Neutron Diffraction Studies of Antiferromagnetism in Manganous Fluoride and Some Isomorphous Compounds*

R. A. ERICKSON[†],[‡]

Oak Ridge National Laboratory, Oak Ridge, Tennessee and Agricultural and Mechanical College of Texas, College Station, Texas (Received Februrary 24, 1953)

Neutron diffraction studies of MnF₂, FeF₂, CoF₂, and NiF₂ are reported. At low temperatures each compound showed the superlattice structure characteristic of antiferromagnetism. The data are accounted for with a magnetic cell of the same dimension as the chemical unit cell; the moments of the magnetic ions at the lattice corners being antiparallel to the moments of the body centered ions. The alignment of the magnetic moments is along the tetragonal axis in all cases except NiF_2 where the alignment direction makes an angle of about 10° relative to the *c* axis. The intensity of the magnetic scattering as a function of sample temperature follows a Brillouin curve of the form suggested by Van Vleck. Extrapolating the saturation data to zero peak intensity gives the Néel temperatures for threshold antiferromagnetism. These are MnF_2 -75° K; FeF₂ -90° K; CoF₂ -50° K; NiF₂ -83° K.

I. INTRODUCTION

HE work of Shull, Strauser, and Wollan¹ on a number of iron group oxides has demonstrated the fruitful application of neutron diffraction techniques to studies of magnetism in paramagnetic and antiferromagnetic compounds. In this work the diffraction of neutrons is used to determine the magnetic behavior of MnF₂, FeF₂, CoF₂, and NiF₂ over a wide range of temperatures. These compounds are of particular interest in that (a) they all have the tetragonal crystal structure of SnO₂, (b) magnetic susceptibility measurements show that MnF₂ and FeF₂ are antiferromagnetic, and (c) considerations of crystal structure make it likely that at least MnF2 has a magnetic structure much like the two-sublattice model of antiferromagnetism discussed by Néel² and Van Vleck.³

The powder magnetic susceptibilities of these compounds have been reported by Bizette and Tsai,4,5 Bizette,⁶ and de Haas, Schultz, and Koolhaas.⁷ According to these results MnF2 and FeF2 are antiferromagnetic below 72° and 79°K, respectively, whereas C_0F_2 and NiF_2 appear to be paramagnetic to at least 20°K. Griffel and Stout⁸ have measured the susceptibilities of a single crystal of MnF₂ and find the antiferromagnetic moments aligned along the tetrogonal axis.

II. APPARATUS

The diffraction of neutrons by crystalline powders has been treated by Wollan and Shull,9-11 and their diffraction apparatus, as well as the results of their many investigations, have been used throughout this experiment. The neutron wavelength in this work was 1.212A.

Since both MnF₂ and FeF₂ were known to have Néel temperatures near 80°K, it was necessary to have an apparatus capable of maintaining sample temperatures well below that of liquid nitrogen. This was accomplished with an all metal cryostat employing a nitrogen cooled jacket and several floating radiation shields to reduce the heat influx to the sample and its coolant reservoir. The cryostat was evacuated to about 10⁻⁶ mm Hg by continuous pumping with a small oil diffusion pump. The capacity of the inner reservoir was about one liter and at the lowest temperatures the heat leak was approximately 75 calories per hour. Thus a filling of hydrogen at 20°K lasted nearly ninety hours, and about ten hours of operation was obtained from a filling with liquid helium. The nitrogen reservoir had a capacity of two liters and a filling lasted for about twenty-four hours. The sample temperature was taken to be the mean value read from copper-constantan thermocouples located at the top and bottom of the thin wall cylindrical sample tube. The thermocouples were calibrated at several temperatures and referred to Willihnganz's¹² calibration for accurate interpolation.

The samples were prepared by Mr. D. E. LaValle of this laboratory, following the method of Domonge.13 Because of the initially small apparent densities, all of the compounds except FeF₂ were compressed at 10 000 psi and then ground into a fine powder before being loaded into the sample tube. Although the samples were prepared completely dry, in every case a

^{*} Presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Agricultural and Mechanical College of Texas. Presented in part at the Washington Meeting of the American Physical Society, April 26, 1951. [(Phys. Rev. 83, 208 (1951)].

