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Neutron Diffraction Study of Antiferromagnetic $MnTiO_3$ and $NiTiO_3$*

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$MnTiO_3$ and $NiTiO_3$ have a rhombohedral crystal structure similar to $FeTiO_3$ in which layers of Fe and Ti atoms alternate along the rhombohedral axis with oxygen layers between them. A powder neutron diffraction study shows that $MnTiO_3$ has a magnetic structure with the Mn^{2+} spins antiparallel within each layer. On the other hand, $NiTiO_3$ has the same magnetic structure as $FeTiO_3$, in which the spins are parallel within each layer and adjacent layers are antiparallel. The spins are directed along the [111] direction in $MnTiO_3$ and perpendicular to it in $NiTiO_3$. In addition to the magnetic study, the nuclear intensities indicate that the Ni and Ti in $NiTiO_3$ are only 88 per cent ordered.

§ 1. Introduction

Extensive studies have been carried out within the past few years on the magnetic properties of ilmenite-type compounds. Ilmenite ($FeTiO_3$) has a rhombohedral lattice[1] very closely related to the corundum structure of hematite (α–Fe_2O_3). Several solid solution systems between these two types of compounds are known, the most thoroughly studied among them being the ilmenite-hematite system.[2,3,4] The antiferromagnetic spin structures of both the end members of this system were determined by neutron diffraction analysis.[5,6] An interesting feature of the solid solutions is the appearance in some of the ilmenite-rich compositions of a

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strong spontaneous magnetization, which was shown to be due to an ordering of Fe and Ti in the α-Fe_2O_3 spin arrangement.[6)]

Ishikawa and Akimoto[7)] have reported recently on the magnetic properties of other compounds isomorphous with ilmenite, such as $MnTiO_3$, $CoTiO_3$, and $NiTiO_3$, as well as their solid solutions with α-Fe_2O_3. The magnetic behavior of the systems containing $CoTiO_3$ and $NiTiO_3$ was found to be quite similar to that of the $FeTiO_3$ series. The $MnTiO_3$ system, however, showed no appreciable spontaneous moment at any composition, a result suggesting that pure $MnTiO_3$ has a different spin structure from pure $FeTiO_3$ and $NiTiO_3$.

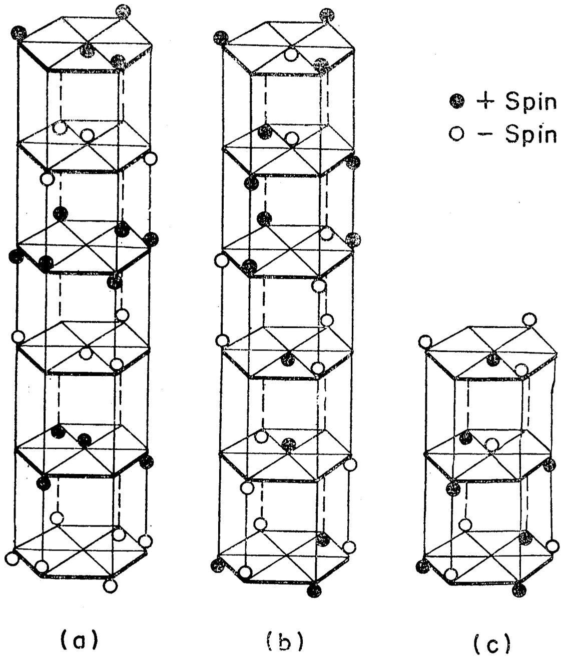


Fig. 1. Three possible magnetic structures for ilmenite-type compounds. The structures are idealized and the Ti layer (the B layer) is omitted. Model (a) is observed in $FeTiO_3$ and $NiTiO_3$ and Model (c) in $MnTiO_3$.

The three possible spin arrangements for ilmenite are illustrated in Fig. 1, in which a hexagonal unit cell containing only the magnetic atoms has been adopted. The layers of magnetic atoms, which may be designated the A layers, are separated by O–B–O layers, where O represents an oxygen layer and B a Ti layer. When α-Fe_2O_3 is added to this ilmenite structure, the magnetic atoms enter the B layers and those on the A layers will result in different structures depending upon the spin configuration of the end member, $MeTiO_3$, where Me represents magnetic atom.

