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Magnetic Properties of Some Orthoferrites and Cyanides at Low Temperatures

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The magnetization of some rare-earth orthoferrites and related compounds, and of some iron-group cyanides, has been investigated at temperatures between room temperature and 1.3°K. Some are ferromagnetic, some antiferromagnetic, and some paramagnetic following the Curie-Weiss law.

The compounds $GdVO_3$, $GdFeO_3$, and $ErFeO_3$ are apparently antiferromagnetic with Néel points of 7.5°, 2.5°, and 4.5°K, respectively. Ordering of the Gd and Er ions at low temperatures is indicated. The compounds $NdFeO_3$, $SmFeO_3$, $YFeO_3$, $NdVO_3$, $PrVO_3$, and $SmVO_3$ show a rapid rise in ferromagnetic moment as the temperature is lowered below about 15°K. $GdTiO_3$ is ferromagnetic with 0.54 Bohr magneton per molecule.

Many of the cyanides of type $A(BC_6N_6)$ are ferromagnetic with magnetic moments of 1 to 4 Bohr magnetons per molecule and Curie points of 3 to 50°K.

A null method of measurement is used. Movement of a pendulum in a field gradient is detected with strain gauges and balanced with a coil. In the space containing the specimen and the balancing coil the gradient varies linearly with distance.

INTRODUCTION

THIS paper describes the magnetic properties of some compounds at temperatures down to 1.3°K. The compounds are of two general types. The first type can be represented by the formula $GdFeO_3$, in which the Gd may be replaced by other rare earths or by yttrium; we have used Pr, Nd, Sm, Eu, and Er. The iron may be replaced by Cr, V, Ti, Co, or Sc. The rare earth orthoferrites of this kind were studied first by Forestier and Guiot-Guillain[1] who have found that many of them have a slight or "parasitic" ferromagnetism with a Curie point of several hundred degrees centigrade. Three of these compounds have been studied at temperatures below room temperature, by Pauthenet and others.[2] The magnetic properties of single crystals of $GdFeO_3$ have been reported by Gilleo.[3] The crystal structure of compounds of this type has been worked out by Geller,[4] who finds them to be orthorhombic, pseudo-perovskite in character.

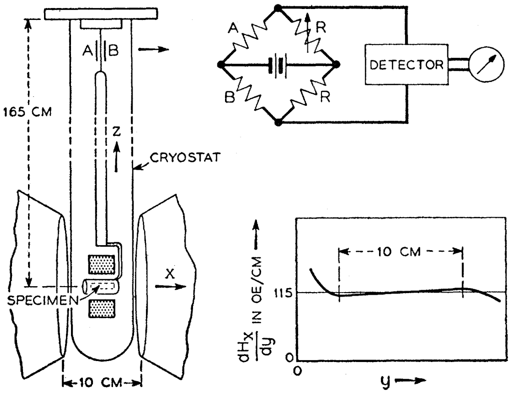

FIG. 1. Schematic diagram of apparatus. Tapered pole faces cause movement of pendulum into plane of paper. Strain gauges (*A*,*B*) are on strip lying in plane of paper, 90° to position shown.

The second type of compound is represented by the formula $Fe(FeC_6N_6)$, ferri-ferricyanide. In the compounds that we have examined the iron of the cation has been replaced by Mn, Co, Ni, Cu, or Zn, and the iron in the anion by Cr, Mn, or Co. All of these compounds contain the radical C_6N_6, and the magnetic moments that we have measured are referred to a formula containing one mole of C_6N_6.

TABLE I. Analysis of ferricyanides, expressed as $M_aFe_bC_6N_6$ + remainder (inert material). Ferromagnetic moments and Curie points.

M ion	*a*, atoms of M	*b*, atoms of Fe	Percent remainder	n_B per C_6N_6	θ, °K
Mn	2.27	0.99	24.5	3.03	11
Co	1.52	0.91	30.7	0.93	21
Ni	1.72	1.03	44.9	2.78	27
Cu	1.86	0.96	28.8	0.69	16
Zn	1.64	1.05	15.3	0.08	···

Although the rare-earth orthoferrites and related compounds of the first type usually have only a small magnetic moment of about 0.05 to 0.4 Bohr magneton/molecule, some of the cyanides have magnetic moments of 3 to 4 magnetons/molecule.

It is hoped that the investigation of a number of compounds containing a wide variety of ions will aid in understanding the nature of magnetic interactions in structures of these types.

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[1] H. Forestier and G. Guiot-Guillain, Compt. rend. **230**, 1844 (1950). See also G. H. Jonker and J. H. Van Santen, Physica **16**, 337 (1950).

