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Antiferromagnetic Properties of the Iron Group Trifluorides

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A neutron diffraction study has been made of the trifluorides of $3d$ transition group elements. The arrangement of the magnetic ions and the anions in these trifluorides is similar to that in the compounds LaMO$_3$ for which the antiferromagnetic properties have been studied earlier. No antiferromagnetic transition was observed in VF$_3$. In the compounds CrF$_3$, FeF$_3$, and CoF$_3$ the magnetic ions are observed to couple antiferromagnetically *via* the intervening anion to each of their six nearest neighbors. This is the same structure as that found in the compounds LaCrO$_3$ and LaFeO$_3$. In the trifluorides the distortions from cubic symmetry have made it possible to determine the orientation of the spin moments relative to the crystallographic axes and in one case (CrF$_3$) the antiferromagnetic domain properties have been studied with magnetic fields applied to the sample. In MnF$_3$ an antiferromagnetic layer structure is found of the type previously observed for LaMnO$_3$. The indirect magnetic coupling in these compounds is correlated with the orbitals which result from the splitting of the d levels by the crystalline field.

1. INTRODUCTION

THE trifluorides of the $3d$ transition group elements crystallize as modifications of a cubic structure in which the metal ions lie on the corners of the cube and the fluorine ions are near the centers of the cube edges. This arrangement is similar to that of the $3d$ metal ions (M) and the oxygen ions in the perovskites of the form LaMO$_3$ in which there is also the nonmagnetic La (or other) ion at the center of the cube. It was thus thought of interest to see if the antiferromagnetic properties of the trifluorides would be similar to those observed[1,2] in the corresponding perovskite type compounds.

2. CRYSTAL STRUCTURE CONSIDERATIONS

It was a fortunate circumstance that at about the time this investigation was begun the reports of a careful x-ray study by Hepworth, Jack, Peacock, and Westland[3,4] of the structure of these compounds had just appeared. Their work shows that the trifluorides of V, Cr, Fe, and Co crystallize with a bimolecular rhombohedral cell of space group $R\bar{3}C$, with 2 metal atoms at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and 6 fluorine atoms at $\pm(x, \frac{1}{2}-x, \frac{1}{4})$; $\pm(\frac{1}{2}-x, \frac{1}{4}, x)$; $\pm(\frac{1}{4}, x, \frac{1}{2}-x)$. The parameter x varies from -0.164 in FeF$_3$ to about -0.12 for CrF$_3$, this latter having been determined from the neutron data since no published values were available for this compound. The degree of distortion of the structure from cubic symmetry is indicated by the fact that the angle for the unimolecular cell is near 88° instead of 90°.

The crystal structure of MnF$_3$ was shown by Hepworth and Jack[4] to be of lower symmetry (monoclinic) than the other members of this group. Accurate fluorine parameters were also obtained and these are of significance in connection with the antiferromagnetic studies. These crystallographic data will be considered in the discussion of the antiferromagnetic structure.

3. RESULTS

Neutron powder diffraction patterns were obtained at various sample temperatures in the range from 4.2°K to 380°K on the compounds VF$_3$, CrF$_3$, FeF$_3$, CoF$_3$, and MnF$_3$.

VF$_3$

In the case of VF$_3$ there was no evidence of magnetic ordering in the lowest temperature (4.2°K) pattern. The diffuse scattering in the low-temperature and room-temperature patterns showed a paramagnetic angle-dependent contribution consistent with a V^{3+} ion with a spin only moment of $2\mu_B$.

CrF$_3$, FeF$_3$, and CoF$_3$

Patterns obtained on the compounds CrF$_3$, FeF$_3$, and CoF$_3$ showed superlattice reflections characteristic of an antiferromagnetic structure which has previously been referred to as of the G type in which the magnetic ions are coupled antiferromagnetically via the intervening anions to all six nearest neighbors. This is the

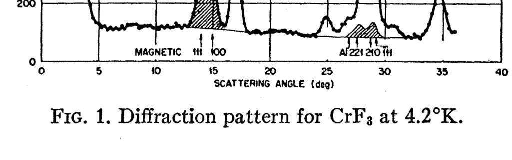

FIG. 1. Diffraction pattern for CrF$_3$ at 4.2°K.

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[1] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 345 (1955).

[2] W. C. Koehler and E. O. Wollan, J. Phys. Chem. Solids **2**, 100 (1957).

