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SOME FERRIMAGNETIC AND ANTIFERROMAGNETIC MATERIALS AT LOW TEMPERATURES

By R. M. BOZORTH and VIVIAN KRAMER,

Bell Telephone Laboratories, Inc. Murray Hill, New Jersey, U. S. A.

Résumé. — Nous avons étudié l'aimantation de monocristaux et de polycristaux de quelques substances aux températures de 1,3 à 300 °K, dans les champs jusqu'à 12 500 oersteds. Nous avons fait des mesures sur des monocristaux de LiMnPO_4 (orthorhombique), $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (monoclinique) et HoFeO_3 (orthorhombique); les substances polycristallines étudiées sont HoFeO_3 , Ho_2O_3 et Er_2O_3 , $\text{PbO} \cdot \text{Fe}_{12-x}\text{Al}_x\text{O}_{18}$, FeTiO_3 et $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$ en solution solide, CoMnO_3 et NiMnO_3 , $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, MnF_3 , et CrF_3 . Pour les monocristaux ferromagnétiques, on observe une aimantation spontanée le long d'un axe cristallin spécifique; dans le cas du $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ il ne fut pas possible de faire dévier l'aimantation spontanée de la direction de l'axe monoclinique; dans le cas de l' HoFeO_3 il est possible aux basses températures de la faire dévier de l'axe privilégié orthorhombique. L'aimantation spontanée de l' HoFeO_3 augmente jusqu'à 3 magnéttons de Bohr environ si on baisse la température du cristal.

Abstract. — The magnetization of single crystals and of polycrystals of a number of materials has been investigated at temperatures from 1.3 to 300 °K, in fields up to 12,500 oersteds. Measurements were made on single crystals of LiMnPO_4 (orthorhombic), $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (monoclinic), and HoFeO_3 (orthorhombic); polycrystalline materials were HoFeO_3 , Ho_2O_3 , and Er_2O_3 , $\text{PbO} \cdot \text{Fe}_{12-x}\text{Al}_x\text{O}_{18}$, FeTiO_3 and $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$ solid solutions, CoMnO_3 and NiMnO_3 , $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, MnF_3 , and CrF_3 . The ferromagnetic single crystals show spontaneous magnetization along one crystallographic direction; in $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ it was not possible to rotate the spontaneous magnetization out of the direction of the axis, in HoFeO_3 it is readily rotated away from the preferred orthorhombic axis at low temperatures. The spontaneous magnetization in HoFeO_3 rises to about 3 Bohr magnetons as the temperature is lowered.

 LiMnPO_4 Crystal

Mays [1] has reported shifts in the nuclear resonance of ^{31}P with temperature in a number of phosphates, and on the basis of the behavior of these shifts has suggested the presence of antiferromagnetic or ferrimagnetic transitions. Miss Walsh and the present authors have found by measurement of magnetic susceptibility that lithiophilite, $\text{Li}(\text{Mn}, \text{Fe})\text{PO}_4$, is antiferromagnetic below 42 °K. A single crystal was cut from a natural crystal corresponding approximately to the formula $\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$, and measurements were made along the three orthorhombic axes.

Results are given in figure 1. The molar susceptibility, χ_m , measured parallel to the a axis ($a : b : c = 6.04 : 10.37 : 4.71$) [2], decreases with decreasing temperatures below the Néel point and extrapolates nearly to zero at 0 °K, according to the theory for an antiferromagnetic with spins parallel and antiparallel to the direction of the applied field. The values of χ_m parallel to the b and c axes are nearly constant below the Néel temperature, θ_N , but have a somewhat irregular course at these temperatures. No ferrimagnetism was observed. Above θ_N the molar susceptibility parallel to the a -axis is given by

$$\chi_m = 4.65/(T + 80),$$

from which follows $\mu_{\text{eff}} = 6.1$. This is slightly higher than that expected for Mn^{++} (5.9). Meas-

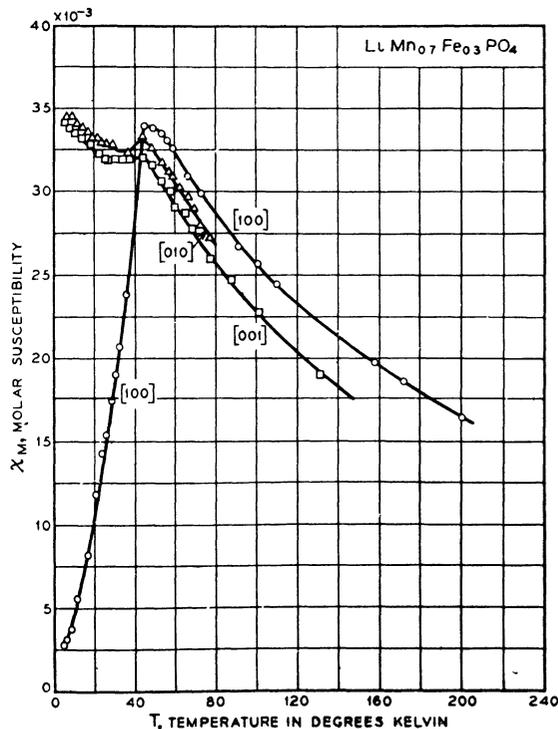


FIG. 1. — Ferrimagnetism in lithiophilite. At low temperatures spins are aligned parallel and antiparallel to [100]. Measurements parallel to [010] and [001] give slightly lower values of χ_m and μ_{eff} .

Since at 0 °K, χ_m along the a axis approaches a value almost zero, it may be concluded that the spin of each Mn ion (as distinguished from the *net* spin of all Mn ions) is aligned closely $\parallel [100]$. This direction lies in the (puckered) plane of the Mn^{++} ions, parallel to the line connecting next-nearest Mn^{++} neighbors.