[2] R. Pauthenet and P. Blum, Compt. rend. **239**, 33 (1954); Guiot-Guillain, Pauthenet, and Forestier, Compt. rend. **239**, 1955 (1954).

[3] M. A. Gilleo, Phys. Rev. **99**, 1641 (1955); J. Chem. Phys. **24**, 1239 (1956).

[4] S. Geller, Phys. Rev. **99**, 1641 (1955); J. Chem. Phys. **24**, 1236 (1956); Acta Cryst. (to be published) and private communication. See also F. Bertaut and F. Forrat, J. phys. radium **17**, 129 (1956).

METHOD OF MEASUREMENT

The method of measurement is shown schematically in Fig. 1. The material is placed in the middle of a small "balancing" coil located at the end of a rather long pendulum which is hung in the cryostat from a flexible metal strip. Strain gauges are placed on either side of the strip so that any movement of the pendulum is transmitted to the gauges. The gauges are placed in two arms of a bridge and the motion of the pendulum is detected by measuring the bridge output. The pole-pieces of the electromagnet are tapered according to the method of Sucksmith[5] to produce a uniform horizontal gradient at right angles to the field so that the motion of the pendulum is in this direction.

When the field is applied and a deflection occurs, a current is passed through the balancing coil until the pendulum comes to its original zero position as indicated by the detector of the bridge. The magnetic moment of the coil gives a proper measure of the moment of the specimen provided the gradient is constant or linear with distance over the volume of the coil and specimen. this is true in our magnet as shown by the insert in the figure.

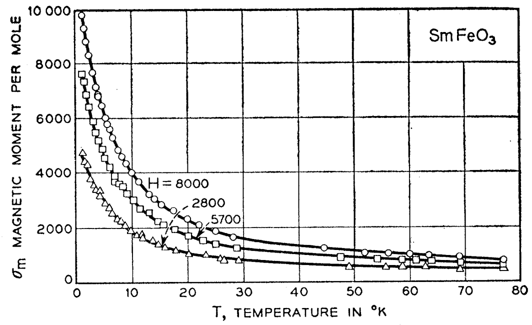

FIG. 2. Results for $SmFeO_3$ for 3 field strengths.

The constant of the balancing coil was determined by measuring a specimen of pure iron, and was in close agreement with that calculated from the geometry of the coil. Magnetic moments are expressed in cgs emu per mole.

Measurements were ordinarily made between 77°K and 1.3°K, the temperature obtained with helium under reduced pressure. A small correction, proportional to the field strength, was normally applied for temperatures below about 20°K, based on measurements made with no specimen present. This has been traced to impurity in the copper wire. The amount of specimen used was usually one-half to one gram.

PREPARATION OF MATERIALS

Some of the rare-earth orthoferrites were prepared from the oxides by ceramic methods, others were obtained in macrocrystalline form by J. P. Remeika by crystallization from molten PbO, and all were finely powdered and pressed. The ceramic materials were ball-milled, pressed, and fired at 800 to 1500°C in air or oxygen. The vanadites and titanites were prepared in a similar way but were fired in a helium atmosphere. Spectroscopic analysis showed that the purity of the metallic component of the rare-earth oxides was about 99.9%, except for Gd_2O_3 which contained over one percent of Sm_2O_3, and for Sm_2O_3 which contained several tenths percent of Gd_2O_3 and Nd_2O_3.

The cyanides containing the C_6N_6 group were prepared by A. N. Holden and C. E. Miller by adding a solution of the potassium salt of the anion to a sulfate solution of the cation containing a stoichiometric excess of the latter. An article[6] reporting the discovery of their ferromagnetism is now in course of publication. The precipitates so obtained are generally uncertain in

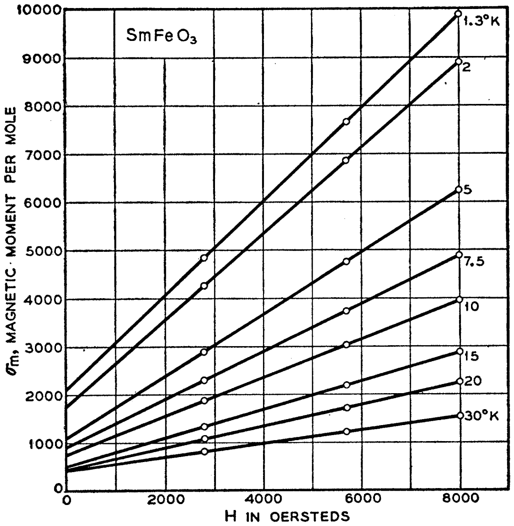

FIG. 3. Extrapolation to separate ferromagnetic from paramagnetic moment.