[3] Hepworth, Jack, Peacock, and Westland, Acta Cryst. **10**, 63 (1957).

[4] M. A. Hepworth and K. H. Jack, Acta Cryst. **10**, 345 (1957).

magnetic structure which was observed in the similar perovskite type compounds $LaCrO_3$ and $LaFeO_3$.

A sample diffraction pattern taken below the Néel temperature ($T_N = 80°K$) is shown in Fig. 1 for CrF_3 in which the magnetic reflections are represented by the cross-hatched areas. The first two barely resolved reflections in this pattern are seen to be of magnetic origin. If the structure of this compound had been cubic, there would have been a single reflection at this point which would have been indexed as (111) for a magnetic cell with all three axes double those of the cubic chemical cell. Due to the distortion from cubic symmetry in this case, there are two reflections which are indexed as (111) and (100) of the rhombohedral cell. In the case of the similar perovskite-type compounds, a single cubic-type reflection was observed at this point. The group of magnetic reflections (221), (210), and $(\bar{1}11)$ all fall under a strong nuclear peak. The total magnetic contributions from these lines as shown by the cross-hatched areas were determined approximately in this case from the difference of patterns taken above and below the Néel temperature. For FeF_3 and CoF_3 the Néel points were found to be above room temperature (see Table IV) and no difference patterns were obtained.

TABLE I. Calculated intensity ratio, $P(111)/P(100)$, for various spin orientations.

For spin parallel to (111) planes	For spin along rhombohedral axis	For spin perpendicular to (111) planes
0.71 (Cr, Fe)	0.125	0 (Co)

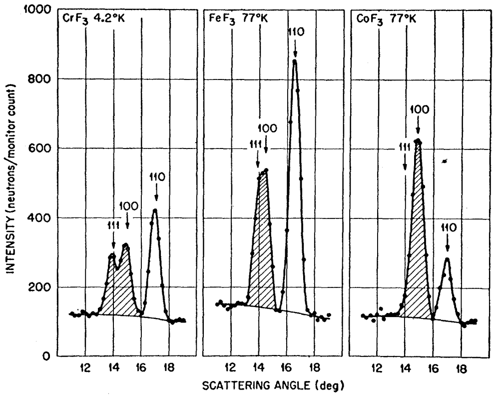

FIG. 2. Low-angle diffraction patterns showing rhombohedral splitting of magnetic reflections.

Since the structure of these compounds is distorted from cubic symmetry, it should in principal be possible to obtain information about the orientation of the spins relative to the axes of the rhombohedral cell. The ratio of the intensities of the (111) and (100) reflections, for example, depend strongly on this spin orientation. The calculated ratios of the intensities of these reflections, $P(111)/P(100)$, are given in Table I for three assumed orientations of the spins relative to the rhombohedral axes of the unit cell. The related experimental data are shown in Fig. 2 which gives the diffraction patterns over the region of the (111) and (100) magnetic reflections and incidentally also over the range of the first nuclear reflection for these three trifluoride compounds. In the case of CrF_3, the (111) and (100) reflections are partially resolved and the ratio of their intensities is found to be close to the value 0.71 which corresponds to the spins being parallel to the (111) planes. In FeF_3 these magnetic reflections are not resolved but the shape of the broad unresolved peak strongly suggests that in this case also the spins are parallel to the (111) planes. In CoF_3 the intensity of the (111) reflection is very small. A zero value of this ratio places the spin vector perpendicular to the (111) planes, whereas if the spin vector were along one of the rhombohedral axes the intensity ratio would be 0.125. The data favor the case of spins perpendicular to the (111) planes.

In the case of CrF_3, intensity measurements of the (111) and (100) reflections were made with magnetic fields of up to 10 kilo-oersteds applied to the sample along the respective scattering vectors. No intensity change was observed for the (111) reflection. This is to be expected since the spins were found to be parallel to the (111) planes; and since the field was applied to the sample along the scattering vector, any effect would thus require the breaking down of the magnetic exchange coupling, and for this the applied field was much too small. When the field was applied along the scattering vector of the (100) planes, however, the intensity increased by about 50% over the no-field value. This effect can be accounted for on the basis of a reorientation of the spins within the (111) sheets so as to bring them parallel to (100) planes in a larger

