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Magnetic Anisotropy of the Iron-Group Fluorides

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The magnetic anisotropy of single crystals of FeF_2 and CoF_2 has been measured over the temperature range 11 to 340°K. Like MnF_2, the anhydrous difluorides of iron and cobalt have the tetragonal rutile crystal structure, and the anisotropy results are compared with those found by Stout and Griffel for MnF_2. In all three compounds the magnetic susceptibility parallel to the crystallographic c axis is at room temperatures greater than that in a direction perpendicular to this axis. Because of the orbital magnetic moment the high temperature anisotropy is much greater for FeF_2 and CoF_2 than for MnF_2. As the temperature is lowered, the anisotropy changes sign and at 11°K has large negative values, indicating that the susceptibility parallel to the c axis becomes small. This indicates that at low temperatures there is an ordered antiferromagnetic arrangement with the elementary magnetic moments aligned parallel and antiparallel to the c axis. Such a magnetic structure has been found from neutron diffraction measurements by Shull and Erickson. The anomalous behavior of the magnetic anisotropy, associated with the antiferromagnetic ordering, is in the case of CoF_2 spread out over a much wider temperature range than in the case of MnF_2 and FeF_2. At the lowest temperatures the anisotropy of MnF_2 varies as T^2, whereas those of FeF_2 and CoF_2 vary as the fourth power of the temperature.

THE anhydrous difluorides of the elements manganese, iron, cobalt, and nickel all have the rutile-type crystal structure.[1] The tetragonal unit cell, containing two molecules, has values of c_0/a_0 in the neighborhood of two-thirds. The structure of the positive ion lattice may be thought of as made up of chains running parallel to the c axis. A given magnetic ion and its two nearest magnetic neighbors all lie in the same chain. The eight next nearest neighbors, in the directions of the body diagonal of the tetragonal unit cell, are more distant than the nearest neighbors by factors ranging from 1.12 in FeF_2 to 1.18 in NiF_2. The structure of MnF_2, which is typical, is shown in Fig. 1. Because of the tetragonal symmetry there is a possibility of anisotropy in the magnetic susceptibility. The symmetry requires that one of the principal axes of magnetic susceptibility lie along the c axis of the crystal, while the susceptibility must be the same in all directions normal to the c axis.

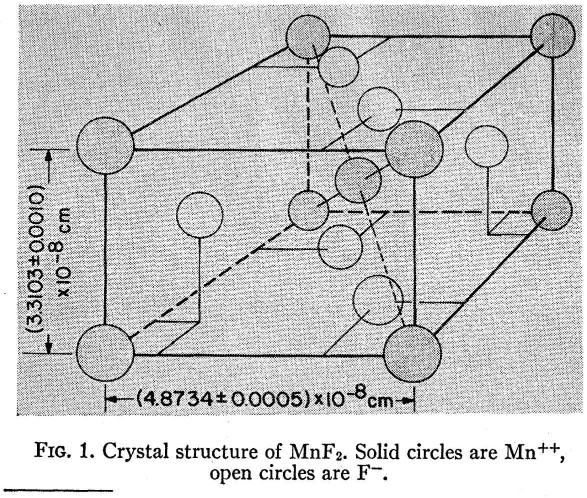

FIG. 1. Crystal structure of MnF_2. Solid circles are Mn^{++}, open circles are F^-.

From measurements of the magnetic susceptibiltiy by Bizette and Tsai,[2] and by de Haas, Schultz, and Koolhaas,[3] and from the heat capacity measurements of Stout and Adams,[4] manganese fluoride is known to be a typical antiferromagnetic material. It exhibits a maximum in the powder magnetic susceptibility and at about the same temperature a region of anomalously high heat capacity which is indicative of a cooperative phenomenon. The susceptibility data of Bizette and Tsai[5] indicate that FeF_2 is also antiferromagnetic, but, according to Bizette,[6] CoF_2 and NiF_2 are not.