We are indebted to J. L. Durand for supplying us with an oriented crystal of weight about 1 gram, and to J. M. Mays for discussion of the structure.

Ludlamite Crystal, $Fe_3(PO_4)_2 \cdot 4H_2O$

Ludlamite is monoclinic [3] (C_{2h}^5), the point-group having only one plane of symmetry which is perpendicular to the two-fold axis, b . A crystal was cut from the same specimen as that used by Mays [1] in his study of nuclear resonance, and

was in the form of a short cylinder with its axis

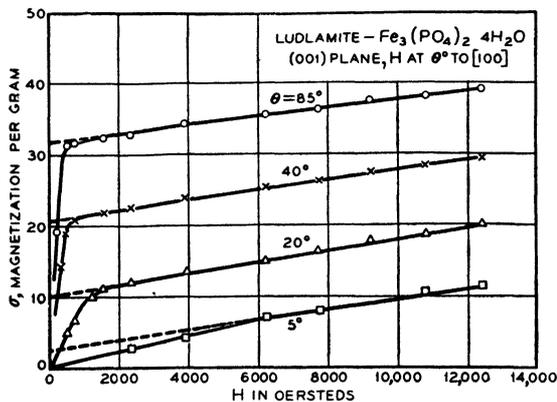


FIG. 2. — Magnetization curves of ludlamite in the (001) plane, when H is inclined to a axis at angle θ .

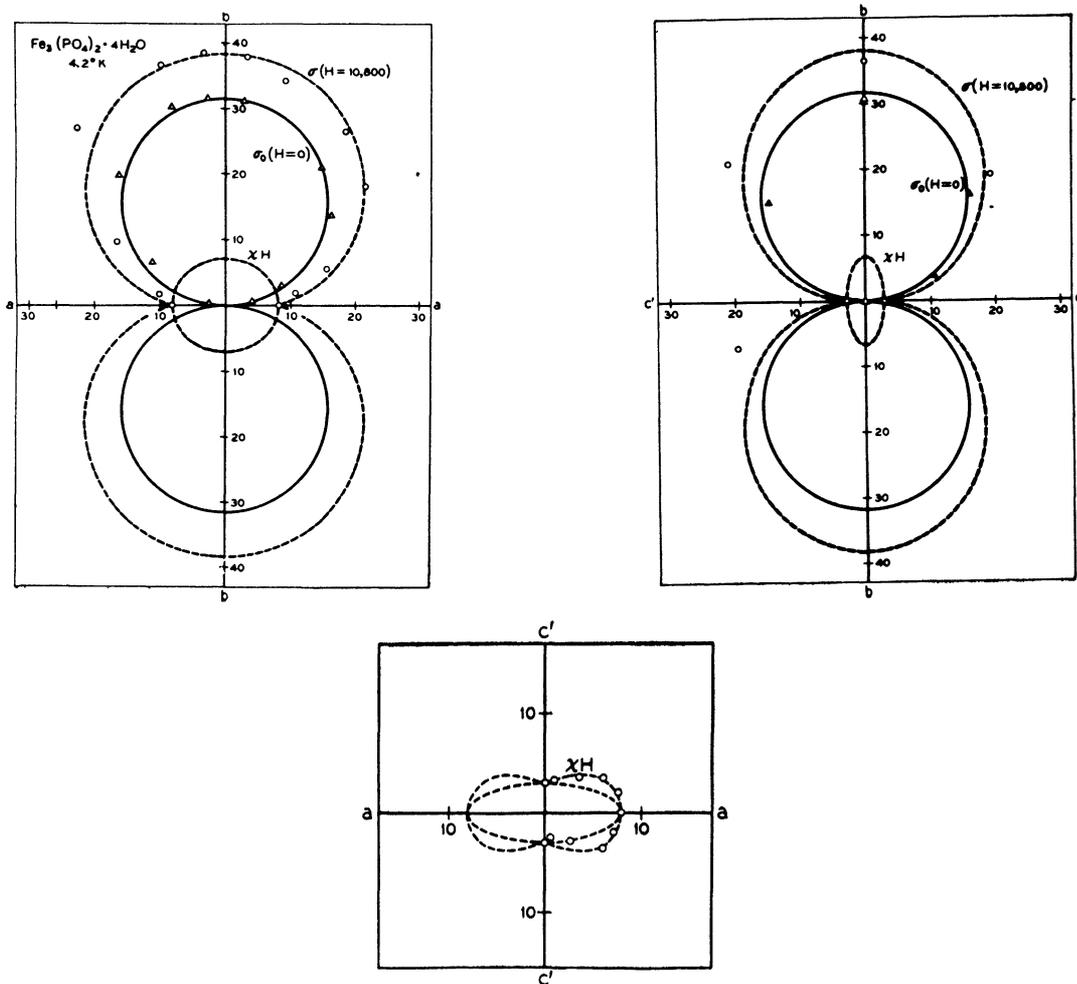


FIG. 3. — Magnetization of ludlamite in the three principal planes perpendicular to the a , b and c' axes. Broken curves are those calculated from the observed values of spontaneous magnetization σ_0 and paramagnetic magnetization χH at $H = 10\,800$ Oe, the points are observed.

perpendicular to the cleavage plane, the ratio of length to diameter being 0.84. This axis, desi-

gnated c' , is about 10° from the crystallographic c axis and is perpendicular to the a and b axes.

Data were taken in the three planes perpendicular to a , b and c' . Measurements showed the Curie point to be 20 °K.