[†] This work was performed while the author was a Graduate Fellow of the Oak Ridge Institute of Nuclear Studies.

[‡] Now at the University of Tennessee, Knoxville, Tennessee. ¹ Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

² L. Néel, Ann. phys. 5, 256 (1936).

² J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941). ⁴ H. Bizette and B. Tsai, Compt. rend. **209**, 205 (1939).

⁵ H. Bizette and B. Tsai, Compt. rend. 212, 119 (1941). ⁶ H. Bizette, Ann. phys. 1, 295 (1946).

 ⁷ de Haas, Schultz, and Koolhaas, Physica 7, 57 (1940).
⁸ M. Griffel and J. W. Stout, J. Chem. Phys. 18, 1455 (1950).

 ⁹ E. O. Wollan and C. G. Shull, Phys. Rev. **73**, 830 (1948).
¹⁰ E. O. Wollan and C. G. Shull, Nucleonics **3**, 8 (1948).
¹¹ C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

¹² E. Willihnganz, thesis, Pennsylvania State College (1934), unpublished.

¹³ H. Domonge, Ann. Chem. Justus Liebigs 7, 225 (1937).



FIG. 1. Neutron diffraction patterns for MnF_2 in the paramagnetic state (295°K) and in the antiferromagnetic state (23°K). The unit cells for antiferromagnetic and nuclear scattering are of the same size.

small water content was subsequently inferred from neutron transmission measurements. The presence of water does not complicate an analysis of the coherent scattering, but the angular dependence of the diffuse scattering from hydrogen makes the analysis of magnetic diffuse scattering uncertain.

III. EXPERIMENTAL RESULTS

MnF_2

The powder diffraction patterns from MnF_2 at room temperature and 23°K are shown in Fig. 1. The pattern at 295°K shows the expected nuclear peaks as well as some angularly dependent magnetic diffuse scattering. At 23°K the diffuse scattering is considerably reduced, and several large magnetic reflections are in evidence.

An analysis of the diffuse magnetic scattering in these patterns, as shown in Fig. 2, indicates that even at room temperature the magnetic scattering is not entirely paramagnetic. Similar liquid-like patterns were observed by Shull, Strauser, and Wollan¹ (S-S-W) and attributed to a short-range ordering of the ionic magnetic moments. An estimate of the forward scattering from a true paramagnetic lattice is made according to the dashed line in Fig. 2. The intercept agrees favorably with the value 1.69 barns/steradian calculated from the Halpern and Johnson¹⁴ (H-J) expression for the Mn⁺⁺ ion (S=5/2).

As the temperature is reduced and the antiferromagnetic order is perfected, the coherent magnetic scattering should increase with a consequent reduction in the diffuse magnetic scattering. According to H-J, however, some diffuse magnetic scattering may persist even at the lowest temperatures if inelastic collisions which alter the ionic spin orientation are permitted. This result is confirmed by Tamor¹⁵ who finds that, in the limiting case where the neutron energy is large compared with the magnetic energy of an ion in its local field, the residual diffuse magnetic scattering in the forward direction should be 1/(S+1) of the paramagnetic forward scattering. The diffuse magnetic scattering at 23°K thus seems to be a real effect, and though its angular dependence is rather unlike the paramagnetic scattering, the forward intercept agrees nicely with the value predicted by Tamor.

The magnetic form factor of Mn^{++} , as obtained from the extrapolated scattering cross section at 295°K, is shown in (a), Fig. 3. Also shown (c) is the form factor



FIG. 2. Diffuse magnetic scattering from MnF_2 and CoF_2 at room temperature and at 23°K. The bump in the high temperature curves is attributed to a short-range ordering of the magnetic moments.

obtained by S-S-W. Form factor values consistent with the observed magnetic peaks in MnO (S-S-W) and MnF₂ are shown and curve (b) is drawn as the best fit to all the magnetic peak data. Because of the uncertainties in correcting the MnF₂ for a small amount of water, it is felt that (a) is too large and that the true form factor is better described by (b) or (c).