The theory of antiferromagnetism proposed by Van Vleck[7] predicted that below the Curie temperature the magnetic susceptibility of an antiferromagnetic material should decrease with decreasing temperature in that direction along which the spins of two sublattices are aligned parallel and antiparallel, and should approach zero at the absolute zero of temperature. The susceptibility perpendicular to this direction would, according to the theory, remain constant below the Curie temperature. However, Van Vleck did not discuss why the direction of spin alignment should correspond to any particular direction with respect to the crystallographic axes. The exchange forces, which presumably cause the antiferromagnetic ordering, are themselves isotropic, so in a substance like MnF_2, where the magnetic ions are in an S state and consequently the anisotropy energy due to crystalline electrostatic fields would be

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* Lindsay Light and Chemical Company Fellow, 1951.

[1] See (a) MnF_2, M. Griffel and J. W. Stout, J. Am. Chem. Soc. **72**, 4351 (1950); (b) FeF_2 and CoF_2, A. Ferrari, Atti Acad. Lincei, [6] **3**, 324 (1926); (c) NiF_2, Haendler, Patterson, and Bernard, J. Am. Chem. Soc. **74**, 3167 (1952).

[2] H. Bizette and B. Tsai, Compt. rend. **209**, 205 (1939).

[3] de Haas, Schultz, and Koolhaas, Physica **7**, 57 (1940).

[4] J. W. Stout and H. E. Adams, J. Am. Chem. Soc. **64**, 1535 (1942).

[5] H. Bizette and B. Tsai, Compt. rend. **212**, 119 (1941).

[6] H. Bizette, Ann. phys. [12] **1**, 295 (1946).

[7] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).

very small, it was doubtful if any preferential direction of spin alignment would exist in a crystal.

In an investigation of this point Stout and Griffel[8] discovered by measurements on a single crystal of MnF_2 that at high temperatures the magnetic anisotropy is, as was expected, very small, but as the temperature is lowered below 70°K a rapid increase in anisotropy begins, reaching extraordinarily large values in the hydrogen temperature range. Figures 2 and 3 show the data on MnF_2. At high temperatures (Fig. 2) the magnetic susceptibility is greater parallel to the *c* axis; at 300°K the anisotropy is about 0.1 percent of the susceptibility. As the temperature is lowered the anisotropy rises at first as one would expect from the effect of an anisotropic crystalline field. At 120°K the curve reaches a maximum and then rapidly drops. The anisotropy passes through zero at about 77°K and at lower temperatures the greater susceptibility is perpendicular to the *c* axis. In Fig. 3, which shows the anisotropy, $\chi_{\parallel}-\chi_{\perp}$, below 100°K, the scale is one thousand times smaller than that of Fig. 2. By combining the results of the anisotropy measurements with the powder susceptibility data of de Haas, Schultz, and Koolhaas[3] one can calculate the susceptibilities parallel and perpendicular to the *c* axis. The curves for MnF_2 are shown in Fig. 4. Within the limits of error of the powder susceptibility data the susceptibility parallel to the *c* axis approaches zero at the absolute zero of temperature.

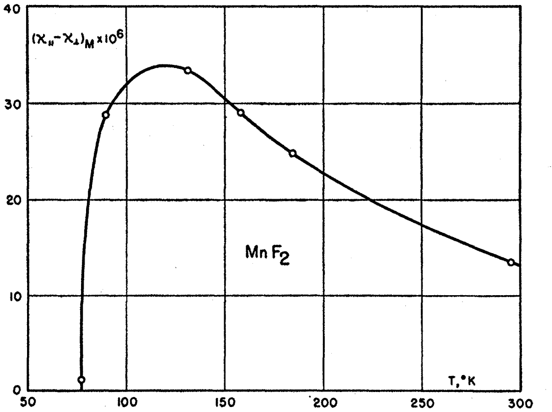

FIG. 2. Molal magnetic anisotropy of MnF_2. $\chi_{\parallel}$ and $\chi_{\perp}$ are molal susceptibilities parallel and perpendicular to the *c* axis. Note that the ordinate scale is 1000 times that of Fig. 3.

The observed magnetic behavior of MnF_2 at low temperatures is in qualitative agreement with the theory of Van Vleck,[7] provided one assumes that the alignment of the spins is parallel and antiparallel to the *c* axis of the crystal. This alignment of the spins has been confirmed by neutron diffraction measurements of Erickson and Shull[9] which, besides showing that the *c* axis is the direction along which alignment occurs, also demonstrate that the spins in a nearest-neighbor chain in the direction of the *c* axis are all aligned parallel to one another. Each chain is surrounded by four others with spin alignment antiparallel to it. The ordered magnetic structure consistent with the magnetic susceptibility and neutron diffraction data is shown in Fig. 5.