Measurements in the two planes containing b showed immediately that the crystal was ferromagnetic along the b axis, and that in all directions perpendicular to b the magnetization was proportional to the field. Some data for the magnetization per gram, σ , in the ab plane are shown in figure 2. In figure 3 are plotted the values of σ in the three planes for $H = 10\,800$ and $H = 0$, the latter obtained by extrapolating σ along the straight portion of the σ vs H line to $H = 0$. The latter values, designated σ_0 , plot as circles in the ab and bc' planes; this shows that they exhibit characteristic ferromagnetic properties in the b direction only. There is no apparent rotation of σ_0 out of the direction of the b axis in the highest fields used, 12 500 Oe, consequently we have not been able so far to place any limit on the amount of anisotropy of the spontaneous magnetization.

The magnitude of σ parallel to b corresponds to $n_B = 0.8$ Bohr magneton per atom of iron. Two plausible models may be suggested to account for this magnitude, in terms of the crystal structure :

The Fe^{++} ions in the structure occupy two non-equivalent positions, and occur in straight lines of three; the lines are "over" each other in the b direction and form a plane parallel to the b axis. The iron ions in the line are equally spaced, and each is surrounded by six oxygen atoms at the corners of distorted octahedra. The end Fe^{++} ions of the line of three are crystallographically equivalent to each other but not to the center Fe^{++} ion. If the three ions are ferromagnetically coupled and are strictly parallel, the b component of the magnetization is $4\cos\theta_b$ Bohr magnetons per ion, where θ_b is the angle between the spin direction and the b axis; θ_b must then be about 80° to agree with the observed value of 0.8. Other lines of ions are so aligned in the crystal structure that the components $\perp b$ cancel to zero.

It seems more likely that the Fe^{++} ions in the line of three are antiferromagnetically coupled. In this case the component of the moment parallel to b is $(4/3)\cos\theta_b$, and θ_b must then be about 50°. The deviation of the alignment of the three spins from exact parallelism with each other is, of course, not ruled out.

Since there is no plane of symmetry in the crystal parallel to the b axis, the symmetry of the structure does not require the minimum in susceptibility in the ac' plane to have any special direction. Therefore the observed direction of minimum susceptibility, parallel to the c' axis, must be normal to the direction of the resultant spin, or at least nearer to 90° to this direction than is any

other direction in the ac' plane. This is shown schematically in figure 4.

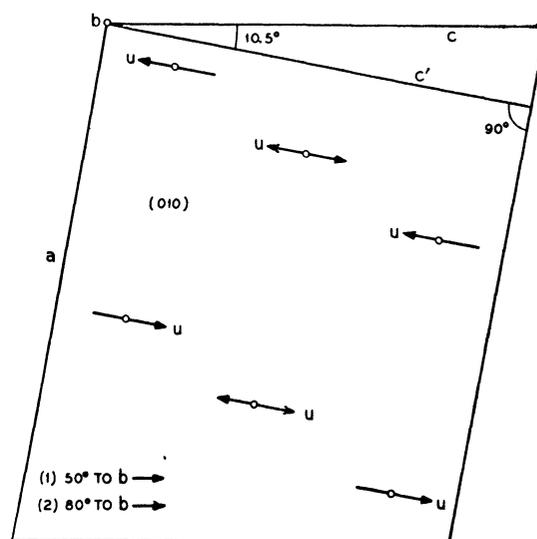


FIG. 4. — Proposed alignments of moments in crystals of ludlamite.

On the assumption of either antiferromagnetic or ferromagnetic coupling, the spin directions are thus determined. These assumption, and the true spin directions, could be checked with neutron diffraction; a study of this kind is being undertaken by Dr. S. C. Abrahams.

We are indebted to J. L. Durand for supplying the oriented crystal specimen, and to J. M. Mays for discussion of the structure.

HoFeO₃ Crystal

Magnetic measurements have previously been made [4] on several of the rare-earth orthoferrites between room temperature and 1.3 °K, and

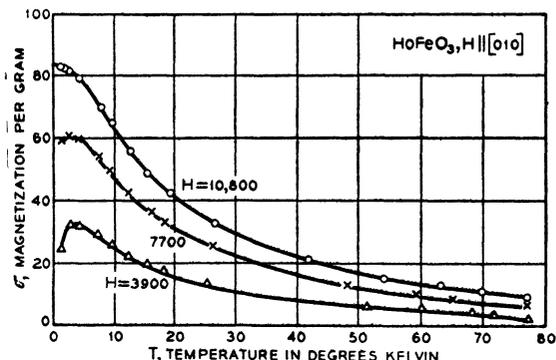


FIG. 5. — Magnetization vs temperature for $H \parallel [010]$ in $HoFeO_3$ crystal.

Gilleo [5] has measured a single crystal of $GdFeO_3$ at temperatures down to 77 °K. The present work on a $HoFeO_3$ crystal at temperatures down

to 1.3 °K shows spontaneous magnetization that changes in direction with change in temperature and increases rapidly in magnitude when the temperature is lowered below 40 °K.

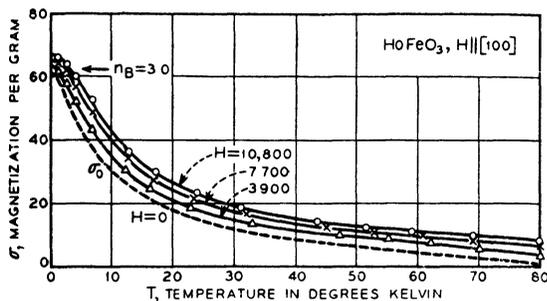


FIG. 6. — Magnetization vs temperature for [100] direction, showing spontaneous magnetization of 3 Bohr magnetons at low temperatures.