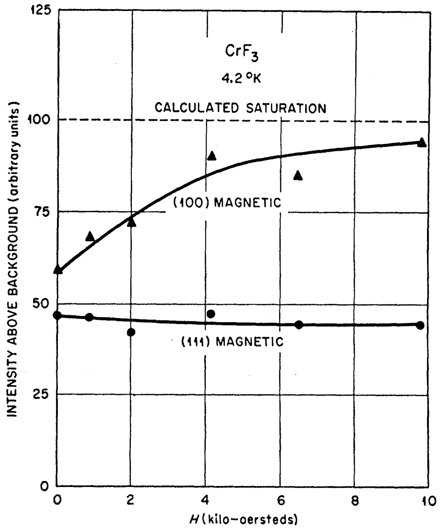

FIG. 3. Magnetic field orientation of antiferromagnetic domains in CrF_3.

TABLE II. Comparison of observed and calculated magnetic intensities.

Rhombohedral indices		FeF_3 Calculated ($S=5/2$)	FeF_3 Observed total intensity	CoF_3 Calculated ($S=2.2$)	CoF_3 Observed total intensity	CrF_3 Calculated ($S=3/2$)	CrF_3 Observed total intensity
111		287	272	0	0	140	146
100				289	289	197	204
200							
222	Nuclear	198		367			
210	Total	351	355	579	593		
221	Magnetic	153		266		171	∼150
$\bar{1}11$							

fraction of reflecting crystallites. These field effects are shown in Fig. 3 where the dashed line represents the expected saturation value. These magnetic field effects thus indicate the existence of antiferromagnetic domains in CrF_3 in which in the absence of a magnetic field the spins in the ordered state have equal probability of being parallel and antiparallel to any one of the three a axes of the hexagonal cell.

The absolute intensities associated with the magnetic scattering in these compounds are shown in Table II, where a comparison is made between the observed intensity at saturation and that calculated for a particular value of the spin of the magnetic ion. In the case of iron and chromium, the intensities calculated on the basis of the expected spin-only values of $\frac{5}{2}$ and $\frac{3}{2}$, respectively, for the trivalent ions are seen to be in good accord with the measured values. For cobalt the observed magnetic scattering is larger than that given by the spin-only value $S=2$ for a trivalent cobalt ion. There appears thus to be some orbital contribution to the magnetic moment in this case.

MnF_3

Manganous trifluoride also shows the growth of superlattice reflections at low temperatures ($T_N=43$°K), but the antiferromagnetic structure which develops in this compound is different than in the other trifluorides of this group. The situation is identical to that observed in the corresponding perovskite-type compound $LaMnO_3$.

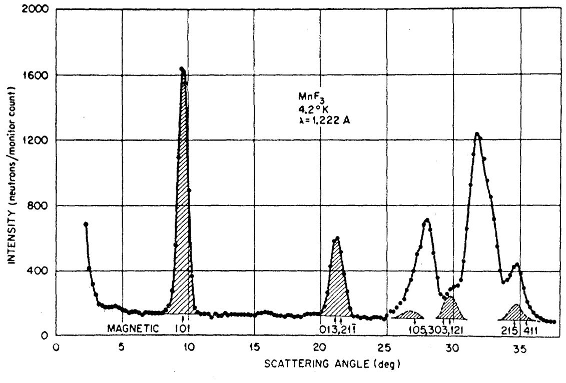

FIG. 4. Diffraction pattern for MnF_3 at 4.2°K.

A low-temperature powder pattern (4.2°K) for MnF_3 is reproduced in Fig. 4. The cross-hatched areas represent the magnetic contributions to the pattern. The small contributions which lie underneath strong nuclear reflections were determined by taking the difference between the coherent contributions in patterns taken above and below the Néel temperature.