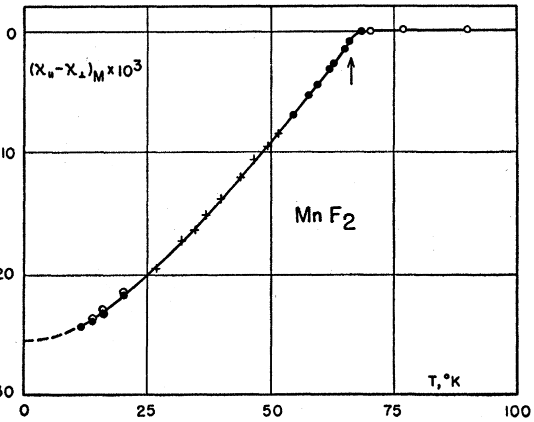

FIG. 3. Molal magnetic anisotropy of MnF_2. $\chi_{\parallel}$ and $\chi_{\perp}$ are molal susceptibilities parallel and perpendicular to the *c* axis. The arrow indicates the temperature of the heat capacity maximum.

The small anisotropy observed in MnF_2 at high temperatures indicates that for each magnetic ion there is an anisotropy energy of a few tenths of a wave number favoring alignment of the spins along the *c* axis as compared to a perpendicular alignment. In the neighborhood of 100°K the long-range order, caused by the energetically much larger exchange forces, begins to appear in the crystal. As the temperature is lowered the extent of order continues to grow. One may think of the magnetic ions as clustered together in ordered

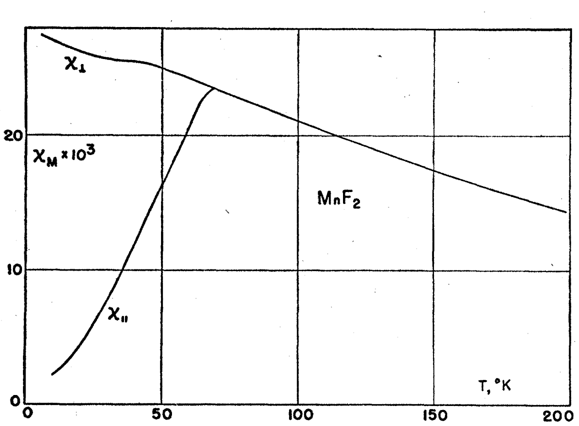

FIG. 4. Molal magnetic susceptibility of MnF_2 parallel and perpendicular to *c* axis of crystal.

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[8] J. W. Stout and M. Griffel, (a) Phys. Rev. **76**, 144 (1949); (b) J. Chem. Phys. **18**, 1455 (1950).

[9] (a) R. A. Erickson and C. G. Shull, Phys. Rev. **83**, 208 (1951); (b) R. A. Erickson, thesis, Agric. and Mech. College of Texas, June, 1952.

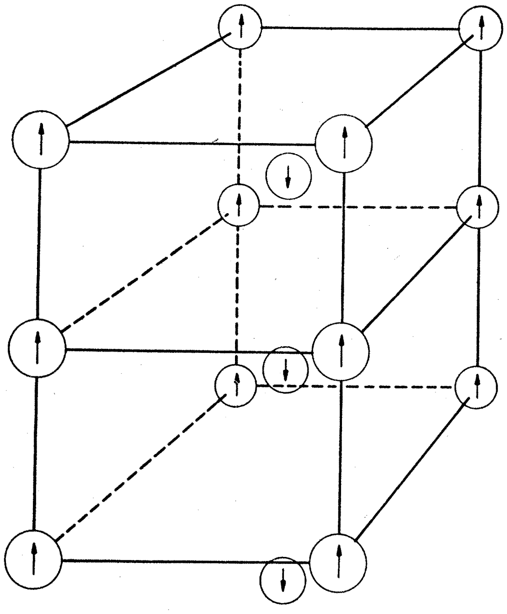

FIG. 5. Ordered magnetic structure of MnF_2, FeF_2, CoF_2. The arrows indicate the spin alignment parallel and antiparallel to the *c* axis. Only the positive ions are shown.

