The Magnetic Anisotropy of Manganous Fluoride between 12 and 295°K

Maurice Griffel and J. W. Stout

Additional information on J. Chem. Phys.

The Magnetic Anisotropy of Manganous Fluoride between 12 and 295°K

MAURICE GRIFFEL* AND J. W. STOUT

Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received July 13, 1950)

The magnetic anisotropy of single crystals of MnF_2, a typical antiferromagnetic substance, has been measured over the temperature range 12 to 295°K. At temperatures above 100°K the anisotropy is of the order of 0.1 percent of the susceptibility and the greater susceptibility is in the direction of the c axis of the tetragonal crystal. Below 70°K the anisotropy becomes extraordinarily large and the susceptibility in the direction of the c axis is smaller than that perpendicular to this axis. Within the limit of experimental error, the anisotropy was independent of field strength up to 10,000 gauss. From the present measurements, combined with those of previous investigators on the powder susceptibility, the directional susceptibilities parallel and perpendicular to the c axis have been calculated. As the temperature is lowered from 70 to 14°K, the perpendicular susceptibility increases by about 12 percent and the parallel susceptibility approaches zero at zero temperature. These results are discussed in connection with the theory of antiferromagnetism proposed by Van Vleck.

INTRODUCTION

MANGANOUS fluoride is an example of that class of paramagnetic substances which are called antiferromagnetic. In ferromagnetic materials the exchange forces between neighboring paramagnetic ions favor a parallel alignment of the electronic spins and the ordered arrangement stable at low temperatures has a permanent magnetic moment within each domain consisting of many atoms. In antiferromagnetic materials the exchange forces favor an antiparallel alignment of the spins and the low temperature ordered arrangement has no permanent moment and a magnetic susceptibility less than would be obtained if there were no interaction between the magnetic ions. The magnetic susceptibility of powdered MnF_2 as measured by Bizette and Tsai[1] and de Haas, Schultz, and Koolhaas[2] has a maximum in the neighborhood of 70°K and decreases at lower temperatures, reaching at 15°K a value roughly three-fourths of the maximum. The heat capacity measurements of Stout and Adams[3] show a sharp maximum at 66.5°K. About 34 percent of the total magnetic entropy of $k \ln 6$ per Mn^{++} ion, corresponding to the change from a completely ordered state to one of complete randomness of the spins, was found in that portion of the heat capacity curve which was clearly anomalously high. The remainder of the magnetic entropy is presumably gradually acquired at higher temperatures in such a fashion that the corresponding heat capacity could not be distinguished from the ordinary vibrational heat capacity.

Van Vleck[4] has derived a theory of antiferromagnetism which is formally similar to the Weiss-Heisenberg theory of ferromagnetism. In Van Vleck's theory the magnetic ions are divided into two subclasses, each of which is acted on by an internal field proportional to the magnetic moment of the other. Since the two subclasses have opposite orientations, there is no net magnetic moment. As in the Weiss theory, there is a Curie temperature at which long-range order appears. Below the Curie temperature the magnetic susceptibility parallel to the direction of alignment of the spins decreases to zero as the temperature is lowered to 0°K while that perpendicular to this direction remains constant. Van Vleck did not consider the identification of these susceptibilities with any crystallographic directions but by averaging calculated that the powder susceptibility at 0°K should be two-thirds its value at the Curie temperature.

Recent accurate measurements of Corliss, Delabarre, and Elliott[5] on the powder susceptibility of MnF_2 at temperatures above 180°K may be represented by the Curie-Weiss formula, $\chi = C/(T+\Delta)$, with the Curie constant equal to that calculated for the ^6S state of gaseous Mn^{++} ion and a Δ of 97°K. The large value of Δ is presumably associated with the exchange coupling between the magnetic ions. The energy associated with the exchange forces depends only on the relative orientations of the spins of the interacting ions and is independent of the orientations of the spins with respect to the crystallographic directions.[6] MnF_2 has the tetragonal rutile crystal structure[7,8] with each Mn^{++} ion surrounded by two nearest neighbors at a distance of 3.3103A in the direction of the c axis, eight neighbors at a distance of 3.8229A in the 111 directions and four at a distance of 4.8734A in the ab plane. Although the exchange forces, which are primarily responsible for the ordering that begins near 70°K, cannot directly produce a magnetic anisotropy, it was conceivable that this ordering could affect the small anisotropy expected from other causes. Our measurements show that in the ordered state the anisotropy becomes extraordinarily