$FeTiO_3$ was found to have the structure shown in Fig. 1(a). in which the arrangement within each layer is ferromagnetic. The addition of Fe on the B layers in this case destroys the ferromagnetic ordering on the A layers, as shown by the neutron diffraction study. The ferrimagnetic ordering based upon the hematite spin lattice develops when the concentration of α-Fe_2O_3 reaches a critical value of about 15 per cent.

Models (b) and (c) have the common feature that the spins in the A layers are antiparallel. In the light of a molecular field calculation[7)] showing that the moments on the B layer are parallel in (b), the observed moment should increase linearly with increasing concentration of α-Fe_2O_3. On the other hand, model (c) results in antiparallel spins on the B layer, and on this basis model (c) was predicted for $MnTiO_3$.

The present paper describes a neutron diffraction study of $MnTiO_3$ and $NiTiO_3$. Besides the magnetic structure there is additional interest, for the case of $NiTiO_3$, in the degree of order of Ni and Ti. Because the two metal positions in the lattice are almost equivalent, some disorder might be expected. Neutron diffraction offers a particular advantage over x-ray diffraction in fixing the degree of order, since the scattering amplitude of Ti (-0.38×10^{-12}cm) and Ni ($+1.03\times10^{-12}$cm) have opposite signs. The same is not true for $MnTiO_3$ because of the manganese scattering amplitude (-0.36×10^{-12}cm).

Approximately 30 grams of $NiTiO_3$ and $MnTiO_3$ powder were prepared for the neutron diffraction study. $NiTiO_3$ was fired according to the method described previously.[8)] A mixture of NiO and TiO_2 was heated in air at 1350°C for three hours, then cooled in the furnace at a rate of approximately 300°C/hr. This compound is quite stable in air and exhibits high electrical resistivity. A chemical analysis of the sample gave the stoichiometric ratio within experimental limits. $MnTiO_3$ was obtained by the reaction of $Mn_3O_4+3TiO_2$ in a vacuum furnace with 10^{-4}mm Hg pressure. The sample was kept at 1300°C for 24 hours and cooled in the furnace to room temperature, the total cooling time being 5–6 hours. Chemical analysis revealed a slight deficiency in Mn content (about 2 per cent). However, an X-ray powder picture did not show any trace of impurities, and the lattice constants are identical with a sample[7] having a Néel temperature of 41°K and an effective moment corresponding to Mn^{2+}. In the present calculation for $MnTiO_3$, the stoichiometric ratio was used with the assumption of divalent manganese. The possible implication of non-stoichiometry will be discussed later.

§ 2. Crystal Structures

Although a hexagonal unit cell is used in Fig. 1 for the magnetic models, the crystal structure can be described more conveniently by using a rhombohedral cell containing two molecular units. The atomic positions are given by the following five parameters for the space group $R\bar{3}$:

2 Me at $\pm(u_1, u_1, u_1)$ Me=Fe, Mn or Ni
2 Ti at $\pm(u_2, u_2, u_2)$
6 O at $\pm(x, y, z)$

If Me and Ti are incompletely ordered, as in the case of $FeTiO_3$, the ordering parameter S must be treated as an additional parameter. Since the magnetic atoms Me constitute the A layers of Fig. 1, S is the fraction of Me at $\pm(u_1, u_1, u_1)$, which ranges from unity for complete order to one half for complete disorder. These six parameters determine the X-ray intensities as well as that part of neutron intensities due to nuclear scattering.

When a magnetic order develops, the total neutron intensity can be written as (see Bacon[9].)

$$I_{hkl}=K(F^2_{\text{nucl}}+q^2F^2_{\text{mag}})$$

where q is determined by the direction of the spins with respect to the scattering vector. The magnetic structure factor, F_{mag}, depends only on the magnetic stoms and is therefore a function of u_1 and S, as well as p, the magnetic scattering amplitude. It should be noted that

$$p=0.269\,\mu f$$

where f, the form factor, is not a well established quantity. The effective magnetic moment μ depends upon the degree of quenching of orbital moment and must be determined experimentally together with the form factor.