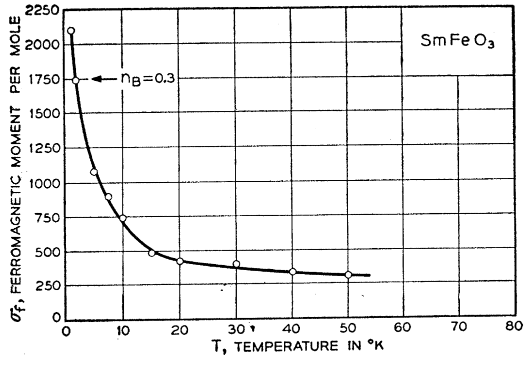

FIG. 4. Ferromagnetic moment of $SmFeO_3$ increases rapidly at low temperatures.

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[5] W. Sucksmith, Proc. Roy. Soc. (London) **A170**, 551 (1939).

[6] Holden, Matthias, Anderson, and Lewis (to be published).

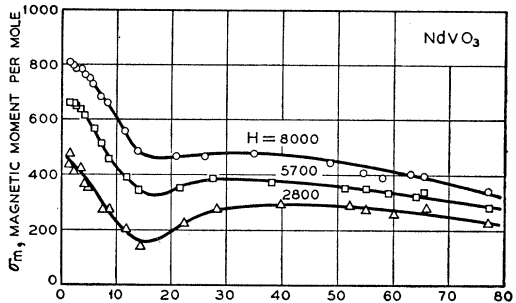

FIG. 5. Results for $NdVO_3$.

constitution,[7] and the compositions of our specimens have not yet been established. Calculation of the magnetic moment per molecule from our measurements was based on the formula $A(BC_6N_6)$, A and B being respectively, the cation and anion elements. This means that a given weight of ferro-ferricyanide, for example, is assumed to contain the same number of molecules as the same weight of ferriferrocyanide; according to our measurements the ferromagnetism of these two compounds is the same.

At the present time only the ferricyanides have been analyzed chemically. These show considerable variation in the ratio of cation to C_6N_6, but a rather constant ratio Fe/C_6N_6 of nearly one, in the specimens containing Mn, Co, Ni, Cu, and Zn. A certain amount of extraneous material (oxide, sulfate and potassium) is present and is indicated in Table I as "percent remainder." The results may then be put in the form $M_aFe_bC_6N_6$+inert material, and the moments calculated for this formula weight containing one C_6N_6.

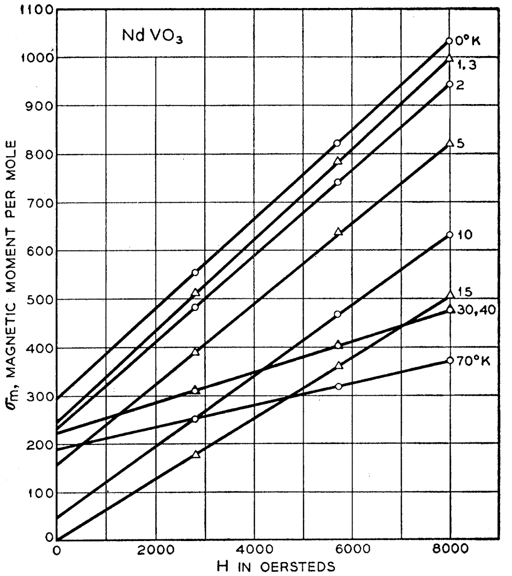

FIG. 6. Paramagnetic and ferromagnetic moment (slopes and intercepts) of $NdVO_3$ change markedly with temperature. Upper line by extrapolation.

Further work must be done to establish the moments of the stoichiometric compounds.

RARE-EARTH FERRITES AND RELATED COMPOUNDS

The results of measurements are illustrated for $SmFeO_3$ in Fig. 2. Readings are ordinarily made at 8000, 5700, and 2800 oersteds as shown. Figure 3 shows how the data so obtained are extrapolated for various temperatures to zero field; we assume that the extrapolated magnetization is the ferromagnetic moment and that the slope of the line represents the paramagnetic susceptibility. This analysis follows the work of the French[1,2] who have shown that the magnetization of these compounds can be represented by the formula

$$\sigma_m = \sigma_f + \chi_p H,$$

σ_m being the total molecular moment, σ_f the ferromagnetic moment, and χ_p the molar paramagnetic susceptibility. When the ferromagnetic moment is plotted against temperature as in Fig. 4, we note a rather rapid rise of moment as the temperature falls below about 20°K. At the lowest temperatures the moment may be as high as 0.3 or 0.4 Bohr magneton per molecule. At the temperatures of liquid nitrogen the moment drops to about 0.05 Bohr magneton per molecule. Presumably this decreases with increasing temperature to the Curie point in accordance with the measurements of the French.