---

* AEC Predoctoral Fellow 1948–49. Present address: Iowa State College, Ames, Iowa.
[1] H. Bizette and B. Tsai, Comptes Rendus 209, 205 (1939).
[2] de Haas, Schultz, and Koolhaus, Physica 7, 57 (1940).
[3] J. W. Stout and H. E. Adams, J. Am. Chem. Soc. 64, 1535 (1942).
[4] J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941).

[5] Corliss, Delabarre, and Elliott, J. Chem. Phys. 18, 1256 (1950).
[6] See J. H. Van Vleck, Phys. Rev. 52, 1178 (1937).
[7] P. P. Ewald and C. Hermann, *Strukturbericht* (Leipzig, 1931), Vol. I, p. 192.
[8] M. Griffel and J. W. Stout, J. Am. Chem. Soc. (to be published).

large. The measurements and the interpretation will be discussed below. A preliminary account of them has been published.[9]

EXPERIMENTAL

The magnetic anisotropy was determined with a torsion balance which measured the couple on an oriented single crystal in a homogeneous magnetic field. The apparatus and method of measurement have been described previously.[10] The preparation and properties of the single crystals of MnF_2 used have also been described.[8] Two crystals, designated as A and B, were used for the measurements. Crystal A was in the form of a right circular cylinder 0.9 cm tall and 0.9 cm in diameter, and weighed 2.224 g. The boule from the single crystal furnace was first oriented approximately by observation through crossed polaroids. It was then attached to the goniometer head of a Laue back reflection x-ray camera and adjusted until the c axis coincided with the direction of the incident x-rays. An accurately milled miter box was then placed around the crystal and lined up with respect to the camera. The

TABLE I. Couple produced at various angular positions. The angular position, θ, is measured from a position of zero torque. The couple produced by the magnetic field is proportional to the rotation, Δ, of the torsion head needed to bring the crystal in the magnetic field back to its position, θ, in zero field. $\Delta = 1000$ corresponds to one complete rotation. All measurements are on crystal A.

	θ	Δ	Average
$T = 295.7°K$	45°	41.05 ⎫	
0.005-in. suspension	225°	39.23 ⎭	40.14
9845 gauss	135°	40.19 ⎫	
	315°	41.11 ⎭	40.65
$T = 90.15°K$	45°	85.15 ⎫	
0.005-in. suspension	225°	84.30 ⎭	84.73
9860 gauss	135°	87.55 ⎫	
	315°	81.50 ⎭	84.53
$T = 20.34°K$	45°	163.85 ⎫	
0.010-in. suspension	225°	164.05 ⎭	163.95
2045 gauss	135°	163.70 ⎫	
	315°	164.50 ⎭	164.10

crystal was cemented to the miter box with a beeswax-rosin mixture. The miter box was then rotated on the bed of the camera by 180° and an x-ray picture taken of the opposite side of the crystal. The perfect agreement of the two pictures as well as the uniform extinction of polarized light proved that the crystal was indeed single.

The miter box was then mounted on the cross feed of a lathe and the ends of the crystal ground down parallel to the ends of the box against a rotating flat sanding plate. These faces contained the c axis of the crystal and were used as reference planes in the further machining operations. The crystal was next cut with a

jeweler's saw, the selected half removed from the miter box and the reference surface cemented to a flat-surfaced brass piece held in the collet of the lathe. The crystal was then ground with sandpaper into the form of a right circular cylinder with the c axis lying in the basal plane. The orientation was confirmed to within 1° by an x-ray picture taken perpendicular to the c axis. The crystal was etched in HCl solution to remove any possible ferromagnetic impurities on the surface and was mounted in the torsion balance with the c axis accurately perpendicular to the axis of the suspension and the direction of the c axis in the basal plane known roughly by a mark on the crystal. The exact angular orientation of the c axis was determined from the positions of zero torque.