groups which grow in size as the temperature is lowered. The energy required to turn a group in the crystalline field is the small anisotropy energy per ion times the number of ions in a group, and if the number in a group increases rapidly this energy soon becomes large compared to kT. This explanation, suggested in qualitative form by Stout and Griffel,[8] has been quantitatively treated by Yosida[10] and by Keffer.[11] The latter author emphasizes the importance of the dipole forces which cause an anisotropy energy in addition to that of the crystalline field. Griffel and Stout[8b] had pointed out that the dipole forces would contribute to an anisotropy energy and, from their result that the spin alignment was along the *c* axis, suggested the magnetic structure shown in Fig. 5 as the one favored by the dipole forces. However, the possibility of other directional dependent forces made any theoretical prediction uncertain, and it was not until after the neutron diffraction results[9] were obtained that the magnetic structure was proved.

The magnetic ions Fe^{++} and Co^{++} are in *D* and *F* states, respectively. The interaction between the orbital motion of the electrons and the crystalline electrostatic fields produces in magnetically dilute salts of these ions a large magnetic anisotropy.[12] In the anhydrous fluorides the anisotropy energy should be much larger than was the case in MnF_2. As the number of electrons in the *d* shell increases beyond the half-filled position of manganous ion, one might also expect a decrease in the magnitude of the exchange energy. To investigate these effects we have measured the magnetic anisotropy of single crystals of FeF_2 and CoF_2. The detailed results of these measurements will be published elsewhere.

The observed magnetic anisotropy of FeF_2 is shown in Fig. 6. The points shown as filled circles were taken under isothermal conditions. Those indicated by crosses were obtained during a warming curve and because of possible temperature gradients are considerably less accurate. They serve, however, to show the general shape of the curve in the region between 20 and 60°K. Like MnF_2, the susceptibility at high temperatures is greater in the direction of the *c* axis, but the magnitude of the anisotropy at high temperatures is much greater, amounting at 300°K to 20 percent of the powder susceptibility. This is comparable to the anisotropy observed in dilute ferrous salts.[12] At high temperatures the anisotropy rises with decreasing temperature, but the curve bends over, reaching a maximum at about 95°K, and then drops rapidly. The anisotropy passes through zero at about 72°K and, as the temperature is lowered, rapidly drops to large negative values. In the hydrogen range the variation of anisotropy with temperature decreases at the lower temperatures and it appears that the curve will approach 0°K with zero slope. The magnetic susceptibility of powdered FeF_2 has been measured by Bizette

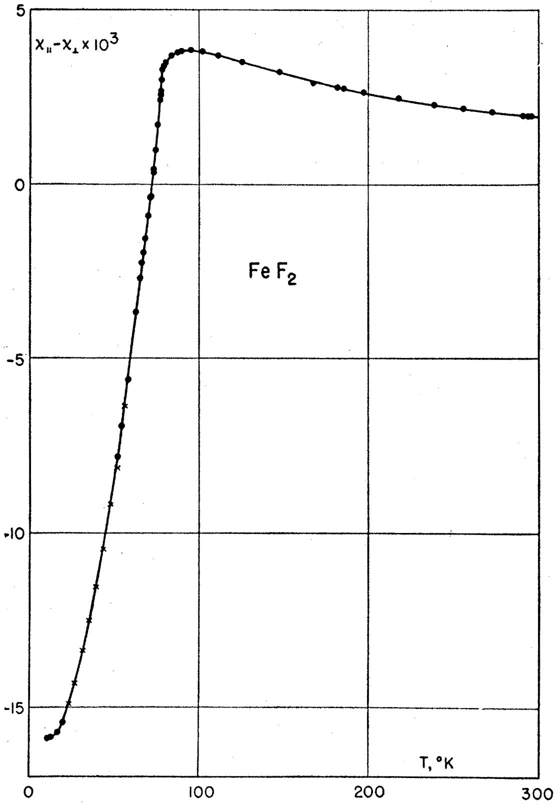

FIG. 6. Molal magnetic anisotropy of FeF_2. $\chi_{\parallel}$ and $\chi_{\perp}$ are molal susceptibilities parallel and perpendicular to the *c* axis.

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[10] K. Yosida, Prog. Theoret. Phys. 6, 691 (1951).

[11] F. Keffer, Phys. Rev. 88, 608 (1952).