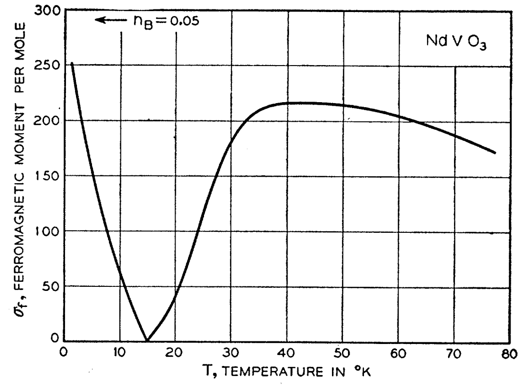

FIG. 7. Ferromagnetic moment of $NdVO_3$ passes through zero at 15°K.

Measurements on another compound, $NdVO_3$, and the extrapolations to zero field, are shown in Figs. 5 and 6. In this compound we find that the ferromagnetic moment passes through zero at about 15°K and then rises again at higher temperatures (Fig. 7). A similar behavior has been noted by the French in $GdFeO_3$.[2] This phenomenon has already been explained by Néel[8]

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[7] Weiser, Milligan, and Bates, J. Phys. Chem. **46**, 99 (1942).

[8] L. Néel, Ann. Physik **3**, 137 (1948); Compt. rend. **239**, 8 (1954).

on the following basis: In a number of ferrites there are two sublattices of magnetic ions, one of which has a high magnetic moment and a low molecular field, the other of which has a low moment and a high molecular field, the two sublattices being held antiparallel to each other. As the temperature rises, the spontaneous magnetization in the two sublattices varies differently, so that the net moment will pass through zero at a virtual Curie point, and then at higher temperatures will reverse and finally approach zero again at the true Curie point. In the rare-earth orthoferrites virtual Curie points of this kind, and also additional virtual Curie points, are observed and are covered by the theory.

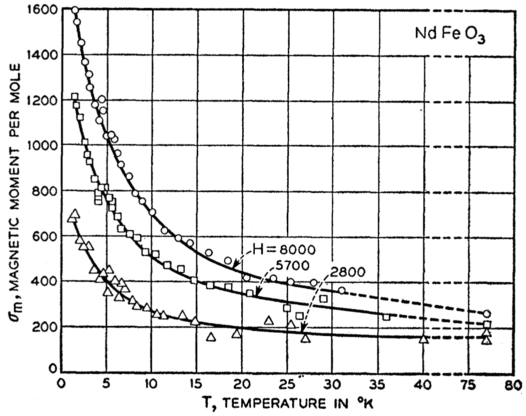

FIG. 8. NdFeO$_3$ has large paramagnetic susceptibility, small superposed ferromagnetism.

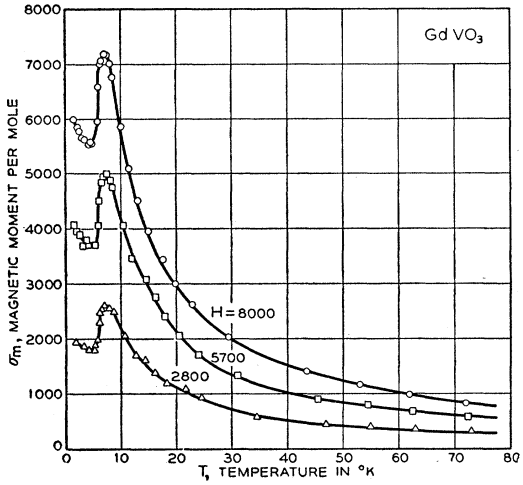

FIG. 9. GdVO$_3$ has susceptibility peak at 7.5°K indicating antiferromagnetism.

The difference in behavior of NdVO$_3$ and NdFeO$_3$ is apparent when one compares Figs. 5 and 8; in the latter material there is relatively little ferromagnetism, but at liquid nitrogen temperatures some slight residual or parasitic ferromagnetism can be measured. This has also been observed in NdFeO$_3$ by the French at higher temperatures.