Crystal B, prepared from another boule, was a small square plate approximately 0.6 cm along an edge and 0.15 cm thick. It was similarly oriented by x-rays to within 1° and weighed 0.2054 g.

Before the measurements were made it was expected that the magnetic anisotropy of MnF_2 might be quite small and so some pains were taken to grow a large crystal and to form it into a geometrical shape with circular symmetry about the axis of rotation of the balance suspension. There is a torque on a magnetically isotropic crystal of non-symmetrical shape in a uniform magnetic field because of demagnetization effects.[11] Thus an isotropic paramagnetic needle tends to align itself with the direction of the magnetic field. This effect is not important for moderately anisotropic paramagnetic salts, as was the case, for example, with our measurements on $NiSO_4 \cdot 6H_2O$, but in the case of MnF_2, when the anisotropy is small and the susceptibility relatively large, it can be of importance unless care is taken to have a symmetrical sample. After the measurements on crystal A had shown the anisotropy at hydrogen temperatures to be very large, we prepared crystal B, which has square symmetry, for the measurements at these temperatures.

When the anisotropy is small there is another effect that is of importance. The quartz rod to which the crystal is attached is neither perfectly straight, nor perfectly centered, nor is the field absolutely uniform. Consequently, if the field exerts a slight lateral force on the paramagnetic sample or the quartz rod, because of the lack of perfect alignment and centering of the suspension, rod and sample, a torque on the suspension is observed. To a good approximation this torque varies as $\sin\theta$ where θ is the angular position of the suspension. It was found experimentally that this effect could be minimized by selecting straight rods and by careful alignment. The total couple measured in an arbitrary position is then

$$C = C_1 \sin(\theta + \alpha) + C_2 \sin2(\theta + \psi). \qquad (1)$$

[9] J. W. Stout and M. Griffel, Phys. Rev. 76, 144 (1949).
[10] J. W. Stout and M. Griffel, J. Chem. Phys. 18, 1449 (1950).

[11] E. C. Stoner, *Magnetism and Matter* (Methuen and Company, Ltd., London, 1934), p. 40.

TABLE II. Molal magnetic anisotropy of MnF₂.
(Molecular weight 92.93.)

Crystal	T, °K	H, gauss	$(\chi_{||}-\chi_{\perp})\times10^3$
A	295.7	9845	0.0133
A	185.1	9850	0.0248
A	158.8	9840	0.0290
A	131.7	9850	0.0334
A	90.15	9860	0.0279
A	90.15	6040	0.0282
A	90.15	3910	0.0282
A	77.30	9870	0.0009
A	77.27	6030	0.0012
A	73.42	9920	− 0.0237
A	70.38	9840	− 0.0603
B	68.70	9790	− 0.1109
A	68.4±0.1	9870	− 0.114
A	67.34	9890	− 0.184
B	66.19	9815	− 0.884
B	62.98	9800	− 2.76
B	62.35	9850	− 3.10
B	59.80	9820	− 4.46
B	58.00	9830	− 5.32
B	54.76	9820	− 6.87
B	20.37	9806	−21.8
B	20.37	7755	−21.8
B	20.37	6040	−21.7
B	20.37	3955	−21.7
B	20.37	2075	−21.8
A	20.34	4015	−21.5
A	20.34	2045	−21.5
A	20.34	1010	−21.3
A	16.40	2040	−23.0
B	16.24	9820	−23.2
A	13.92	2040	−23.7
B	13.92	9820	−23.9
B	11.9	9815	−24.4