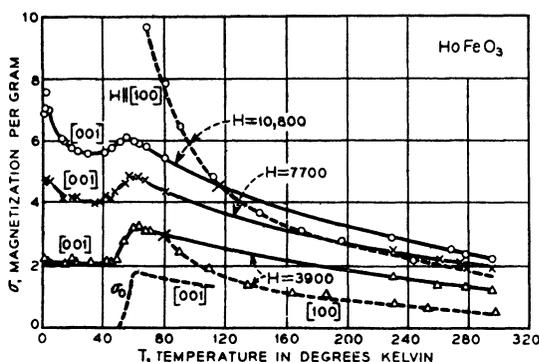


FIG. 7. — Solid curves, magnetization vs temperature for $H \parallel [001]$. Broken curves, same for [100] to indicate reversal of direction of easy magnetization. Also, σ_0 for [001].

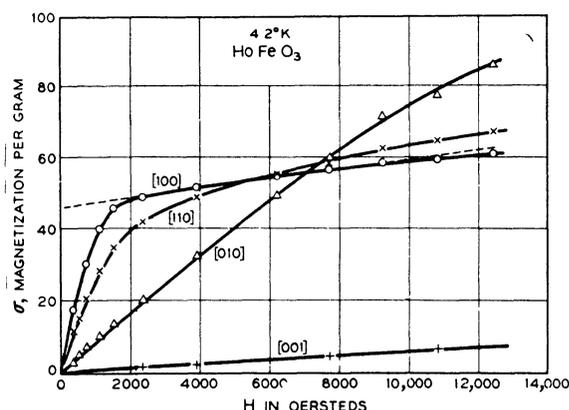


FIG. 8. — Magnetization curves of HoFeO_3 in various crystallographic directions at 4.2 °K.

The crystal is isomorphous with GdFeO_3 , the structure of which was determined by Geller [6]. It is orthorhombic, and axes are chosen so that $a < b < c$. Magnetization vs temperature was measured at several field strengths in four directions in the orthorhombic crystal, namely [100],

[010], [001] and [110]. Results are given in figures 5 to 8.

The direction of spontaneous parasitic magnetization at room temperature is [001], and its magnitude is about $n_B = 0.04$ Bohr magneton per molecule. Superposed on this is the rare-earth paramagnetism, the total magnetization being:

$$\sigma = \sigma_0 + \chi H,$$

as pointed out by Pauthenet and Blum [7]. On cooling to about 60 °K, the direction of σ_0 changes and becomes parallel to [100], and its magnitude increases rapidly to about 3 Bohr magnetons at the lowest temperature.

In our experiments we measure only the component of magnetization parallel to the applied field, designated σ . The direction in which a given field will give rise to the greatest σ we will call the direction of easy magnetization, and this will depend not only on the spontaneous magnetization σ_0 but also on the induced magnetization χH . At room temperature [001] is the direction of easy magnetization in all fields used. At 77 °K σ is greatest \parallel [100] in weak fields, and \parallel [010] in strong fields.

At 4 °K the spontaneous magnetization is \parallel [100] and is about 2 Bohr magnetons per molecule. At this temperature the spontaneous magnetization cannot easily be rotated out of the [100] direction into the [001] direction, but it can readily be rotated into the [010].

The higher values of σ obtained in the [010] direction in high fields would be expected if the spins of the Fe^{3+} ions lie in the (010) plane at rather large angles to the [100] direction, and are held by such anisotropy forces that they can be rotated much more easily toward [010] than toward [001].

When $H \parallel [010]$ the susceptibility χ increases with decreasing temperature down to about 5 °K, so it is concluded that the Ho^{3+} ions are responsible for the paramagnetism in the way generally assumed. A value of $\mu_{\text{eff}} = 10.9$ is derived from the curve of $1/\chi$ vs T when $T > 60$ °K.

The maxima in the σ vs T curves for the [010] direction, at about 4 °K, suggest ordering of the Ho^{3+} ions below this temperature. They might also be accounted for by a change in the anisotropy in the (001) plane with temperature, a higher anisotropy corresponding to a stronger fixing of $\sigma_0 \parallel [100]$ at lower temperatures, would mean that a given field \parallel [010] would cause less rotation in this direction and consequently lower σ 's would be observed. The curve of σ vs T at $H = 1200$ oersteds bends downward below 4 °K and extrapolates approximately to zero at 0 °K, as one expects below an antiferromagnetic transition.

A specimen of polycrystalline HoFeO_3 showed no maxima on curves of σ vs T , with constant H , and only a small amount of spontaneous magne

tization. The large values of χ and the ease of rotation of σ_0 apparently obscure the effects readily observed in single crystals.

Koehler and his colleagues at Oak Ridge have found by neutron diffraction that below 4 °K the moments of the Ho^{3+} ions are ordered $\parallel [010]$, the Fe^{3+} ions being $\parallel [100]$. These results fit in nicely with our magnetic results, which show $\sigma_0 \parallel [100]$. We are indebted to Dr. Koehler for permission to quote these results.

Measurements were also made on powdered Ho_2O_3 and Er_2O_3 , in which Koehler et al. [8] observed some kind of ordering at helium temperatures by neutron diffraction. Our magnetic data indicate the possibility of antiferromagnetic ordering below 4 °K in Er_2O_3 but show no evidence of this in Ho_2O_3 . It seems probable, however, that the high value of χ in the Ho^{3+} ion would obscure a transition in the latter material just as it did in powdered HoFeO_3 . An indication of antiferromagnetism in powdered ErFeO_3 at 4 °K has already been reported [4].

Experiments have also been made on single crystals of the orthoferrites of the rare-earth ions from Sm to Lu.

We are greatly indebted to J. P. Remeika for supplying the single crystals of HoFeO_3 and other orthoferrites, which were grown [9] from a PbO melt, and to H. J. Williams, M. A. Gilleo, P. W. Anderson and R. C. Sherwood for discussion of the properties of HoFeO_3 and other rare earth orthoferrites.

