes would give the observed diffraction pattern. The crystal platelets were so thin that x-ray patterns from different sections along the c axis could not be obtained. Thus, it is not known whether the crystals contain only one twin boundary or whether there is multiple twinning.

Alternatively, metal atoms arranged at random could also give a first level diffraction pattern with symmetry $3m$. If this were the case the diffraction pattern of $NiMnO_3$ would be similar to that of a compound M_2O_3 where the scattering factor of M is the average of the scattering factors of Ni and Mn. It is apparent from Table I, which compares the reflections observed from $NiMnO_3$ and $CoMnO_3$ crystals with those observed from single crystals of corundum (Al_2O_3) and natural ilmenite, that $NiMnO_3$ and $CoMnO_3$ do not have the M_2O_3 structure. Therefore, it is concluded that these compounds have the symmetry $R\bar{3}$ (C_{3i}^2) of ilmenite.

TABLE I. First upper level x-ray reflections of rhombohedral crystals.

Corundum Al_2O_3	Ilmenite $FeTiO_3$	$NiMnO_3$ or $CoMnO_3$
Absent	201	201 $0\bar{2}1$
Absent	021	021 $\bar{2}01$
Absent	$\bar{2}\bar{2}1$	$\bar{2}\bar{2}1$ 221
$1\bar{2}1$	Absent	Absent
$\bar{2}11$	$\bar{2}11$	$\bar{2}11$ $\bar{1}21$
$\bar{3}\bar{1}1$	Absent	Absent
$\bar{1}\bar{3}1$	$\bar{1}\bar{3}1$	$\bar{1}\bar{3}1$ 311
231	Absent	Absent
321	321	321 $\bar{2}\bar{3}1$

TABLE II. Observed x-ray diffraction lines.

	$NiMnO_3$			$CoMnO_3$		
	d_{obs} (A)	d_{calc} (A)	$\lvert F_{hkl}\rvert^2$	d_{obs} (A)	d_{calc} (A)	$\lvert F_{hkl}\rvert^2$
110	3.60	3.60	16	3.63	3.63	15
211	2.65	2.65	51	2.67	2.67	72
$\bar{1}\bar{1}0$	2.45	2.45	55	2.67	2.47	55
210 120	2.15	2.155	23	2.17	2.17	26
221	1.80	1.80	43	1.81	1.815	57
321 231	1.66	1.66	100	1.68	1.675	100
310 130	1.45	1.44	55	1.46	1.46	61
211	1.415	1.42	64	1.43	1.425	77

III. ANALYSIS OF POWDER DATA

Diffraction patterns of $NiMnO_3$ and $CoMnO_3$ powders were taken using cobalt $K\alpha$ radiation. The observed structure factors were obtained from line intensities using the methods outlined in the international tables.[5] Since the measurements were made with a Norelco diffractometer, the absorption factor could be taken as a constant independent of the Bragg angle.[6] Interplanar spacings listed in Table II were calculated using the cell dimensions given by Swoboda, Vaughan, and Toole[3]: $a=4.905\pm 0.001$ A, $c=13.59$ ± 0.01 A for $NiMnO_3$ and $a=4.933\pm 0.001$ A, $c=13.71$ ± 0.01 A for $CoMnO_3$. Since intensity calculations are simpler for the rhombohedral cell than for the hexagonal cell, a rhombohedral indexing is used in Table II. The rhombohedral cell constants are $a_r=5.343$ A, $\alpha=54°39'$ for $NiMnO_3$ and $a_r=5.385$ A, $\alpha=54°31'$ for $CoMnO_3$.

The best fit between observed and calculated structure factors was obtained for the lines of Table II by minimizing the reliability factor

$$\frac{\sum \big| |F_{hkl}|_{obs} - |F_{hkl}|_{calc} \big|}{\sum |F_{hkl}|_{obs}},$$

as is common practice. Values of atomic scattering factors and equations for structure factors for the space group $R\bar{3}$ were obtained from the International Tables[5] (see Table III). Corrections to the atomic scattering factors due to dispersion by the K electrons were obtained from tables given by James.[7]

The positions in the rhombohedral cell for compounds

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[5] *Internationale Tabellen zur bestimmung von Kristallstrukturen* (Borntraeger, Berlin, 1935), Vols. I and II.

[6] H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures* (John Wiley and Sons, Inc., New York, 1954), pp. 376–7.

[7] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1954), p. 608.

TABLE III. Observed and calculated values of $|F_{hkl}|$.