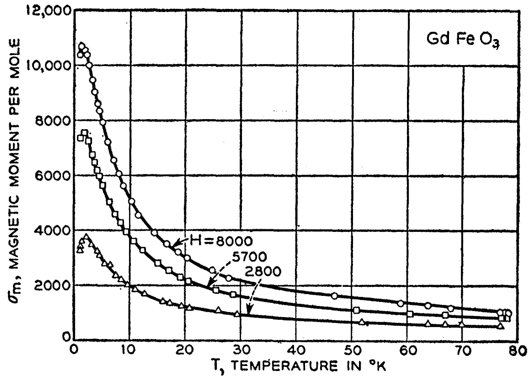

FIG. 10. GdFeO$_3$ has indication of Néel point at 2.5°K.

An interesting behavior is observed for GdVO$_3$ (Fig. 9). The form of the curve indicates that the phenomena of antiferromagnetism occurs, with a Néel point of about 7.5°K. We have not been able to observe any superposed ferromagnetism in this case. The rise of the magnetic moment on cooling at the lowest temperatures should be noted.

The data for GdFeO$_3$ (Fig. 10) give an indication of antiferromagnetism with a Néel point of about 2.5°K. Our ferromagnetic moments observed at 1.3 to 77°K differ definitely from some of those first reported[2] but agree with the more recent results of Gilleo.[3] In trying to explain these differences, two additional specimens were prepared with 10% excesses of Gd$_2$O$_3$, and of Fe$_2$O$_3$ respectively, but in neither case could the observed changes account for the discrepancies.

The maxima in the σ *vs* T curves for GdVO$_3$ and GdFeO$_3$ (Figs. 9 and 10) at the lower field strengths (2800 oe) occur at 7.5° and 2.5°K, respectively, while

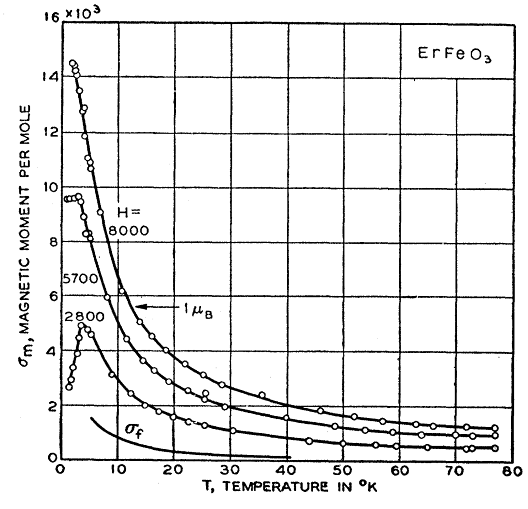

FIG. 11. Results for ErFeO$_3$, showing antiferromagnetism with susceptibility peak shifted or eradicated in high fields.

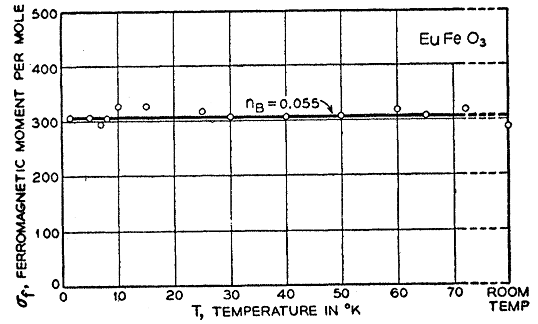

FIG. 12. Ferromagnetic component of $EuFeO_3$ is constant at low temperatures.

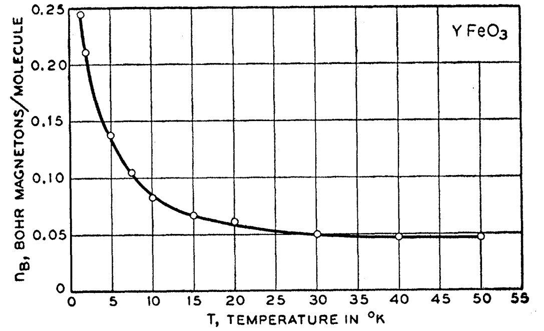

FIG. 13. $YFeO_3$ shows rapid rise of ferromagnetic component at low temperatures.

in $GdFeO_3$ at the higher field strengths (8000 oe) they occur at a somewhat lower temperature. In $ErFeO_3$ (Fig. 11), the low-field maximum is at 4.5° and at higher fields the maximum is completely absent at the temperature used. These characteristics are similar to those observed in $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ by Garrett,[9] and in detail in $CuCl_2 \cdot 2H_2O$ by Poulis, van den Handel, Ubbink, and Gorter,[10] and show that in $ErFeO_3$ the critical field for the transformation of antiparallel into parallel spins has been exceeded. Our results thus add three more materials for which the critical field can be investigated in the temperature range of 1.5° to 10°K. Also, data for $GdScO_3$ suggest a Néel point below 2°K.