Polycrystalline $\text{PbO} \cdot \text{Al}_x\text{Fe}_{12-x}\text{O}_{16}$

E. W. Gorter [10] has proposed a model of the arrangement of spins in barium ferrite, $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$, which has the same structure as magnetoplumbite $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$. By replacing various amounts of Fe in magnetoplumbite by Al, and by measuring the saturation magnetization down to liquid helium temperatures, it was hoped that the model could be tested and the behavior of Al in these crystals determined. Measurements of magnetic saturation at room temperature in solid solutions of Al in Ca and Ba ferrites, by Van Uitert and Swanekamp [11] have already indicated that Al replaces Fe in octahedral sites in these materials.

A series of crystals was prepared by J. P. Remeika [9] by crystallization from molten PbO , with $x = 0$ to 8. For ease in attaining saturation the specimen was prepared from rather coarse crystalline powder; this was placed in a strong field at room temperature and vibrated to align the crystals as nearly as possible so that the direction of easy magnetization was parallel to the direction of the field to be used during measurement. Extrapolation of σ to its value at $T = 0$

and $H = \infty$ then left an uncertainty of only a few per cent of the value for pure magnetoplumbite.

The results are shown in figure 9. The broken lines correspond to various possibilities of replacement of Fe by Al, to be discussed below.

According to Gorter's model, based on the structure of Adelsköld [12], the Fe^{3+} ions in $\text{PbO} \cdot \text{Fe}_{12}\text{O}_{16}$ are arranged in layers perpendicular to the hexagonal axis, and the spins in each layer are parallel to each other and antiparallel to the spins in the adjacent iron layers. Starting with the layer containing Pb, the number of Fe ions in successive layers, and the coordination number of each Fe ion in the layer, may be described as follows: 1(5), 1(6), 3(6), 1(4), 1(6), 1(4), 3(6) and 1(6), then repeated. (The coordination number of 5 gives only a rough idea of the oxygen environment of the iron atoms in the Pb plane.) The spins corresponding to the 12 Fe ions in these layers are then:

+ 5, - 5, + 15, - 5, + 5, - 5 + 15, and - 5, and the net moment is 20 Bohr magnetons. Our observed moment extrapolated to $T = 0, H = \infty$, is about 19. For simplification of discussion let us designate the layers (beginning with the layer containing Pb), and the number of Fe ions in other layers, together with their spin directions, in the order of their distance from the first layers, as follows:

$$A(+1), B(-2), C(+6), D(-2), E(+1).$$

If Al replaced Fe ions in the C positions (octahedral), the moments should lie on the straight line C of figure 9, as in fact they do until about

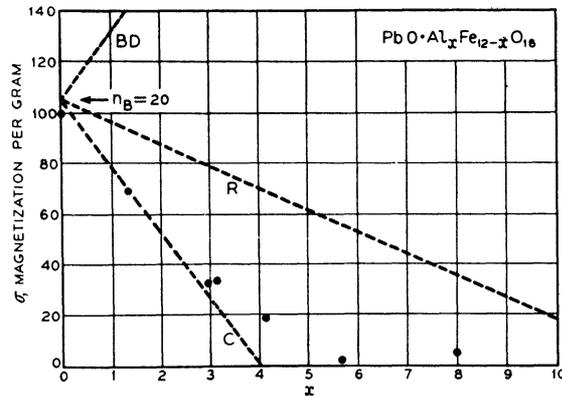


FIG. 9. — Variation of saturation in magnetoplumbite with Al content. See text for assumptions corresponding to broken lines.

$x = 3$ when half of the C ions are replaced. Replacement by Al of the tetrahedral iron ions in layer D or the octahedral ions in B would give line BD, and random replacement of Fe by Al would give line R. In the magneto-plumbite structure the Al evidently prefers the octahedral position, if we accept the assumptions of Gorter.

The observed moment goes to about zero when $x = 6$. There are several ways of explaining this fact, but the data are inconsistent with the replacement of all 6 C ions of Fe by Al.

When $x = 8$ the moment is greater than for $x = 6$. There are also a number of ways in which this may be explained if we do not have direct knowledge, such as that obtainable by X-ray or neutron diffraction, of the positions of the Al atoms. It seems probable, however, that σ_0 goes through zero near $x = 6$, and that therefore the orderly arrangement of Al ions persists beyond this point. It is planned to test this point by diffraction studies, and to measure specimens with other values of x .

The magnetoplumbite structure has not been obtained from PbO melts beyond $x = 8$. It may be that the random distribution of Al and Fe atoms makes the structure unstable and that the α - Al_2O_3 structure, with some Fe_2O_3 in solid solution, is then the stable phase in PbO solution.

Ilmenite Structures

Bizette and Tsai [13] have shown that a natural specimen of ilmenite, FeTiO_3 , has a Néel point of about 65 °K. Shomate [14] had previously prepared a specimen and observed a heat effect at about 60 °K.

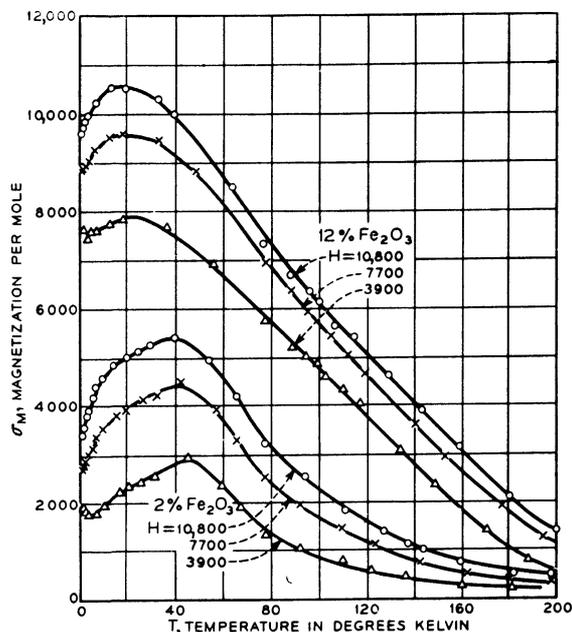


FIG. 10. — Magnetization of FeTiO_3 containing 2 and 12 atomic per cent of Fe_2O_3 .