	NiMnO$_3$		CoMnO$_3$	
	obs	calc	obs	calc
110	4.0	3.4	3.8	3.2
211	7.2	7.5	8.5	8.5
$1\bar{1}0$	7.4	7.1	7.4	7.4
210 120	4.8	4.7	5.1	5.0
220	6.6	6.9	7.5	7.4
321 231	10	10	10	10
310 130	7.4	8.2	7.8	8.9
$\bar{2}11$	8.0	9.1	8.8	9.8

of the ilmenite structure are as follows[5]:

$$\text{metals: } \pm u,u,u;\ v,v,v;$$

$$\text{oxygens: } \pm(xyz,zxy,yzx).$$

A Patterson series[8] along the [111] diagonal was used to select a range of trial values for the metal positions. In order to limit the number of trial values for the oxygen positions, the condition $x+y=2z$ was imposed. This condition, which is required by symmetry for compounds of the corundum structure, is found to hold for ilmenite[9] and most ilmenite-type titanates.[10] The best over-all fit to the data was obtained for the following positions[11]:

NiMnO$_3$		CoMnO$_3$	
Ni:	$u=0.352$	Co:	$u=0.354$
Mn:	$v=0.148$	Mn:	$v=0.146$
O:	$x=0.56$	O:	$x=0.57$
	$y=-0.06$		$y=-0.07$
	$z=0.25$		$z=0.25.$

As would be expected, the calculated structure factors were not very sensitive to oxygen positions because of the low atomic scattering factor of oxygen. The reliability factor was 6% for both NiMnO$_3$ and CoMnO$_3$.

IV. EXCHANGE INTERACTIONS IN NiMnO$_3$ AND CoMnO$_3$

A discussion of the superexchange interaction between two metal atoms and the intervening oxygen atom has been given by Li[1] for the rhombohedral oxides Cr$_2$O$_3$, $\alpha-$Fe$_2$O$_3$, and FeTiO$_3$. In this discussion, he makes use of Anderson's[12] conclusions that the most favorable metal-oxygen-metal angle is 180°. The possible configurations listed by Li for Cr$_2$O$_3$ and $\alpha-$Fe$_2$O$_3$ have the following analogs in NiMnO$_3$ and CoMnO$_3$:

	NiMnO$_3$	CoMnO$_3$
(1) $A_1-\text{O}-B_1$		
qq	$q=2.06$ A	$q=2.13$ A
	$\beta=84°42'$	$\beta=84°11'$
(2) $A_2-\text{O}-\text{B}_4$	$q=2.06$ A	$q=2.13$ A
$B_4-\text{O}-A_3$	$p=1.91$ A	$p=1.89$ A
qp	$\beta=132°14'$	$\beta=131°03'$
(3) $B_2-\text{O}-B_4$	$q=2.06$ A	$q=2.13$ A
$A_4-\text{O}-A_3$	$p=1.91$ A	$p=1.89$ A
qp	$\beta=92°52'$	$\beta=92°27'.$

A diagram of the unit cell is shown in Fig. 1 where the large open circles and the large cross-hatched circles represent the two different metals and the small circles represent the oxygen atoms. This figure is similar to that presented by Li for equivalent metals.

Li assumed that configuration (3) would produce a very weak interaction because the near 90° angle is most unfavorable for a superexchange interaction. He assumed that the magnetic lattice was extended in three dimensions by combination of interactions (1) and (2). Interaction (2) should be favorable for exchange because of the obtuse angle. The acute angle of configuration (1) makes it seem unfavorable for a superexchange interaction. However, there are three equivalent oxygen atoms in this configuration. Li concluded that a stong interaction could be expected because of an appreciable overlap between the π orbitals of the group of three equivalent oxygen ions and the $3d\pi$ orbitals of the metal ions. It should be noted, however, that Li assumed that this interaction was necessary in order to extend the magnetic lattice in three dimensions. This assumption is not necessary. As pointed out by Iida,[13] there is a fourth interaction which Li did not discuss,

	NiMnO$_2$	CoMnO$_3$
(4) $B_2-\text{O}-A_3$		
pp	$p=1.91$ A	$p=1.89$ A
	$\beta=122°18'$	$\beta=123°47'.$

This fourth interaction has an obtuse angle and also smaller average metal-oxygen distances than configuration (2). If (2) is considered to be one of the principal interactions, then (4) cannot be neglected, and a combination of (2) and (4) is sufficient to extend the magnetic lattice in three dimensions. These two interactions should be considered as the principal magnetic interactions in the rhombohedral oxides of the corundum or ilmenite structure.

The sign of interactions (2) and (4) determines the nature of the magnetic ordering. Obviously if both are positive, a ferromagnetic oxide results. No rhombohedral ferromagnetic oxide is known. The magnetic lattice of Cr$_2$O$_3$[14] in which the spins of the chromium

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[8] See, for example, H. S. Lipson and W. Cochron, *The Determination of Crystal Structures* (G. Bell and Sons, London, 1953).

[9] R. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. I.

[10] E. Posnjak and J. F. W. Barth, Z. Krist. **88**, 271 (1934).

[11] After this paper had been written there appeared a paper by E. F. Bertaut and F. Forrat [J. Appl. Phys. **29**, 247 (1958)], that gave a brief discussion of ferrimagnetism and crystal structure of NiMnO$_3$. The metal positions given do not agree with values reported here. This recent paper is discussed briefly in the appendix.

[12] P. W. Anderson, Phys. Rev. **79**, 350 (1950).

[13] S. Iida, J. Phys. Soc. Japan **12**, 222 (1957).