In the low temperature diffraction pattern from MnF_2 it is observed that the superlattice magnetic peaks can be indexed as (100), (111), (210), and (201). It follows that the magnetic unit cell has the same dimensions as the chemical unit cell. Furthermore, since the chemical unit cell contains two Mn^{++} ions, it is

 ¹⁴ O. Halpern and M. H. Johnson, Phys. Rev. 55, 898 (1939).
¹⁵ S. Tamor, private communication.

necessary that the moments of the Mn⁺⁺ ions at the (0, 0, 0) cell positions be antiparallel to the moments at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This conclusion is confirmed in detail by the



FIG. 3. Magnetic form factors for Mn^{++} and Co^{++} . The solid curves are obtained from paramagnetic scattering data and the points are from the low temperature coherent magnetic scattering. Curve (c) for Mn^{++} was reported by Shull, Strauser, and Wollan.

crystal structure factors and peak intensities. These, together with the complete absence of any intensity in the (001) reflection, lead uniquely to a spin alignment direction that is parallel to the tetragonal axis. The magnetic structure is thus determined completely and is as shown in Fig. 4. According to this model the local environment of each Mn^{++} ion is as follows: (1) two parallel neighbors at 3.31A (along the *Co* axis); (2) eight antiparallel at 3.81A; (3) four parallel at 4.87A; (4) eight antiparallel at 6.03A. Although this lattice can be uniquely divided into two sublattices with opposing spins, it does not fulfill Van Vleck's³ assumption that nearest neighbors be oriented antiparallel. If, however, the exchange potential is assumed to vary exponentially with the distance between ions, then the actual configuration is approximately equivalent to having four antiparallel neighbors at 3.81A. Within the limits of this modification it should be permissible to apply Van Vleck's results to this material.

The direct exchange interaction between two electrons is spherically symmetric and as such cannot account for the anisotropy or preferred orientation of the magnetic moments in the lattice. On the other hand, the magnetic dipole interaction is strongly anisotropic. Thus, for an aligned dipole interaction between a Mn++ ion and its ten nearest neighbors, the proposed magnetic structure is about 3 cm^{-1} (per ion) more stable than the structure in which the moments are normal to the tetragonal axis. Kittel¹⁶ has suggested that even such relatively small forces, when accompanied by a large isotropic exchange force, are capable of producing a large anisotropy field. It seems likely that the field dependence of the magnetic susceptibility below the Néel temperature, as shown in the results of Bizette and Tsai,⁴ is closely related to the modification in the directional local field as a result of the superposition of the dipole and applied magnetic fields.

Diffraction patterns of the first magnetic peak (100) have been obtained at several temperatures below the Néel temperature, as shown in Fig. 5. From these the crystal structure factors of Fig. 6 are calculated. It is seen that the peak intensity saturates over a relatively greater temperature interval than was observed in MnO by S-S-W.



FIG. 4. Magnetic structure of MnF_2 showing the order and orientation of the Mn^{++} magnetic moments. The small circles correspond to fluorine sites.

¹⁶ C. Kittel, Phys. Rev. 82, 564 (1951).



FIG. 5. Diffraction patterns for the (100) magnetic reflection in MnF_2 at several temperatures.

If the antiferromagnetism in MnF_2 follows that of Van Vleck's model, then the thermal dependence of the magnetic structure factor will be as the square of the Brillouin function. That is,

$F_{hkl}^2(mag) = 0.289 \times 10^{-24}$

$$\times [gS\{fqe^{-W}\}_{hkl}]^2 B_S^2(y) \text{ cm}^2, \quad (1)$$

 $B_S(y)$ is where the Brillouin function for the ionic spin S, $y=3B_S(y)ST_N/(S+1)T$, f the magnetic form factor, q the magnitude of the sine of the angle between the neutron scattering vector and the ionic magnetic moment, W the Debye-Waller temperature factor, and g an anomalous factor such that the effective magnetic moment of the ion (for neutron scattering) is gS Bohr magnetons. Thus, the departure from g=2 is a measure of the contribution from the unquenched orbital momentum to the total magnetic moment. In writing Eq. (1) it is assumed that the results of both H-J and Van Vleck are yet valid when a small part of the ionic moment is due to orbital angular momentum, that is when g is nearly 2.