[12] Krishnan, Chakravorty, and Banerjee, Trans. Roy. Soc. 232, 99 (1932).

and Tsai.[5] By combining these data with out anisotropy values, the susceptibilities parallel and perpendicular to the *c* axis have been calculated. The curves are shown in Fig. 7. The powder susceptibility data do not extend below 63°K and the dotted portion of the curves is an extrapolation upon the assumption that the parallel susceptibiltiy, $\chi_{\parallel}$, approaches zero at 0°K. The powder susceptibility data do extend to a low enough temperature to show definitely the maximum in $\chi_{\parallel}$. Aside from the expected much larger anisotropy at high temperatures the curves for FeF_2 resemble those of MnF_2 and are in qualitative agreement with the behavior predicted by the theory of Van Vleck. The anisotropy data show that the alignment of the elementary magnets is in the direction of the *c* axis, in agreement with the neutron diffraction measurements of Erickson and Shull.[9] Figures 4 and 7 show the perpendicular susceptibility rising below the Curie temperature for MnF_2 and falling in the case of FeF_2. On the theory of Van Vleck[7] $\chi_{\perp}$ should be independent of temperature in this region. The variation in $\chi_{\perp}$ is much larger than the error in out anisotropy measurements, but because of possible errors in the powder susceptibilities, and the lack of data at hydrogen temperatures for FeF_2, the knowledge of the details of the variation of $\chi_{\perp}$ with temperature below the Curie points must await precise determination of the powder susceptibility, or preferably, measurements of the susceptibility of a single crystal along a known crystallographic direction.

The data for the magnetic anisotropy of CoF_2 are shown in Fig. 8. As was the case with MnF_2 and FeF_2, at the lowest temperatures the greater susceptibility of CoF_2 is that perpendicular to the *c* axis. The magnitude of the low temperature anisotropy in CoF_2 is unusually large, being twice that observed for MnF_2. On the Van Vleck theory[7] the Curie temperature, T_C, is related to the constant perpendicular susceptibility below the Curie temperature, $\chi_{\perp}$ (which is equal to the anisotropy at 0°K), by $T_C = \frac{1}{2}C/\chi_{\perp}$, C is the constant in the Curie-Weiss law, $\chi = C/(T+T_C)$, that describes the high temperature susceptibility. The observed Curie constants for colbalt salts[13] range from 2.4 to 3.4, so one might expect a Curie temperature for CoF_2 between 24 and 33°K. A similar calculation for MnF_2 and FeF_2 yields Curie temperatures of 88 and 120°K, respectively. These temperatures are roughly in agreement with those at which the rapid fall in anisotropy begins. However, in CoF_2 the anomalous behavior of the anisotropy extends to temperatures much higher than the Curie temperature calculated from the low temperature anisotropy data. By fitting Brillouin functions to his observed magnetic scattering intensity data, Erickson[9b] estimates the Curie temperatures as 75°K for MnF_2, 90°K for FeF_2, and 50°K for CoF_2.

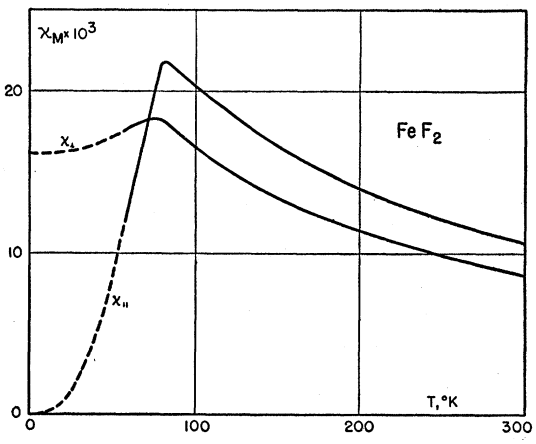

Fig. 7. Molal magnetic susceptibility of FeF_2 parallel and perpendicular to *c* axis of crystal.