Nagata, Akimoto and Ishikawa [15] in a series of articles, have shown that some of the solid solutions of FeTiO_3 - Fe_2O_3 are strongly ferromagnetic at room temperature. In the present measurements the temperature range has been extended to

1.3 °K, and Bohr magneton numbers determined. These results have already been reported briefly and their implications discussed [16].

Our measurements of prepared ilmenite containing by analysis an impurity of about 2 mole per cent of Fe_2O_3 , and of a solid solution containing 12 mole per cent Fe_2O_3 in FeTiO_3 , are shown in figure 10. The Néel point of the former material is about 40 °K, somewhat lower than that previously reported, and ferromagnetism is observed below 4 °K. The 12 per cent material shows strong ferromagnetism, and a marked maximum in the curves at about 20 °K.

Values of the molar moment in a field of 10 800 oersteds have been plotted for a number of compositions in figure 11 for the temperatures

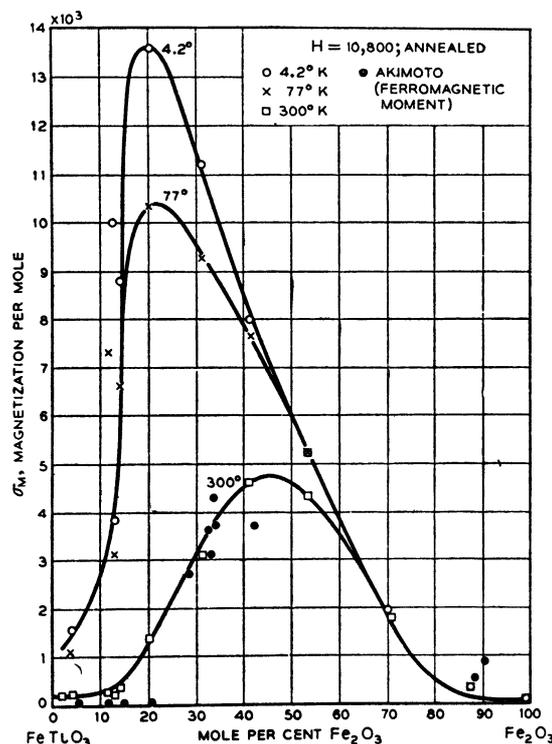


FIG. 11. — Magnetization of solid solutions of FeTiO_3 - Fe_2O_3 series at various temperatures ($H = 10\ 800$).

300, 77, and 4 °K, and additional data of Akimoto for natural crystals at room temperature have been added. In determining the saturation magnetization the procedure has been followed of extrapolating the moment at low temperatures to infinite field when the molar moment was large (greater than 4 000 when $H = 10\ 800$) and to $H = 0$ when the moment was small. This is based on the assumption, possibly not always valid, that paramagnetism is superposed on ferromagnetism when the moment is small, and that it is the anisotropy which prevents saturation when the material is strongly magnetic. Bohr magneton numbers

determined from saturation at low temperatures are given in figure 12.

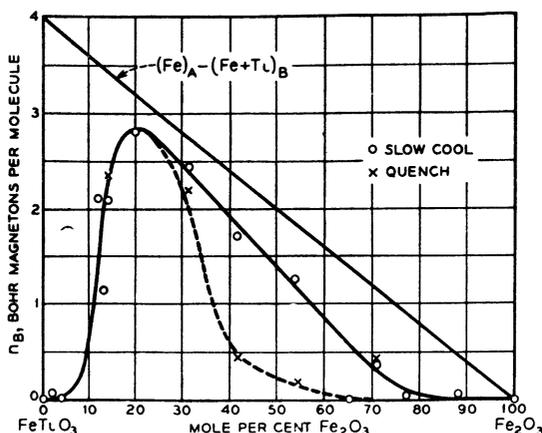


FIG. 12. — Bohr magneton number of $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$, as compared with proposed spin model.

In the neighborhood of 40 mole per cent Fe_2O_3 the saturation depends markedly on cooling rate, as illustrated in figure 13. In the quenched spe-

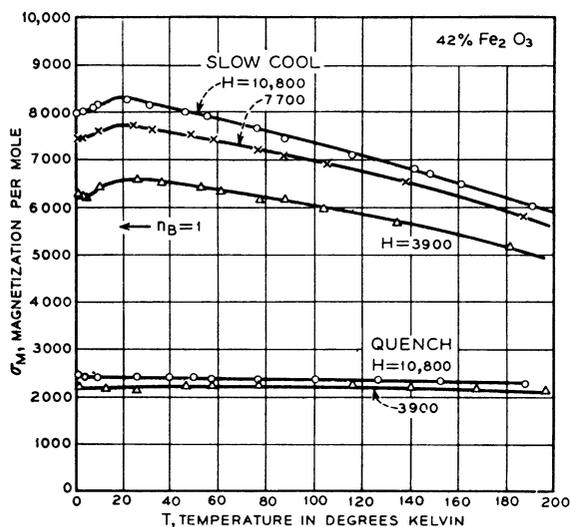
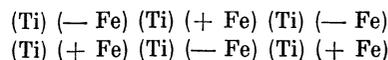


FIG. 13. — Effect of cooling rate on magnetization of specimen with 42 atomic per cent Fe_2O_3 .

cimen the maximum in the σ vs T curve has disappeared; presumably the arrangement of Fe and Ti ions is then more disordered and the resemblance to the regular FeTiO_3 structure is less.