TABLE II. Ferromagnetic moments, n_B, of some vanadites and orthoferrites at 1.3°K, in Bohr magnetons per molecule (of kind ABO_3).[a] θ' is the temperature (°K) at which the moment reduces to about 0.05 Bohr magneton per molecule.

	Vanadites		Orthoferrites	
Cation	n_B	θ'	n_B	θ'
Pr	0.23	70	0.21	>300
Nd	0.05	· · ·	0.05	· · ·
Sm	0.17	15	0.42	40
Eu	· · ·	· · ·	0.05	· · ·
Y	0.05	· · ·	0.27	25

[a] Note also: $LaCoO_3$, $n_B = 0.10$; $GdTiO_3$, $n_B = 0.54$, $\theta = 21$°K.

The low Néel points of these compounds suggest that the rare-earth ions become antiferromagnetically ordered at these temperatures. It has already been postulated[8] that the iron ions in the orthoferrites are so ordered at temperatures up to several hundred degrees centigrade.

In contrast with most of the orthoferrites, $EuFeO_3$ is found to have a constant ferromagnetic moment per molecule down to the lowest temperatures (Fig. 12). The moment does not vary appreciably from room temperatures to 1.3°K. In this connection one recalls that the paramagnetic susceptibility of the Eu^{+++} ion is known to be constant at low temperatures[11] in accordance with the Van Vleck theory.

In the compounds so far described, both metal ions have considerable magnetic moments. For this reason it was desirable to find the effect of yttrium, which has zero magnetic moment. Yttrium orthoferrite was examined, with the results shown in Fig. 13. It is to be noted that we have here also a parasitic magnetic moment which again increases strongly as we go below 5°K. It is known from the work of the French that this moment persists well above room temperature. The magnitude of the moment at these higher temperatures is about 0.05 Bohr magneton per molecule, the same in order of magnitude as the other (parasitic) ferromagnetic moments of the rare-earth orthoferrites.

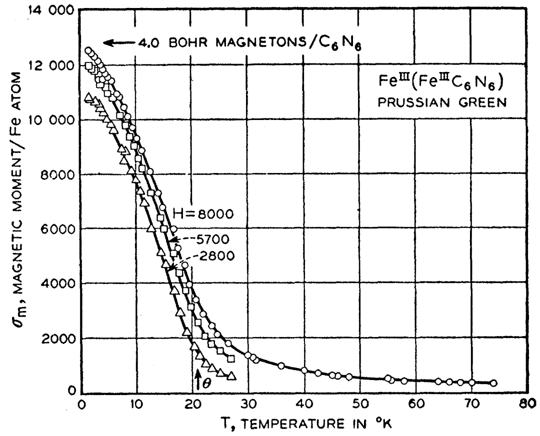

FIG. 14. Results for $Fe(FeC_6N_6)$ show substantial ferromagnetism.

Table II is a summary of some of the results on the compounds of the orthoferrite type.

CYANIDES

Some results for Prussian green, ferri-ferricyanide, $Fe(FeC_6N_6)$, are shown in Figs. 14 and 17(a). At the lowest temperatures the Bohr magneton number per molecule is almost 4. The Curie point is 22°.

The Bohr magneton number of ferro-ferricyanide, Turnbull's blue, is almost as large as that of ferri-

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[9] C. G. B. Garrett, Proc. Phys. Soc. (London) **A63**, 1043 (1950); Proc. Roy. Soc. (London) **A206**, 242 (1951).

[10] Poulis, van den Handel, Ubbink, and Gorter, Phys. Rev. **82**, 552 (1951); Physica **18**, 862 (1952).

[11] B. M. W. Trapnell and P. W. Selwood, Nature **169**, 841 (1952).

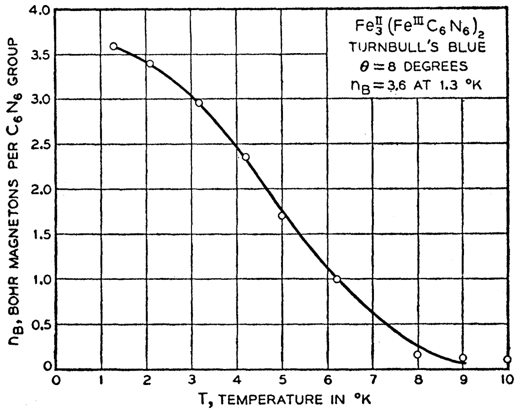

FIG. 15. Ferromagnetic component of ferro-ferricyanide.

ferricyanide but it has a Curie point of about 8°K (Fig. 15). The same result is obtained when a ferric salt is added to a potassium ferrocyanide; thus Turnbull's blue and Prussian blue seem to have identical ferromagnetic behavior. Previous work[7] has indicated that they have the same composition and structure. However, as noted in Table IV below, the Curie constants of these materials are not the same.