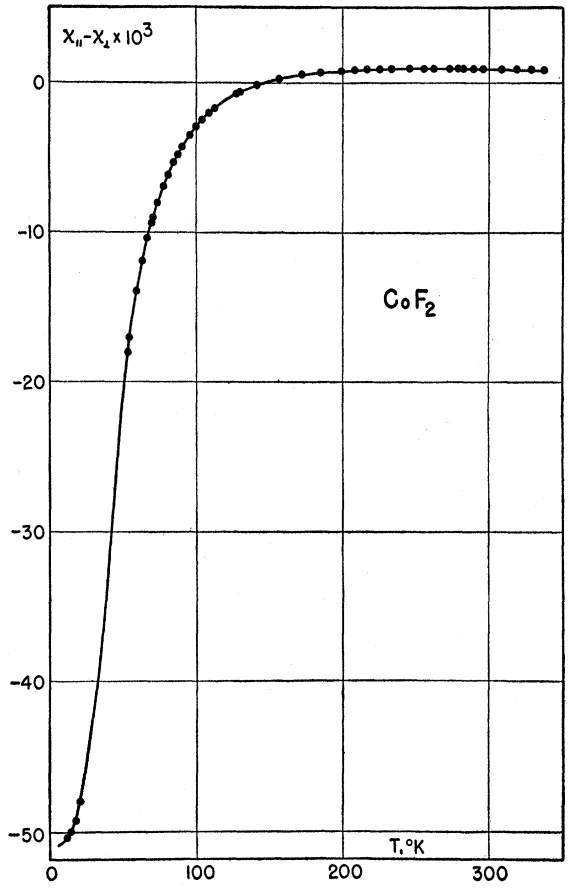

FIG. 8. Molal magnetic anisotropy of CoF_2. $\chi_{\parallel}$ and $\chi_{\perp}$ are molal susceptibilities parallel and perpendicular to the *c* axis.

The curve drawn in Fig. 8 between 20.4 and 53° is a smooth interpolation between these points. We have made measurements during warming between 20 and 60°K, and a preliminary calculation of the data indicates that at temperatures slightly above 20°K the anisotropy rises more steeply than the curve drawn and then decreases in slope until at a temperature of around 40°K it again rises steeply. Although these results may

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[13] E. C. Stoner, *Magnetism and Matter* (Methuen and Company, London, 1934), p. 312.

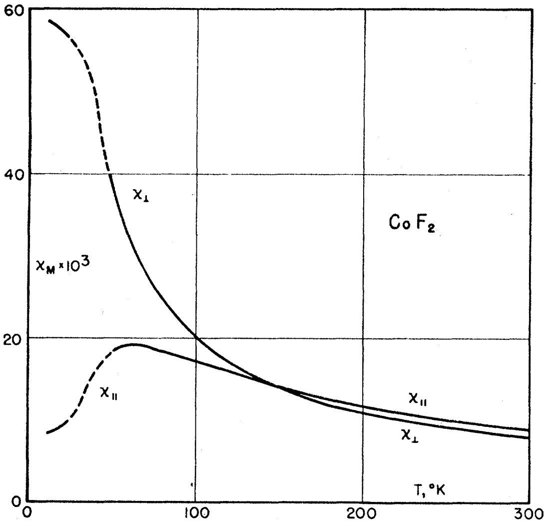

FIG. 9. Molal magnetic susceptibility of CoF$_2$ parallel and perpendicular to c axis of crystal.

be revised upon more complete calculation of the warming curve data, there is no question that between 20 and 60°K the absolute value of the anisotropy decreases monotonically with temperature.

Unlike MnF$_2$ and FeF$_2$ there is in CoF$_2$ no rapid change of slope in the anisotropy curve as the maximum is approached from the low temperature side. The anisotropy of CoF$_2$ passes through zero at about 146°K and rises slowly to a broad maximum in the neighborhood of 260°K. At higher temperatures there is a gradual fall in $\chi_\parallel - \chi_\perp$.

In CoF$_2$ we observed a small field dependence of anisotropy energy at the temperature of liquid hydrogen. The anisotropy increased by about 2 percent in going from 2000 to 10 000 gauss. No field dependence of anisotropy was observed for CoF$_2$ at higher temperatures, nor for MnF$_2$ and FeF$_2$ at any temperature.

Measurements of the powder susceptibility of CoF$_2$ have been made by de Haas and Schultz.[14] From these data and the anisotropy measurements we have calculated the susceptibilities parallel and perpendicular to the c axis. The curves are shown in Fig. 9. The data of de Haas and Schultz show a considerable decrease of the powder susceptibility with field at 14°K, whereas we found a slight increase in the anisotropy with field. In drawing the curves we have used the powder susceptibilities at high fields. The curve in Fig. 9 for $\chi_\parallel$ does not extrapolate to zero at 0°K; the value of the powder susceptibility would have to be decreased by 20 percent in order to obtain a curve extrapolating to zero. This rather surprising result should be verified by measurements of one of the principal susceptibilities using a single crystal specimen.