Although the crystal structure of MnF_3 is monoclinic with 12 molecules per unit cell, the basic antiferromagnetic structure can most easily be described in terms of an idealized cubic form. The antiferromagnetic structure consists of ferromagnetic layers in which the spins in alternate layers are oppositely oriented. The antiferromagnetic cell is then the tetragonal one for which half of the cell is shown in Fig. 5. The orbital representation in the figure will be considered in the next section. This antiferromagnetic cell gives rise to the reflections shown in Table III. The high intensity observed for the first line (101) of this structure (Fig. 4) corresponds to the spins lying in or nearly in the plane of the ferromagnetic sheets. The observed magnetic intensities from this pattern are listed in the last column of Table III. The corresponding intensities calculated on the basis of the true monoclinic cell and for the spins in the ferromagnetic sheets are shown in the third column of this table. The agreement is good except for the first reflection for which the difference

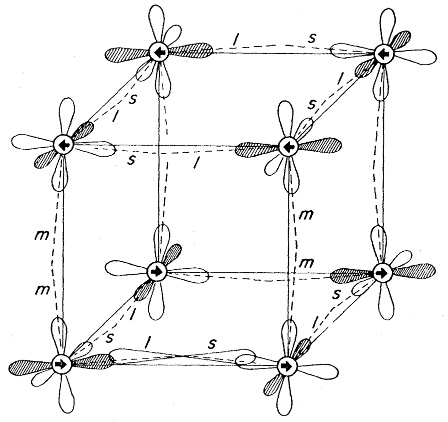

FIG. 5. Magnetic structure (half-cell) of MnF_3 with suggested d-orbital magnetic coupling. The letters l, m, and s represent long, medium, and short distances to fluorine ion.

seems to be somewhat outside the apparent experimental uncertainty. The magnetic moment of the Mn^{3+} ion is within experimental error equal to the spin only value of $2\mu_B$.

Concurrent with the present investigation, R. M. Bozorth and V. Kramer[5] have measured the magnetic susceptibility of MnF_3. They observed a susceptibility maximum at 47°K which is in reasonably good accord, with the value of the Néel temperature observed here ($T_N = 43$°K).

The Néel temperatures obtained from the neutron diffraction measurements for the trifluorides and for the corresponding perovskite compounds studied previously are listed in Table IV.

4. DISCUSSION

The antiferromagnetic structure properties of the $3d$ transition group trifluorides (MF_3) are very similar to the corresponding perovskite type compounds ($LaMO_3$). This is not too surprising in view of the similar disposition of the magnetic cations relative to the intervening anions in the two cases. In both series the vanadium compound showed no detectable magnetic ordering, and the chromium and iron compounds were found in both series to order antiferromagnetically with the same G-type structure. The previous results on $LaCoO_3$ showed no magnetic ordering whereas the corresponding CoF_3 compound showed magnetic ordering of the same type as in the iron and chromium compounds. There is evidence[6] that the spin state of cobalt in $LaCoO_3$ is very sensitive to the presence of some Co^{4+} ions which is difficult to eliminate in these preparations. The evidence suggests that in a pure compound the Co^{3+} ions are in the high spin state ($S=4/2$) whereas in the presence of some Co^{4+} the Co^{3+} ions become diamagnetic. This would then account for the apparent difference in the two systems in regard to the cobalt compound. In the case of the manganese compounds the same antiferromagnetic structure (A type) was observed in both series.

TABLE III. MnF_3 magnetic intensities. Spins parallel to (101) monoclinic planes.

Monoclinic indices	P_{hkl}(calc) ($S=2$)	P_{hkl}(obs)
101	1530	1402
013 $21\bar{1}$	571	587
$10\bar{5}$	65	~70
121 303	180	~190
215 411	134	~125

The antiferromagnetic structure data on the perovskite-type compounds was shown by Goodenough[7] to have some striking correlations with a hybrid orbital interpretation of the magnetic structure data. This picture, however, failed in some respects to account for the indirect exchange mechanisms involved in the magnetic ordering. It appears now that the orbitals which results from the splitting of the d levels by the crystalline field are better suited to account for the magnetic properties of these compounds. These orbitals have recently been used by Dunitz and Orgel[8] in accounting for the distortions in spinels and other systems.

TABLE IV. Néel temperatures of $3d$ group trifluorides and perovskites.

	T_N (°K)		T_N (°K)
CrF_3	80	$LaCrO_3$	320
MnF_3	43	$LaMnO_3$	100
FeF_3	394	$LaFeO_3$	750
CoF_3	460		

The crystal field splits the $3d$ levels of an ion in an octahedral site into a lower triplet (t_{2g}) and an upper doublet (e_g). The electron occupation of these orbitals for the trivalent $3d$ ions under consideration here are shown in Table V. The two e_g orbitals are of the form $d_{x^2-y^2}$ and d_{z^2}. The d_{z^2} orbital is directed along the z axis and the $d_{x^2-y^2}$ orbital is of the square type whose lobes lie along the x and y axes of the cubic structure. These cation orbitals are thus the ones which overlap the p orbitals of the intervening anions in the trifluoride type of structure and hence these are the orbitals which would be expected to be associated with the indirect magnetic exchange coupling in compounds of this type.