[14] B. N. Brockhouse, J. Chem. Phys. **21**, 961 (1953).

ions are arranged in $+-\ +-$ sequence along the [111] diagonal is established if (2) is positive and (4) is negative. The $+-\ -+$ sequence for $\alpha-Fe_2O_3$[15] is achieved if both (2) and (4) are negative. The fourth possibility, a $++\ --$ sequence, results from (2) being negative and (4) being positive. It can be seen from Fig. 1 that the $+-\ -+$ sequence of $\alpha-Fe_2O_3$ is the only one of these four possibilities which will give rise to ferrimagnetism in a compound ABX_3 of the ilmenite structure. The sequences $+-\ +-$ or $++\ --$ result in cancellation of magnetic moments within the individual A and B lattices. Thus, if a compound of the ilmenite structure is ferrimagnetic, interactions (2) and (4) must both be negative.

Ilmenite, itself, is antiferromagnetic below approximately 68°K.[16] Li concluded that this antiferromagnetic ordering arose because the titanium ion is not purely Ti^{+4} but has some Ti^{+3} character. He pointed out that ilmenite must then have a Cr_2O_3 type magnetic lattice rather than the $\alpha-Fe_2O_3$ magnetic lattice. However, antiferromagnetic ordering only within the iron layers by means of the weaker interaction (3) could give parallel and perpendicular susceptibilities of the form reported for ilmenite.[16]

The observed saturation magnetization of approximately 0.7 Bohr magneton/molecule for $NiMnO_3$ and $CoMnO_3$[4] indicates that these compounds are ferrimagnetic, and must therefore have the $\alpha-Fe_2O_3$ magnetic lattice. All metal ions in a given nickel (or cobalt) layer have parallel moments that are antiparallel to those of the adjacent manganese layers.

The work of Bozorth and Walsh[4] suggests that there is considerable orbital contribution to the magnetic moments of the metal ions in $NiMnO_3$ and $CoMnO_3$. Other measurements[17] show that $NiMnO_3$ has a large negative anisotropy, i.e., the direction of easy magnetization is in the basal plane perpendicular to the [111] axis. In this connection, Néel[18] has shown that the magnetic moments of the Fe^{+3} ions in $\alpha-Fe_2O_3$ are also oriented perpendicular to the [111] axis above approximately 260°K, but parallel to the [111] axis below 260°K. In Cr_2O_3[19] and $FeTiO_3$,[16] the magnetic moments of the metal ions appear to be oriented parallel to the [111] axis. Any comprehensive treatment of exchange phenomena in transition metal oxides of the corundum or ilmenite structure must account for the manner in which the magnetic moments of the ions are coupled to the crystal lattice. Since experimental data on the antiferromagnetic compounds Cr_2O_3, $\alpha-Fe_2O_3$, and $FeTiO_3$ can now be augmented with data on the ferrimagnetic compounds $NiMnO_3$ and $CoMnO_3$, these rhombohedral oxides offer an interesting system for theoretical study.

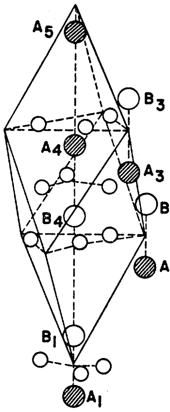

FIG. 1. The $NiMnO_3$ structure. Large open circles represent Mn atoms. Cross-hatched circles represent Ni atoms. Small circles represent O atoms.

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APPENDIX. RECENT PUBLICATION ON $NiMnO_3$

The paper of Bertaut and Forrat[20] gives the nickel and manganese positions as $u=0.363$ and $v=0.153$. Structure factors calculated from their values of u and v do not give good agreement with our experimental data regardless of what oxygen positions are chosen. Their reliability factor is in the order of 18% which is to be compared with 6% when the values $u=0.352$ and $v=0.148$ reported here are used.

The discussion of Bertaut and Forrat suggests that the principal magnetic interaction is between Ni and Mn ions involving an Ni−Mn distance of approximately 3.5 A and that the interaction involving a smaller Ni−Mn distance (2.9 A) is weak. However, the discussion presented here shows that two Ni−O−Mn superexchange interactions are necessary to propagate the magnetic lattice. Crystal parameters presented here give Ni−Mn distances of 3.63 and 3.38 A.

The work of Bozorth and Walsh[4] gives a value of 0.61 Bohr magnetons per molecule for the magnetization of $NiMnO_3$ compared to the higher value of 0.76 Bohr magnetons per molecule given by Bertaut and Forrat. Measurements made in this laboratory gave a value in better agreement with that reported by Bozorth and Walsh.

Bertaut and Forrat do not mention how their $NiMnO_3$ was prepared and present no chemical analysis or x-ray data. For complete information about methods of preparation and chemical analysis of $NiMnO_3$ and also $CoMnO_3$, attention is directed for reference 2 and also to U. S. Patent No. 2 770 523, November 13, 1956 (R. C. Toole), which discloses $NiMnO_3$ and $CoMnO_3$ and methods of preparation.

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[15] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

[16] H. Bizette and B. Tsai, Compt. rend. **242**, 2124 (1956).

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[20] E. F. Bertaut and F. Forrat, J. Appl. Phys. **29**, 247 (1958).