α and ψ are phase angles which in general are not equal and $C_2=\frac{1}{2}(m/M)H^2(\chi_1-\chi_2)$ where the notation is the same as used in the previous paper.[10] The validity of Eq. (1) was checked by several series of measurements at ten to twenty equally spaced intervals around a complete circle and treating the data by Fourier analysis. Only the coefficients of the "1θ"- and "2θ"-terms were found to be appreciable. It is sometimes difficult to keep the temperature constant for the time required to take a large number of readings. Since generally $C_2\gg C_1$ and since the torque at the maximum is not sensitive to small changes in angle a simpler procedure of eliminating the "1θ"-terms was adopted. A zero torque position is found; the torsion head is rotated 45° to the position of maximum torque and a reading taken. The torsion head is then rotated by 180° and another observation made. The average of these two readings is the correct one since the "1θ"-terms cancel. As a check two further readings were often taken at the two remaining maxima. In Table I are presented some typical data. It is evident that at room temperature and at the boiling point of oxygen where the anisotropy is small the "1θ"-correction is important whereas at the boiling point of hydrogen it is smaller than the experimental error. At the boiling point of nitrogen, which is very near the temperature where the anisotropy passes through zero, the "1θ"- and "2θ"-deflections were comparable in magnitude and it was necessary to take

a complete set of readings and make the Fourier analysis.

The results of the measurements are presented in Table II. The results are believed to be accurate to one percent or to an absolute value of 0.3×10^{-6} susceptibility difference per mole, whichever is larger. In the region near 66°K, where the anisotropy is changing very rapidly with temperature, the principal uncertainty is introduced by the temperature measurement which was accurate to 0.05° unless otherwise indicated. The results of the anisotropy measurements below 100°K are shown in Fig. 1. In order to investigate the region between 20 and 55°K where no refrigerant bath was available a warming curve of one-hour duration was taken over this temperature range. Measurements of temperature and anisotropy were made throughout the warming time and the curve in Fig. 1 has been drawn through these points which are indicated by crosses. Since the uncertainty in the temperature of the specimen when there may be appreciable thermal gradients in the apparatus makes the warming curve points considerably less reliable than the ones taken with a refrigerant bath, we have not presented these data in tabular form. However, they show the general nature of the variation of the anisotropy over the temperature range 20 to 55°K.
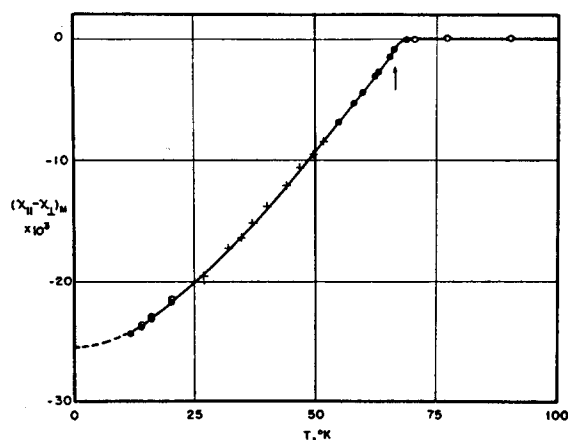

Fig. 1. Molal magnetic anisotropy of MnF₂. The arrow indicates the temperature of the heat capacity maximum.

At high temperatures the susceptibility parallel to the c axis, $\chi_{||}$, is greater than the perpendicular susceptibility, $\chi_{\perp}$, and the anisotropy, $\chi_{||}-\chi_{\perp}$, is of the order of 0.1 percent of the susceptibility. As the temperature is lowered, the anisotropy rises, reaching a maximum at about 120°K and then falls rapidly. The anisotropy passes through zero at about 77°K and as the temperature is lowered becomes large and negative until at the temperatures of liquid hydrogen it is greater than the susceptibility of powdered specimens. The susceptibility of a randomly oriented powder specimen is given by $\chi_{Av}=\frac{1}{3}\chi_{||}+\frac{2}{3}\chi_{\perp}$. By combining our measurements with those of de Haas, Schultz, and
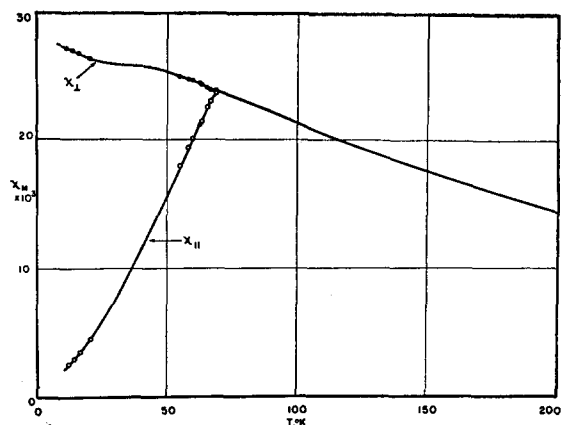
FIG. 2. Molal magnetic susceptibility of MnF$_2$ parallel and perpendicular to c axis of crystal.