The main purpose of the present study, the determination of the magnetic structure, requires the accurate determination of only two parameters from the nuclear scattering peaks, u_1 and S. The oxygen parameters are nevertheless quite important, not only to determine the scale factor K (which in turn decides the magnitude of the magnetic moment for each model considered), but also to calculate the proper metal-oxygen distances. For these reasons a careful analysis of the nuclear diffraction data was carried out. Since only about twenty reflections are available to determine six parameters, the two metal parameters were first fixed by X-ray measurements, and then the remaining four parameters, x, y, z and S, adjusted to obtain the best agreement with the neutron data.

The crystal structures of $MnTiO_3$, $NiTiO_3$, and $FeTiO_3$, were studied by Posnjak and Barth.[1,10] They established the structure of $FeTiO_3$ by using single crystals as well as powder specimens; powder intensities alone were used for $NiTiO_3$. The parameters determined were:

$$u_1(\text{Fe})=0.358 \quad u_2(\text{Ti})=\frac{1}{2}-u_1\,,$$
$$u_1(\text{Ni})=0.353$$

with the same oxygen parameters in each case

$$x=0.555 \quad y=-0.055 \quad z=0.250\,.$$

Though no intensity calculations were performed explicitly for $MnTiO_3$, parameters similar to those of $FeTiO_3$ were expected because of the close resemblance of the powder intensities in these two compounds.

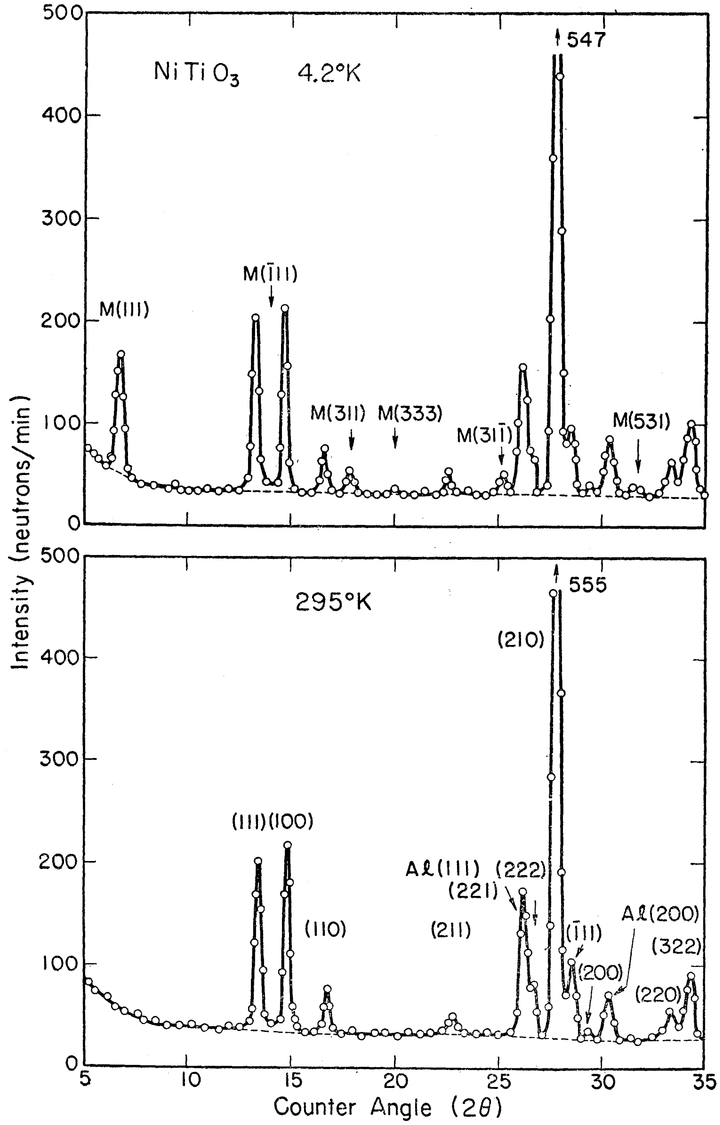
X-ray powder intensities of $NiTiO_3$ and $MnTiO_3$ were taken with a Norelco diffractometer using Cu Kα radiation. The first 13 lines up to (211) were used to determine the metal parameters, by assuming the oxygen parameters given by Posnjak and Barth. The best values are:

$$u_1(\text{Ni})=0.353\pm0.002 \quad u_1(\text{Mn})=0.357\pm0.002$$

is good agreement with the reported values. The assumption $u_2=1/2-u_1$ made in these calculations is borne out by the agreement between calculated and observed values.