Much of the observed magnetic structure data for compounds of the presently considered type can be accounted for on the basis of the following types of indirect exchange:

(a) Whenever half-filled orbitals of two magnetic cations overlap, respectively, the two ends of a given anion p orbital, the magnetic exchange will be antiferromagnetic.

(b) Whenever empty orbitals of two magnetic cations overlap, respectively, the two ends of a given anion p orbital, the magnetic exchange is likewise antiferromagnetic.

TABLE V. Primary crystal level splitting and electron occupation of d orbitals in octahedral surroundings.[a]

		t_{2g}			e_g
Ion	d_{xy}	d_{yz}	d_{xz}	d_{z^2}	$d_{x^2-y^2}$
Cr^{3+}	↑	↑	↑	0	0
Mn^{3+}	↑	↑	↑	↑	0
Fe^{3+}	↑	↑	↑	↑	↑
Co^{3+}	↑↓	↑	↑	↑	↑

[a] $E(\text{triplet}) < E(\text{doublet})$.

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[5] R. M. Bozorth and V. Kramer (to be published).

[6] G. H. Jonker and J. H. Van Santen, Physica **19**, 120 (1953).

[7] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).

[8] J. W. Dunitz and L. E. Orgel, J. Phys. Chem. Solids **2**, 100 (1957).

(c) Whenever an empty orbital of one magnetic ion overlaps one end of an anion p orbital and the other end of the same anion p orbital overlaps a half-filled orbital of another magnetic ion, the magnetic exchange is ferromagnetic.

These exchange situations are undoubtedly to be associated with the superexchange mechanism suggested by Kramers[9] and more completely investigated by Anderson[10] and by Pratt.[11] These processes can be qualitatively interpreted as indicating that the anion electrons involved in the exchange process must simultaneously satisfy the conditions (Pauli principle and Hund's rule) for existing independently on either the anion or the cations involved in the exchange process.

The exchange in the iron and cobalt compounds would thus correspond to case (a) and the octahedral symmetry of the e_g orbitals would logically lead to the observed symmetrical G-type antiferromagnetic structure. The exchange in the chromium compounds is of the (b) type which would lead to the same antiferromagnetic structure.

In the case of MnF_3 one observes the same layer type antiferromagnetic structure (A type) as was previously observed for $LaMnO_3$. This structure appears to be associated with the presence of only one electron in the e_g orbitals. If one assumes that this electron goes into a d_{z^2} orbital, the antiferromagnetic structure can be accounted for by the orbital arrangement shown schematically in Fig. 5. The antiferromagnetic coupling between layers is of the (b) type involving the overlap of empty cation orbitals with both ends of the p orbitals of the intervening anions. The ferromagnetic coupling within the layers is of the (c) type which involves overlap of the p orbital of the intervening anion with an empty orbital on one side and a half-filled orbital on the other side. The same structure can also be developed on the assumption of an empty d_{z^2} orbital and a half-filled $d_{x^2-y^2}$ orbital.

The spacial ordering of the orbitals which is required to account for this type of structure is made reasonable in the case of MnF_3 by the x-ray measurements[4] of the crystal parameters of the fluorine ions. The relation of the observed distances $l=2.1$ A, $m=1.9$ A, and $s=1.8$ A to the pseudotetragonal antiferromagnetic cell is schematically represented in Fig. 5.

Along the c axis of this cell the fluorine ions are observed to lie half-way between antiferromagnetic layers, which suggests overlap of fluorine ion p orbitals with identical magnetic ion d orbitals on both sides which is the required condition for antiferromagnetic coupling. The observed ordered arrangement of long and short fluorine parameters within the ferromagnetic layers suggests the proposed ordering of the magnetic-ion orbitals such that the p orbitals overlap a filled cation orbital on one side and an empty cation orbital or the other, and this is the requirement for ferromagnetic coupling within the layers. The observations that the fluorine ions are displaced from the lines joining neighboring cations would be expected to be involved only with the strength of the indirect exchange.

ACKNOWLEDGMENTS

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