A comparison of Eq. (1) with the curve fitted to the data in Fig. 6, $F_{100}^2 = 5.35B_{\frac{3}{2}}^2(y)$, gives $T_N = 75^{\circ}$ K and g = 1.99. Both of these values are in good agreement with susceptibility measurements.

FeF_2

Neutron diffraction patterns from FeF_2 at room temperature and at 23°K are shown in Fig. 7. Here the

nuclear peaks have quite different relative intensities as compared with the MnF_2 pattern. This results from the iron coherent nuclear scattering amplitude being large and positive whereas the manganese amplitude is small and negative.

The analysis of the magnetic diffuse scattering from FeF_2 is made unreliable by uncertainties in the water contamination; the Mn^{++} (b) form factor is therefore used in analyzing the FeF_2 data.

The magnetic peaks in FeF_2 are seen to arise from the same lattice planes as in MnF_2 and again the (001) reflection seems to have zero intensity. It is concluded therefore that the magnetic structure in these two fluorides is identical.

The crystal structure factors shown in Fig. 6 are obtained from observations of the (100) peak intensity at several temperatures below T_N . Since the spin of the Fe⁺⁺ ion is 2, these data are compared with a $B_2^2(y)$ and a reasonable fit results with $F_{100}^2 = 4.55B_2^2(y)$ and $T_N = 90^{\circ}$ K. Comparison with (1) gives g = 2.32.

The indicated Néel temperature is about 11° higher than the temperature of maximum susceptibility. A departure from the Brillouin behavior would not be unexpected in this case since the Fe⁺⁺ ion seems to retain a fair amount of unquenched orbital momentum.

CoF_2

The room temperature and 23° K diffraction patterns from CoF₂ are given in Fig. 8, and the analysis of the



FIG. 6. Temperature dependence of the (100) peak intensity, in terms of the crystal structure factor, for MnF₂ and FeF₂. The points are fitted with an appropriate Brillouin saturation curve.

diffuse magnetic scattering is shown in Figs. 2 and 3. The uncertainty of correcting for a small water contamination again makes these data somewhat unreliable, but the general features of the diffuse scattering are the same as those noted in MnF_2 . The forward scattering intercept corresponds to a paramagnetic moment with g=2.03.

The low temperature magnetic reflections in Fig. 8 have the same relative positions and intensities as in MnF_2 and FeF_2 . CoF_2 is therefore assigned the same antiferromagnetic structure as the previous fluorides.

Since susceptibility measurements give no evidence of antiferromagnetism in this compound, the saturation of the (100) peak intensity is of special interest in providing a measure of the Néel temperature. These results are given in Fig. 9, showing a best fit for a Brillouin (S=3/2) saturation with $T_N=50^{\circ}$ K. Measurements made at 47°K suggest the Néel point is probably closer to 45°K than 50°K, but coherent peak data near the magnetic threshold are very difficult to analyze.

The T=0 intercept of 1.90×10^{-24} cm² corresponds to g=2.00, which is rather small compared with the value from paramagnetic susceptibility measurements, but consistent with the paramagnetic diffuse scattering result.

NiF_2

From the diffraction patterns shown in Fig. 10 it is seen that NiF₂ is antiferromagnetic at 25°K, but not so at room temperature. The (100), (111), (210), and (201) magnetic reflections are seen as in MnF₂ although they are very much smaller here, and there is additionally a small peak at the (001) position. It appears therefore



FIG. 7. Diffraction patterns for FeF_2 at room temperature and 23°K. The antiferromagnetic peaks occur at the same relative positions as in MnF_2 .



FIG. 8. Diffraction patterns showing the antiferromagnetism in CoF₂ at low temperatures.

that the magnetic cell in NiF_2 is again identical with the chemical cell, but the moments are not directed along the tetragonal axis as in the other fluorides.