Powder neutron data were obtained at room temperature and 4.2°K (Figs. 2 and 3). Samples were placed in a cylindrical aluminium container of 3/8 inch diameter; the intensities were measured at angular intervals of 0.1° in 2θ, the counting time (approximately 10 minutes) being determined by a monitor. The nuclear intensities at the two temperatures agree with each other quite satisfactorily for both compounds. The observed intensities were compared with computed ones after applying appropriate normalization and angular factors; the small correction due to the temperature factor was neglected in the calculation. With the use of the two metal parameters given by the X-ray data, the three oxygen parameters and the ordering parameter S were adjusted to fit the data.

The intensities calculated for $NiTiO_3$ with the reported oxygen parameters did not give satisfactory agreement, especially for (111), (100), and (210), if $S=1$. Reflection with $h+k+l=2n+1$ have a structure factor proportional to (b_1-b_2), were b_1 is the effective scattering amplitude at (u_1, u_1, u_1). On the other hand, reflections with $h+k+l=2n$ are



Neutron diffraction patterns of $NiTiO_3$

Fig. 2. Neutron diffraction patterns of $NiTiO_3$ taken above and below the Néel point. The wave length $\lambda=1.064A$.

proportional to (b_1+b_2) and are independent of the distribution of Ni and Ti on the different sites. The agreement was considerably improved by adjusting S from 1 to 0.92. Still better agreement was obtained by refining the oxygen parameters and then readjusting the ordering parameter. The best values of the parameters are:

$$x=0.555 \quad y=-0.045 \quad z=0.235 \quad S=0.94\,.$$

Agreement with the (210) peak could be obtained only by use of the S parameter. The oxygen parameters are very close to the improved values found for $FeTiO_3$.[6] One may note that the oxygen parameters reported previously satisfy the requirements of the higher symmetry **R$\bar{3}$C** of α-Fe_2O_3, that is, $y=1/2-x$ and $z=1/4$, though these are not necessary for **R$\bar{3}$**. The new oxygen parameters give more reasonable metal-oxygen bond distances, as shown in Table I. The agreement between calculated and observed intensities is presented in Table II (a).