Several models of the ordering of spins in FeTiO_3 and its solid solution have been proposed [17]. Shirane, Nathans, and Pickart have investigated this material with neutron diffraction and have found that the unit cell must be doubled in the direction of the rhombohedral axis, as compared with the "X-ray" cell. This is to be expected if the (puckered) planes of Fe ions, perpendicular to axis, are each ferromagnetically coupled within the plane, the planes being antiferromagnetically

coupled through intervening oxygen ions with neighboring Fe planes. The planes of metal ions that cut one X-ray cell would then have the sequence (Ti) (+ Fe) (Ti) (- Fe) (Ti) (+ Fe) along the axis, and there would have to be twice as many planes in the unit cell:



to satisfy the spin-repetition distance.

Shirane, Nathans, and Pickart have also found that when a substantial amount of Ti is replaced by Fe the spin pattern changes, as inferred from the magnetic data [16], and is consistent with the sequence (+ Fe) (- Fe, Ti) (+ Fe) (- Fe, Ti) (+ Fe) - Fe, Ti). We are greatly indebted to these authors for permission to quote their results before publication.

As the composition of the solid solution changes, the Bohr magneton numbers resulting from the last sequence would fall on the straight line of figure 12, if we assign 4 Bohr units to each Fe^{++} ion. This sequence may be expected to apply to the $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$ solid solution series until the Ti ions become too few to establish an ordered structure. This is in qualitative accord with the data.

Two other compounds having the ilmenite structure, CoMnO_3 and NiMnO_3 , have been prepared by Swoboda, Toole and Vaughan [18] and measured by Bozorth and Walsh [19]. Their Bohr magneton numbers are respectively 0.72 and 0.61. These numbers may be explained by the following sequence of (puckered) planes of metal ions along the rhombohedral axis:

(+ Co) (- Mn) (+ Co) (- Mn), the signs indicating the sense of the spins. Although the spin-only moments of these ions are equal, the orbital moments of Co ions are difficult to quench and the effective moments of the ions of the two metals, derived from paramagnetic data, differ by about the observed moment of CoMnO_3 . This compound may thus be said to have "orbital ferrimagnetism".

If spin-only moments occurred in NiMnO_3 the moment would be one Bohr unit per molecule. If the orbital moments of the Ni ions are not completely quenched the moment becomes somewhat less than one unit per molecule. The observed value of 0.61 is quite consistent with this point of view.

Prince and Abrahams have made a preliminary study of CoMnO_3 by neutron diffraction, and have found that the unit rhombohedral cell that is found by neutrons is the same as that found by x-rays. The cell is not doubled as it is for FeTiO_3 , and the sequence given above for CoMnO_3 is consistent with all known data. We appreciate permission to quote the results of Prince and Abrahams before publication.

Fluorides

The fluorides examined were $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, NnF_3 , and CrF_3 . The first of these, as reported by Bozorth and Nielsen [20], becomes antiferromagnetic at 26 °K. Susceptibilities above this temperature follow the law $\chi_m = 0.46/(T + 37)$, and $\mu_{\text{eff}} = 1.9$, in good agreement with the moments reported for other Cu^{++} salts. In accordance with simple theory, at 0 °K χ_m has about 2/3 of its value at the Néel point. Single crystals (monoclinic) are being prepared for measurement in different crystallographic directions.

Antiferromagnetism in MnF_3 was found [20] after we were told informally by W. C. Koehler and E. O. Wollan of Oak Ridge National Laboratory that they, with H. R. Child and M. K. Wilkinson, had detected magnetic ordering near 45 °K by means of neutron diffraction. According to our measurements $\theta_N = 47$ °K, and above this temperature the molar susceptibility is given by $\chi_m = 3.10/(T - 8)$, from which is derived $\mu_{\text{eff}} = 5.0$. The latter result is in fair agreement with that of Klemm and Krose [21] who worked above 90 °K, and is to be compared with the value 4.9 reported by Nyholm and Sharpe [22]. It is somewhat unusual to find θ_N so much greater than the value of $\theta_F = 8$ appearing in the Curie-Weiss expression.

CrF_3 has been examined by Bizette and Tsai [23] down to 70 °K and reported to become ferromagnetic at about 75 °K on cooling. Our measurements enable us to determine the ferromagnetic moment extrapolated to 0 °K. Extrapolation against field strength was to $H = 0$; this was done because the ferromagnetic moment was small (parasitic) and σ in high fields varied linearly with H . Results,

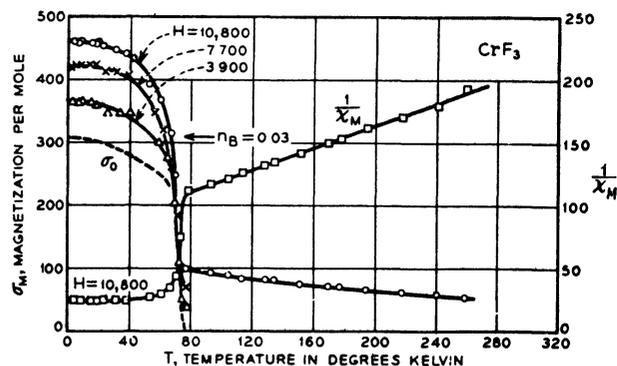


FIG. 14. — Magnetization of CrF_3 , showing parasitic ferromagnetism at low temperatures.

plotted in figure 14, show $n_B = 0.03$. Above the Curie point, $\theta = 74$ °K, $\chi_m = 2.07/(T + 160)$, corresponding to $\mu_{\text{eff}} = 4.1$. This value is somewhat higher than that derived from the data of Bizette and Tsai [23] and of Klemm and Krose [21].