Koolhaas[2] on a powder specimen we have calculated the individual values of $\chi_{\shortparallel}$ and $\chi_{\perp}$ which are illustrated in Fig. 2. Within the accuracy of the powder susceptibility data, $\chi_{\shortparallel}$ approaches zero at zero temperature. The use of the powder susceptibility measurements of Bizette and Tsai[1] combined with our data would extrapolate to a negative value of $\chi_{\shortparallel}$ at 0°K. As is seen from the data in Table II, we found no significant variation of the anisotropy with field strength at the lowest temperatures and at fields up to 10,000 gauss.

DISCUSSION

The small magnetic anisotropy at room temperature is comparable to that observed[12] in more dilute manganous salts which, according to Van Vleck and Penney,[13] is caused by a slight splitting of the sixfold degenerate ground level of Mn^{++} ion by the crystalline electrostatic fields. Since at high temperatures the susceptibility of MnF$_2$ parallel to the c axis is greater than that perpendicular, the states corresponding to the alignment of the spins in the direction of the c axis will be energetically more favored than the others by a few tenths of a wave number. If this effect of the crystalline electric fields were the only one, the anisotropy would be always of the same sign and vary inversely as T^2. However, the heat capacity anomaly near 66.5°K and the large Δ of 97° in the Curie-Weiss formula that represents the powder susceptibility measurements[5] above 180°K are indications of much stronger forces acting on the magnetic ions. These are presumably exchange

[12] K. S. Krishnan and S. Banerjee, Trans. Roy. Soc. A235, 343 (1936).
[13] J. H. Van Vleck and W. G. Penney, Phil. Mag. 17, 961 (1934).

forces which couple together the spins of the Mn^{++} ions. In the neighborhood of 70°K this coupling begins to produce a long-range order and, as the temperature is lowered, the magnetic ions approach a completely ordered arrangement with no net magnetic moment.

The exchange forces cannot in themselves produce any anisotropy. However, once the magnetic ions are coupled together by the exchange forces in ordered groups the energy needed to turn the spins with respect to the crystal lattice is the energy of a few tenths of a wave number for each individual ion times the effective number in a group. Below the Curie temperature of around 70°K the size of the group rapidly increases. With this addition, Van Vleck's theory[4] of antiferromagnetism is in good qualitative agreement with the results we have observed on MnF$_2$. At high temperature, where there is no long-range order, there is a small tendency favoring alignment of the spins parallel to the c axis of the crystal and consequently a slightly greater susceptibility in this direction. Below the Curie temperature, where long-range order sets in, the spins become largely lined up in the direction of the c axis and the susceptibility in this direction becomes small because of an effect analogous to the saturation of a paramagnetic substance in a very large magnetic field.

The magnetic dipole-dipole coupling between neighboring ions in MnF$_2$ could also produce an alignment of the spins with respect to the crystal lattice since the dipole energy contains a term dependent on the orientation of the spins relative to the radius vector between them. For two Mn^{++} ions at the nearest neighbor distance of 3.310A, which are coupled together by strong forces in an antiparallel fashion, the dipole energy would be 0.9 cm^{-1} lower for an alignment of the dipoles perpendicular to the c axis than for alignment with this axis. Taking the nearest and next nearest neighbors into consideration the dipole forces would favor alignment of the spins perpendicular to the c axis provided that the nearest neighbors are coupled together in an antiparallel fashion. This is not in agreement with the alignment of the spins in the direction of the c axis deduced from our measurements. However, if the chains of nearest neighbors running in the c direction are coupled together by the exchange forces in a parallel (ferromagnetic) sense, and if the chains are coupled to one another by antiferromagnetic interaction between the next-nearest neighbors, then the dipole forces would favor the alignment of the spins along the c axis and since the chains are coupled antiparallel the crystal as a whole would be antiferromagnetic.