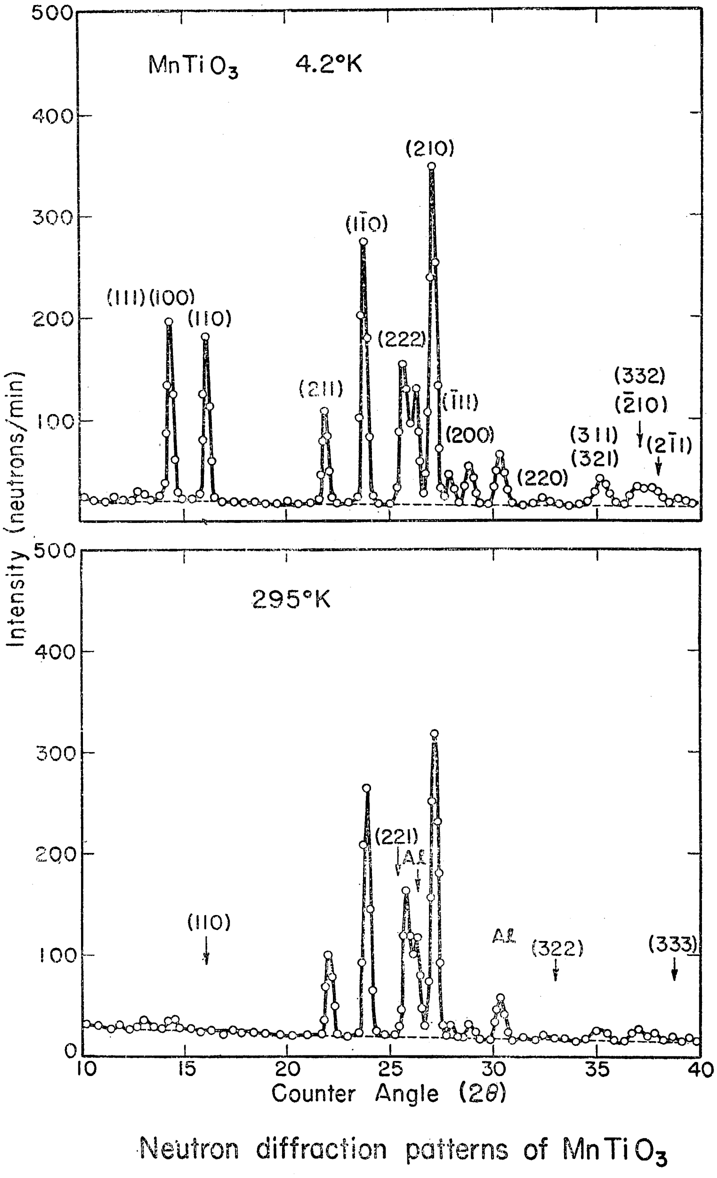


Fig. 3. Neutron diffraction patterns of $MnTiO_3$ taken above and below the Néel point. The wave length $\lambda=1.055$A.

Table I. Structural parameters of $MnTiO_3$ and $NiTiO_3$. The data on $FeTiO_3$ and α-Fe_2O_3 are shown for comparison. The lattice constants are taken from a paper by Ishikawa and Akimoto[7] and the origin is chosen according to Barth and Posnjak.[1]

	$MnTiO_3$	$FeTiO_3$	$NiTiO_3$	α-Fe_2O_3
a	5.610 A	5.538 A	5.437 A	5.424 A
α	54°30′	54°41′	55°07′	55°17′
u_1 (Me)	0.357	0.358	0.353	0.355
x	0.560	0.555	0.555	0.550
y	−0.050	−0.040	−0.045	−0.050
z	0.220	0.235	0.235	0.250
Me-O	2.26, 2.10 A	2.15, 2.03 A	2.14, 2.03 A	2.09, 1.98 A
Ti-O	2.12, 1.86 A	2.14, 1.92 A	2.06, 1.92 A	
r_{Me}	0.91 A	0.83 A	0.78 A	0.67 A
Order S		0.95	0.94	
Spin Direction	$[11\bar{1}]$	[111]	in (111)	in (111) $>$260°K [111] $<$260°K

Table II (a). Calculated and observed nuclear intensities for $NiTiO_3$.

$S=0.94$ $x=0.555$ $y=-0.045$ $z=0.235$

hkl	I_{cal}	I_{obs}	
		295°K	4.2°K
(111)	315	327	334
(100)	295	321	311
(110)	75	72	82
(211)	29	31	31
$(1\bar{1}0)$	7	<5	<5
(210)	1260	1240	1255
$(\bar{1}11)$	152	166	140
(200)	5	13	13
(220)	105	96	90
(322)	205	215	230
(311) (321)	379	380	408
$(\bar{2}10)$	166	150	165
(332) $(2\bar{1}1)$	25	20	25
(333)	44	39	37
(310) $(\bar{2}11)$ (331)	555	529	560
(320) (300) $(22\bar{1})$	231	234	232
(422)	1	<10	<10
(433) (432)	353	343	332
(421)	229	234	232

Table II (b). Magnetic intensities of $NiTiO_3$ at 4.2°K.

Calculated intensities are obtained by assuming $S=0.94$, $\mu_{eff}=2.25\mu_B$, the spin direction in (111) and the form factor of Ni metal. The scale factor was determined by the nuclear intensities shown in Table II (a). (hkl) indices are based on the double rhombohedral cell.

hkl	I_{cal}	I_{obs}
(111)	287	277
$(\bar{1}11)$	18	~15
(311)	41	39
(333)	18	<15
(331)	0	7
$(31\bar{1})$	44	44
(531)	22	25
(553) (511)	2	<7
(555)	2	<10
$(51\bar{1})$	6	<10
(755) (733)	9	~10