For this material the intercept of the extrapo-

lated $1/\chi_m$ vs T line on the T axis at -160 °K, an unusual situation for a material that becomes ferromagnetic and more characteristic of an antiferromagnetic material. This material is best considered as an antiferromagnetic in which, by some mechanism not yet clear, the balance between 2 sublattices is not exact and a small (parasitic) ferrimagnetic moment persists.

The work on $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ has been done in cooperation with Dr. J. W. Nielsen. The MnF_3 was supplied by Dr. R. G. Schulman and was the same material as that used by him and Jaccarino [24] in their measurements of nuclear resonance. We are indebted to Dr. W. C. Koehler and Dr. E. O. Wollan for making known to us their diffraction data for this material before publication. Investigation of CrF_3 was carried out in cooperation with Dr. K. Knox, who supplied the material and contributed to the discussion.

In all of the work described in this paper we have had the able assistance of A. J. Williams.

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DISCUSSION

Dr. Koehler (Comments). — The neutron diffraction measurements on HoFeO_3 and ErFeO_3 which have been made at the Oak Ridge National Laboratory are complementary to the results which Dr. Bozorth has presented. At temperatures above room temperature the Fe^{3+} ions in those compounds are ordered antiferromagnetically with the axis of alignment parallel or nearly parallel to the orthorhombic [100] direction. At temperatures below 43 °K the direction of alignment is observed to change to a [110] plane. The direction of σ_0 is thus normal to the direction of antiferromagnetic alignment. At very low temperatures, both the rare earth and iron ions are ordered, approximately antiferromagnetically, and it is possible, from the interference of the scattering by the two systems to determine the directions of orientations of the moment and their magnitudes. The Er^{3+} ions in ErFeO_3 form a nearly ideal antiferromagnetic configuration in which a chain of parallel moments is surrounded by four chains of oppositely directed moments at nearest neighbor distances. The erbium ion moments are parallel and antiparallel to [001], approximately, and at 1.25 °K have a magnitude of $5.8 \mu_B$. The iron ions are oriented parallel, approximately, to [110]. In HoFeO_3 the Ho^{3+} ions are found in a distorted antiferromagnetic array in which at 1.25 °K each Ho^{3+} ion moment with magnitude of $7.5 \mu_B$ makes an angle, in the (001) plane of about 27° with the [010] direction so as to produce a ferromagnetic moment of $3.4 \mu_B$ parallel to [100]. The Fe^{3+} moments are approximately parallel or antiparallel to [001].

Mr. Kawai. — I should like to make a short communication in connection with one of Dr. Bozorth's studies. About 4 years ago my colleague Dr. Kume and I were also interested in the magnetic character of the solid solutions between hematite and ilmenite. In 1955 [1] Kume published the results which are slightly different from what you have presented just now. The difference is that the point at which the intensity of magnetic moment begins to fall in the Ti-rich region of the solid solution, slightly shifts towards pure ilmenite, the maximum therefore appearing at a point of about 5 mol % or so.

The samples we used are, in most cases, natural specimens which have been made in nature under very high pressure but obviously at low temperature. Ishikawa and Akimoto's results as well as your study indicate that the ordering of the solid-solutions makes σ_s increase. On this point of view, the natural samples we used are much more favorable in getting the ordering, because both the temperature and the time are quite favorable.

Taking this in mind, the difference above mentioned is reasonably explained.

Next, we find Néel-point-like anomalies on the thermomagnetic curve over nearly the whole region of the solid-solution. Those points occur at about 200° higher than the respective Curie-points. I think, in your results, similar kind of anomalies seem to appear which is very interesting. Although we have not yet obtained the final conclusions, have you some model explaining these facts?

[1] SHOICHI KUME, *Proc. Jap. Acad.* 1955, 31, 709.

Mr. Bozorth. — The shift of the maximum of saturation toward lower Fe_2O_3 contents, in specimens subjected to geological aging, seems reasonable to me. One expects the ordering to be more complete, and we have found slow cooling to give an effect in the same direction at higher Fe_2O_3 concentrations.

The Néel temperature in FeTiO_3 has an obvious counterpart in slowly cooled (ordered) ferromagnetic solid solutions containing some Fe_2O_3 . I believe that there is a close relation between these two maxima in the σ vs T curve, but I do not now know the relation in any detail.

Mr. Nagamiya. — As I have written in my manuscript, Ishikawa observed the temperature of ordering of Ti and Fe in hematite-ilmenite solutions. It decreases rapidly towards the ilmenite side. It is possible, therefore, that the ordering in artificial samples is imperfect. Have you any idea about the origin of the Néel-point-like anomaly you also observed?

Mr. Bozorth. — I believe the ordering in the artificial materials is not perfect, even when slowly cooled. The experiments show that slow cooling (ordering) enhances the Néel-point-like anomaly, and this suggests a close connection, about which I have no detailed picture to suggest.

Mr. McGuire. — Did you notice any magnetic field dependence of the susceptibility in the antiferromagnetic materials that you have measured, for example MnF_3 ?

Mr. Bozorth. — No dependence of χ on H was noted in any of the fluorides we investigated except CrF_3 , where the ferromagnetism was reported. Linearity was not tested at the lowest temperature where saturation effects might be expected.

Mr. Hulliger. — Must the slight deviation of the spin direction from the ideal crystalline axes in HoFeO_3 (and other perovskites) not be caused in fact by a real distortion of the lattice? (You have drawn the lattice as ideal).

Mr. Koehler. — Yes. The figure as shown does not clearly display the distortions. The structure is really orthorhombic and there are in the structure two sets of non-equivalent oxygen ions.