Because the magnetic scattering from the Ni⁺⁺ ion (S=1) is so small as compared to the coherent nuclear scattering, it is difficult to obtain good measurements of the peak intensities in this compound. The situation is further complicated because the orientation as well as the magnitude of the magnetic moments must be determined in this case.

The saturation of the (100) structure factor, as shown in Fig. 9, seems to follow the curve $F_{100}^2 = 0.70B_1^2(y)$ with $T_N = 83^{\circ}$ K. Now if the moment orientation were as in MnF₂, then from Eq. (1) g=1.78. This value is certainly too small, confirming the conclusion that the orientation is different from that in the other fluorides.

The best accounting for these saturation data and the measured intensities of the other peaks is obtained with the Ni⁺⁺ moments aligned at an angle of 10° relative to the tetragonal axis. Although the powder diffraction data cannot be interpreted to give more information than the inclination of the moment orientation with respect to the *c* axis, it is to be noted that this angle corresponds closely to the angle between the *c* axis and either of the equivalent F-Ni-F directions. It therefore seems logical to assume the moments to be aligned along one of these lines. For this model then, the (100) structure factor at T=0 gives g=2.04.

An analysis of the paramagnetic diffuse scattering yields the value g=1.98, and no residual diffuse magnetic scattering is detected at low temperatures. Since the latter effect should amount to only 0.2 barn/steradian in the forward direction, its absence is not too surprising.

IV. CONCLUSION

The magnetic structure of the fluorides of Mn, Fe, Co, and Ni are found to be very similar to that in Van



FIG. 9. Temperature dependence of the (100) crystal structure factors in CoF₂ and NiF₂. The saturation curves indicate Néel temperatures of 50°K for CoF₂ and 83°K for NiF₂.

Vleck's simple model in which antiferromagnetism results from direct exchange forces; and the thermal dependence of the intensity of magnetic scattering seems to be accounted for with the Brillouin saturation curve obtained by Van Vleck.

The observed antiferromagnetism in CoF_2 and NiF_2 seemingly constitutes a real contradiction between neutron diffraction and magnetic susceptibility measurements on powdered samples. Since the diffraction work is done in the absence of a magnetic field, and the effect of a field on antiferromagnetism is not well understood, it would be desirable to repeat the susceptibility measurements in very weak magnetic fields to see if this discrepancy is removed. In this connection it is interesting to note that the recent measurements by Stout and Matarrese¹⁷ of the magnetic anisotropy in a single crystal of CoF_2 do indicate an antiferromagnetic behavior in this compound at low temperatures.

Preliminary studies on MnO_2 ,¹⁸ which is isomorphous with the fluorides reported here, show that in this compound the magnetic structure is more complex than that of the fluorides. A more detailed report of this work will be given later.

It is a pleasure for the author to express his gratitude to Dr. C. G. Shull and Dr. E. O. Wollan who suggested this study, made available their apparatus, and gave constant aid during the course of the research. The author is also indebted to Professor J. G. Daunt and Dr. L. D. Roberts for many helpful suggestions in designing the cryostat; to Dr. S. Tamor for many discussions on the theoretical aspects of neutron

¹⁷ J. W. Stout and L. M. Matarrese, Revs. Modern Phys. 25, 338 (1953).



FIG. 10. Diffraction patterns for NiF₂ taken at room temperature and at 25°K. The presence of an (001) reflection at 25°K indicates that the Ni⁺⁺ moments are not aligned along the tetragonal axis.

scattering; to Dr. W. C. Koehler, Dr. M. K. Wilkinson, and Mr. L. A. Rayburn for assistance with the measurements; to Professor J. G. Potter and Professor D. F. Weeks for several discussions and comments on the results; to Mr. B. S. Borie and Mr. R. M. Steele for x-ray analyses of the samples; and to the entire personnel of the Physics Division at the Oak Ridge National Laboratory whose kind cooperation has made this work possible.

The author gratefully acknowledges the grant of a Fellowship from the Oak Ridge Institute of Nuclear Studies.

¹⁸ R. A. Erickson, Phys. Rev. 85, 745 (1952).