$MnTiO_3$ requires somewhat different oxygen parameters than $NiTiO_3$:

$$x=0.560 \quad y=-0.050 \quad z=0.220$$

This is expected because of the difference in the ionic radii of Mn and Ni. As for the ordering of Mn and Ti, no information can be obtained because of the similarity of b_{M_n} (−0.36) and b_{Ti} (−0.38); moreover, it is even difficult to assign Mn to the position $u=0.357$ instead of $u=0.143$. The final assignment of Mn to u_1 gives more consistent interatomic distances and is also slightly favored by the intensity calculations (see Table III). It may be added that the oxygen parameters of this compound could be determined more accurately than in $NiTiO_3$ because of the insensitivity of the diffraction data to the ordering parameter S.

§ 3. Magnetic Structure

The neutron diffraction patterns obtained below the Néel temperature show several changes in the intensities (see Figs. 2 and 3). The new lines in $NiTiO_3$ require the doubling of the rhombohedral unit cell as was the case in $FeTiO_3$; on the other hand, the "magnetic" unit cell of $MnTiO_3$ is identical with the "chemical" unit cell.

All of the observed magnetic lines of $NiTiO_3$, when indexed with the double cell, have h, k, and l all odd. This implies that only the hexagonal **c** axis is doubled but not the **a**, satisfying the condition for models (a) and (b). Model (b) cannot satisfy the strong magnetic (111) reflection with any possible spin direction. The observed intensities can be explained satisfactorily by assuming model (a) and a spin direction lying in the (111) plane, as shown in Table II (b). The specific direction within this plane cannot be defined by powder data alone. Assuming this spin structure, the magnetic moment obtained was 2.25 μ_B, in good agreement with susceptibility measurements⁷⁾, and suggesting a contribution from unquenched orbital moment. The form factor falls off much more slowly than that of Mn^{2+} ¹¹⁾ and Fe^{3+} ¹²⁾, and is closest to that of Ni metal as determined by the polarized neutron technique¹³⁾. It should be noted, however, that because of the limited accuracy of the magnetic intensities at higher angles, the conclusion should be taken with some reserve. In the calculations an ordering parameter $S=0.94$ was used and it was assumed that the remaining Ni on B layers are not magnetically ordered. If their spins form an ordered arrangement such as (a) or (b) within the B layers, they will contribute to the calculated values of the magnetic intensities, but this correction is small.

The magnetic intensities of $MnTiO_3$ can be explained by assuming model (c) and a spin direction along [111]. If we assume $S=1$, the observed intensities require a moment of 4.55 μ_B, which is 91 per cent of the Mn^{2+} moment. This value was determined mainly by the intensities of (100) and (110). With this effective moment and the Mn^{2+} form factor¹¹⁾, quite satisfactory agreement was obtained between observed and calculated values, as shown in Table III.

Table III. Calculated and observed integrated intensities for $MnTiO_3$.

Effective moment, $\mu_{eff}=4.55\mu_B$ Spin direction along [111]

hkl	I_{obs}	I_{cal}			I_{obs}
	295°K	Nucl.	Mag.	Total	4.2°K
$(\bar{1}11)$	6	5	0	5	7
(100)	4	3	152	155	162
(110)	< 2	0	155	155	149
(211)	80	79	5	84	82
$(1\bar{1}0)$	238	250	0	250	244
(221)	<15	0	13	13	<18
(222)	139	134	9	143	153
(210)	321	319	10	329	341
$(\bar{1}11)$	10	8	20	28	31
(200)	23	20	25	45	52
(220)	9	8	2	10	10
(322)	< 4	1	0	1	< 4
(311) (321)	31	27	15	42	46
$(\bar{2}10)$ (332)	27	20	10	30	35
$(2\bar{1}1)$	14	12	12	24	24
(333)	5	5	0	5	5
(310) (331)	46	41	1	42	46
$(\bar{2}11)$	18	19	0	19	19
(320)	16	17	4	21	20
(300) $(22\bar{1})$	< 8	2	1	3	<10
(422)	22	26	1	27	20
(433) (432)	116	122	1	123	113