Results for mangano-manganicyanide are reported in Fig. 16. Here there is a point of irregularity at 10°K the nature of which is not known. Unlike the orthoferrites the cyanides do not appear to have a parasitic magnetization. Results for some other compounds are given in Fig. 17, and a summary of all the cyanides investigated is shown in Table III.

The most complete set of measurements is for the ferricyanides. Values of n_B per unit of C_6N_6 by analysis, and θ, are given in Table I. Comparison with Table III shows differences in values of n_B, since all of the values of Table III are calculated assuming stoichiometirc composition of the sample used.

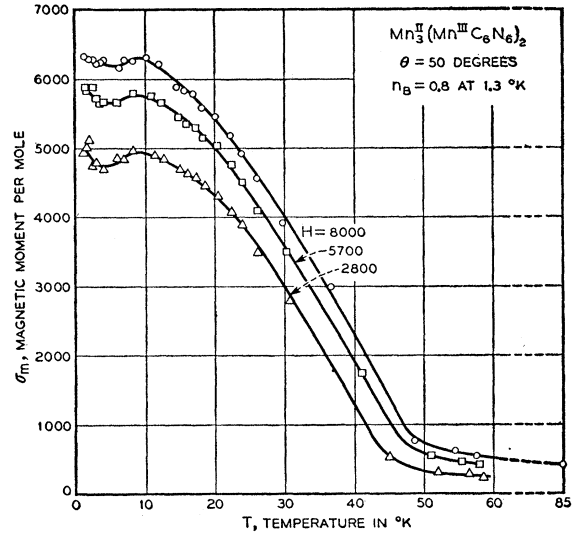

FIG. 16. Results for mangano-manganicyanide.

CURIE-WEISS LAW

The paramagnetic susceptibility χ_p, was determined for some of the compounds. When a ferromagnetic moment was present, χ_p was taken at the slope of the σ *vs* H line. Generally the $1/\chi_p$ *vs* T line was straight over the region investigated, which was usually between the ferromagnetic Curie point (if any) and 75°K. The Curie constants, C, and the values of μ_{eff} derived from them ($\mu_{\mathrm{eff}} = 2.83\sqrt{C}$) are given in Tables IV and V. The accuracy is probably not better than a few percent.

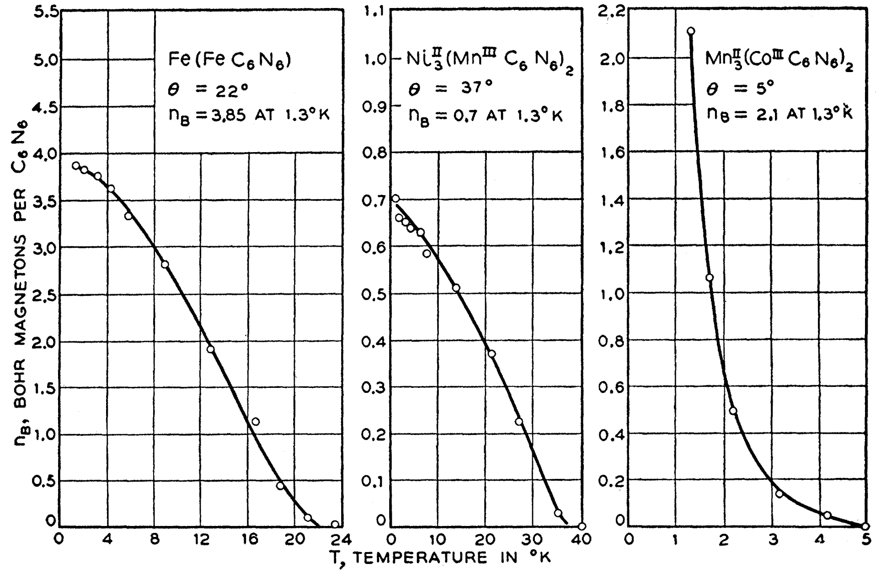

FIG. 17. Ferromagnetism of several cyanides.

TABLE III. Ferromagnetic moment, n_B, in Bohr magnetons per C_6N_6 group, and Curie points in °K.