In the range from 11.5 to 20.4°K the temperature coefficient of the measured anisotropies decreases rapidly at the lower temperatures. This fact, together with the large value of the observed anisotropy, is evidence that the magnetic moments are aligned along the c axis of the crystal. Such an alignment has been found by Shull and Erickson[9] on the basis of neutron diffraction measurements. It appears clear from the neutron diffraction and magnetic anisotropy measurements that CoF$_2$ at low temperatures is antiferromagnetic, if by this term we mean an arrangement of magnetic moments ordered with respect to one another so that the net magnetic moment in the absence of a field is zero, and aligned along a certain direction in the crystal.

The spectacular drop in $\chi_\perp$ between 10 and 100°K and the gradual variation of the anisotropy curve before its maximum at 260°K is not consistent with a simple picture of antiferromagnetism based on exchange interactions between spins, together with an anisotropy energy. It is well known that over the range 1 to 300°K dilute cobalt salts do not obey Curie's law, and Schlapp and Penney[15] have pointed out that for Co^{++} ion the lowest orbital level in the presence of a cubic field will be triply degenerate. In addition, there is a spin degeneracy of four. These twelve lowest-lying states will be split by the spin-orbit coupling and by electrostatic fields of sufficiently low symmetry into six double degenerate levels. The separation in energy will be small enough so that, although at very low temperatures practically all of the magnetic ions are in the lowest level, at room temperature there will be an appreciable population in higher levels. If the exchange interactions, which can remove all spin degeneracy, are comparable in energy to the separation of the levels by spin-orbit interaction and anisotropic crystalline fields, then one would not expect any simple theory of antiferromagnetism to be applicable and it appears reasonable that the magnetic anomalies would be spread out over a larger temperature range than in a

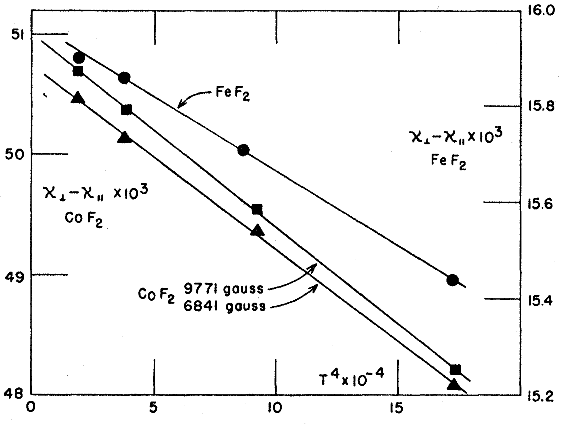

FIG. 10. Molal magnetic anisotropy at hydrogen temperatures *versus* fourth power of the temperature. The scale on the left is for CoF$_2$; that on the right for FeF$_2$.

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[14] W. J. de Haas and B. H. Schultz, Physica 6, 481 (1939).

[15] R. Schlapp and W. G. Penney, Phys. Rev. 42, 666 (1932).

salt like MnF_2 where only the exchange interactions plus a small anisotropy energy need be considered.

By a treatment based on the spin-wave theory, Kubo[16] has shown theoretically that the magnetic anisotropy of a set of spins antiferromagnetically coupled together by exchange forces should at the low temperatures vary as T^2. The observed data[8] on MnF_2, at temperatures obtained with liquid and solid hydrogen, agree well with this relation. From these data Kubo calculates an approximate Curie temperature of 62°K which may be compared with the observed temperature, 66.5°K, of the heat capacity maximum. The observed anisotropies at the lowest temperatures of FeF_2 and CoF_2 do not, however, vary quadratically with temperature, but rather fit closely a function linear in the fourth power of the temperature. In Fig. 10 are shown the anisotropy data for FeF_2 and CoF_2 in the hydrogen range plotted against T^4. Within the accuracy of the measurements the points fall on straight lines. Because of the field dependence found for CoF_2, curves are given for two different magnetic field strengths.

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[16] R. Kubo, Phys. Rev. **88**, 568 (1952).