It is of course possible that the ordering of Mn and Ti is incomplete, as in $FeTiO_3$ and $NiTiO_3$. If we attribute the decrease of the moment from the spin-only value to disorder, S must be 0.91. Though this is not unreasonable compared with the value 0.94 for $NiTiO_3$ and 0.95 for $FeTiO_3$⁶⁾, one might expect a larger activation energy of disorder for $MnTiO_3$, because of the larger difference between Mn-O and Ti-O distances. Moreover, there are several other possible causes for the smaller effective moment. Chemical analysis indicated a slight excess of Ti over Mn, and this departure from stoichiometry is in the correct direction to explain the low observed value. The existence of some manganese in the trivalent state cannot be excluded. In this respect, we may note that the effective Mn moment obtained by the susceptibility measurements⁷⁾ is slightly (2 per cent) smaller than the expected value for Mn^{2+}. Thus the observed effect may be a combination of these factors with disorder playing a major part, and it is not possible, at present, to separate them unambiguously.

§ 4. Discussion

The results of the present neutron diffraction study are in good agreement with the previous magnetic measurements. In particular, the magnetic structure of $MnTiO_3$ proved to be the model predicted by the magnetic measurements on the $MnTiO_3$–α-Fe_2O_3 system. Another important result is the observation of incomplete order of Ni and Ti in $NiTiO_3$. Though direct evidence could not be obtained in the case of $MnTiO_3$, the estimated magnetic moment seems to indicate some disorder in this compound. From these results one might conclude that this is a general characteristic of ilmenite compounds. It would be an interesting problem to investigate the dependence of this disorder on the heat treatment of the specimen and its effect on the magnetic properties.

Superexchange interactions in rhombohedral sesquioxides have been discussed by Li[14] and Iida[15]. There are three important Me-O-Me configurations, two of which, Γ_a and Γ_b, involve metal atoms on different layers and are expected to be stronger than the third one, Γ_c, which is the interaction within the same layer. If, however, the ordering of Me and Ti in $MeTiO_3$ is perfect, and all Ti atoms are in the tetravalent state, the antiferromagnetic order must be propagated three-dimensionally through two layers of oxygen by Me-O-O-Me interactions. As pointed out by Kramers[16], such interactions would normally be expected to be much weaker than the singleanion superexchanges.

When the order is incomplete, some magnetic atoms enter on the B layers, and their role cannot be deduced from the neutron diffraction data. However, indirect evidence was obtained in the study of the $FeTiO_3$-α-Fe_2O_3 system[6], where the addition of α-Fe_2O_3 decreases the antiferromagnetic Néel temperature of $FeTiO_3$. This was interpreted as a destruction of the ferromagnetic coupling within the A layers by a strong antiferromagnetic coupling between the A and B layers. This indicates that at least trivalent magnetic atoms on the B layers are not taking part in the three-dimensional propagation of the $FeTiO_3$-type magnetic order. This conclusion should also apply to $NiTiO_3$, which has essentially the same magnetic structure as $FeTiO_3$ except for the spin direction. Nevertheless, a further study of the $NiTiO_3$–α-Fe_2O_3 system is desirable to provide additional evidence.

$MnTiO_3$ has an antiferromagnetic arrangement within each A layer. A molecular field calculation[7] has shown that the moments introduced on the B layer are arranged antiparallel to each other. In this case strong interactions Γ_a and Γ_b do not disturb the ordering on the A layers, implying that the addition of α-Fe_2O_3 should not change the magnetic structure. Experimental confirmation of this point has yet to be carried out.

If pure $MnTiO_3$ is partially disordered it is possible that Γ_a and Γ_b, as well as a long range Me-O-O-Me interaction, may play a role in the propagation of order between the layers. At present we cannot separate these two effects. It may be worthwhile pointing out that there are two kinds of configuration:

$$\mathrm{Mn}\overset{p}{-}\mathrm{O}-\mathrm{O}\overset{q}{-}\mathrm{Mn} \quad \text{positive}$$

$$\mathrm{Mn}\overset{q}{-}\mathrm{O}-\mathrm{O}\overset{q}{-}\mathrm{Mn} \quad \text{negative}$$

where p and q are bond distances corresponding to 2.10A and 2.26A respectively.[14] This situation is analogous to the case of Cr_2O_3 where the interaction is through only one oxygen.

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