	Fe^{III}		Mn^{II}		Fe^{II}		Co^{II}		Ni^{II}		Cu^{II}		Zn^{II}	
	n_B	θ	n_B	θ	n_B	θ	n_B	θ	n_B	θ	n_B	θ	n_B	θ
$Cr^{III}C_6N_6$							0.3	13						
$Mn^{III}C_6N_6$			0.8	50	0.85	10	0.4	21	0.7	37	0?	···	0	···
$Fe^{III}C_6N_6$	3.85	22	1.9	11	3.5	8	0.7	21	1.15	27	0.45	16	0	···
$Co^{III}C_6N_6$			2.1	5	0.8	5	0.3	3	···		0?	5?	···	···

Representative data for $1/\chi_p$ *vs* T are shown for $SmFeO_3$, $GdScO_3$, $GdTiO_3$, and $NdTiO_3$ in Fig. 18. Solid lines are used above the Curie point, if any, and dotted lines below.

RISE AT LOW TEMPERATURES

Many of the compounds of the $GdFeO_3$ type show an abnormally rapid rise of parasitic magnetization at low temperatures, usually below 15°K. Although the reason for this is not clear, the following suggestions is offered.

It has been shown that the magnetization of very small ferromagnetic particles is subject to thermal fluctuations.[12] Such particles are therefore difficult to saturate when the temperature is too high even though the temperature is well below the Curie point of a normal material. This amounts to a lowering of the Curie point for fine particles, or a change in the form of the curve representing the saturation magnetization *versus* temperature, from concave downwards to concave upwards, in a manner observed for small iron particles.[13] The analogous phenomenon of the lowering of the temperature of maximum susceptibility with decreasing size in small particles of antiferromagnetic nickelous oxide has recently been reported.[14]

In the ideal orthorhombic pseudo-perovskite structure[4] of the orthoferrites and vanadites, there are various distances between magnetic ions. This fact, and also the assumed disturbances caused by lattice imperfections, could well cause these materials to behave like agglomerates of very fine particles in which there would be thermal fluctuations of magnetization. It must be admitted that this explanation cannot apply to $EuFeO_3$, which shows a constancy of ferromagnetic moment down to 1.3°K.

Using neutron diffraction, Erickson[15] has found the spins in NiF_2 to be inclined at 10° to the tetragonal axis, and Stout and Mattarrese[16] found a consequent weak ferromagnetism below the Néel temperature.

TABLE IV. Curie constants C, and effective Bohr magneton numbers μ_{eff}, of ferrites, etc. expected numbers of spins in parentheses.

Cation	Y(0)		La(0)		Nd		Sm		Gd(7)	
Anion	C	μ_{eff}	C	μ_{eff}	C	μ_{eff}	C	μ_{eff}	C	μ_{eff}
$TiO_3(1)$					0.80	2.5			7.9	8.0
$VO_3(2)$							4.9	6.3	8.1	8.0
$FeO_3(5)$	1.75	3.7			0.97		4.8	6.2	11.9	9.8
$CoO_3(4)$			0.57	2.1						

TABLE V. Curie constants C, and effective Bohr magneton number μ_{eff}, of cyanides.

Cation	Fe^{III}		Mn^{II}		Fe^{II}		Co^{II}		Ni^{II}	
Anion	C	μ_{eff}	C	μ_{eff}	C	μ_{eff}	C	μ_{eff}	C	μ_{eff}
$Cr^{III}C_6N_6$							2.2	4.2		
$Fe^{III}C_6N_6$	4.7	6.8	2.2	4.2	4.7	6.1	1.8	3.8	1.1	3.0
$Fe^{II}C_6N_6$	2.9	4.8								
$Co^{III}C_6N_6$			4.7	6.1	2.4	4.4				
$Co^{II}C_6N_6$							2.1	4.1		

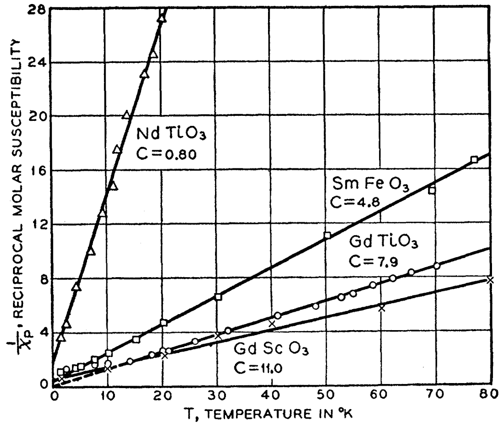

FIG. 18. Curie-Weiss lines for several compounds of orthoferrite type. Note change in slope for $GdTiO_3$ below ferromagnetic Curie point, 21°K.

These results suggest that our observations of the rapid rise in parasitic ferromagnetism at low temperatures may be connected with a change in the angle of spin in the same temperature range.

ACKNOWLEDGMENTS

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