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Rare-Earth Ferricyanides and Chromicyanides $Ln\mathrm{T(CN)_6}\cdot n\mathrm{H_2O}$

F. HULLIGER, M. LANDOLT,* AND H. VETSCH

Laboratorium für Festkörperphysik ETH, CH-8093 Zürich, Switzerland

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Single crystals of the rare-earth ferricyanides and chromicyanides have been grown by a double-infusion technique. These compounds are characterized structurally and magnetically. The complexes with nonmagnetic rare-earth ions are presumably all antiferromagnetic at low temperatures; those with magnetic rare-earth ions are antiferromagnetic or ferrimagnetic. In the first group, magnetic ordering is due to superexchange via five nonmagnetic ions and $\mathrm{LuCr(CN)_6\cdot 4H_2O}$ has the highest ordering temperature ever found for such a long interaction path.

Introduction

Magnetic properties of rare-earth ions in solids have been studied above all in metals and ionic compounds. The chemical bond influences the magnetic properties even of the well-shielded 4*f* electrons via indirect interatomic exchange interactions and effects of the electrostatic crystal field. It is therefore of interest to study magnetic properties in highly covalent compounds. In this paper we present structural and magnetic data of the complex cyanides $Ln\mathrm{Fe(CN)_6}\cdot n\mathrm{H_2O}$ and $Ln\mathrm{Cr(CN)_6}\cdot n\mathrm{H_2O}$.

A detailed study on the crystallization of rare-earth ferricyanides was reported in 1938 by Prandtl and Mohr (*1*). Data on their solubilities were compiled by Marsh (*2*). Some of these cyanides are semipermeable membranes and the growing importance of these membranes in reverse osmosis in connection with the desalination of sea water initiated the structural studies of Milligan *et al.* (*3*, *4*). $\mathrm{LaFe(CN)_6\cdot 5H_2O}$ was found to crystallize in the hexagonal space group $P6_3/m$ and the other lanthanides and large cations were claimed to form isomorphous phases. The detailed structure of $\mathrm{LaFe(CN)_6\cdot 5H_2O}$ was worked out by Bailey *et al.* (*5*). Recently Bonnet and Pâris (*6*) presented structural data and infrared spectra of the rare-earth ferricyanides and studied their thermal dissociation in an oxidizing atmosphere, which leads to stoichiometric $Ln\mathrm{FeO_3}$ as was first pointed out by Gallagher (*7*). A preliminary account of our own studies of the ferricyanides has been reported earlier (*8*, *9*). To our knowledge the corresponding chromicyanides are mentioned in this latter report for the first time. Our studies were initiated by the magnetic investigations of Holden *et al.* (*10*) and Bozorth *et al.* (*11*), who observed ferromagnetic order below ~20°K in transition-element ferri- and manganicyanides.

Sample Preparation

A recrystallization of these salts from aqueous solutions failed. Following the ideas of Prandtl and Mohr (*1*) we prepared single crystals by a new technique, which we describe for Sm ferricyanide as a typical example.

$\mathrm{Sm_2O_3}$ (99.99%, Johnson-Matthey, London) is dissolved in concentrated hydrochloric acid. The resulting solution, filtered and diluted to a concentration of 1 mole/1000 $\mathrm{cm^3}$, is reacted with a freshly prepared

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* Present address: Bell Laboratories, Murray Hill, N.J. 07974.

solution of $K_3Fe(CN)_6$ according to the formal equation

$$SmCl_3(aq) + K_3Fe(CN)_6(aq) \rightarrow SmFe(CN)_6 \cdot 4H_2O(s) + 3KCl(aq).$$

The reaction rate is controlled by the isothermal double-infusion technique developed by Huber (*12*). The two reactants are simultaneously infused into the solute at constant temperature by means of a double-infusion pump of the type used in medical practice. Infusion speed, solute, and temperature are the parameters that have to be optimized. Using water of 65°C as solute and an infusion speed of 0.14 cm^3/hr we obtained single crystals of $SmFe(CN)_6 \cdot 4H_2O$ with edge lengths of 3 mm within 4 days. This method proved to be successful also in the case of the other rare-earth ferricyanides, except with cerium. However, with the heavier rare-earth ions we did not succeed in synthesizing crystals larger than 0.1–0.2 mm.

The Ce, Pr, and Nd ferricyanides synthesized at low temperatures contain $5H_2O$ per formula unit, whereas only $4H_2O$ molecules are incorporated on crystallization at high temperatures.

Growth of the chromicyanides is hampered by the fact that the $[Cr(CN)_6]^{3-}$ anion is hydrolyzed at high temperatures. In the case of the La and Ce chromicyanides, however, fairly large crystals were obtained since these salts crystallize at room temperature. Equivalent amounts of freshly prepared saturated aqueous $K_3Cr(CN)_6$ and 1 *M* $LaCl_3$ or $CeCl_3$ solutions were mixed and kept at room temperature. Crystals of $LaCr(CN)_6 \cdot 5H_2O$ and $CeCr(CN)_6 \cdot 5H_2O$ of up to 3 mm formed within 1 or 2 days. The other rare-earth chromicyanides crystallize only at higher temperatures. In order to prevent hydrolyzation, the reaction time has to be kept as low as possible. Either the cold reactant solutions are mixed and quickly heated at 50–60°C or else a boiling $LnCl_3$ solution is poured into a cold $K_3Cr(CN)_6$ solution. Within a few minutes a large number of small crystallites form. The mother liquor has to be poured off immediately and the crystal powder must be washed with alcohol.

The resulting crystals are transparent and stoichiometric within the accuracy of the chemical analysis. The iron compounds are all dark red while the colors of the Cr^{III} salts are determined by the rare-earth ion. A mass-spectrometric study revealed only minor amounts of K and Cl impurities: K < 600 ppm, Cl < 10 ppm. At room temperature, the crystals are stable in air with certain exceptions connected with the water of hydration.

Crystal Structure

The hexagonal structure of $LaFe(CN)_6 \cdot 5H_2O$ worked out by Bailey *et al.* (*5*) was confirmed on our single crystals by Kietaibl and Petter (*13*, *14*). Discrepancies in the specific-heat and X-ray intensity data led to the discovery of a second modification

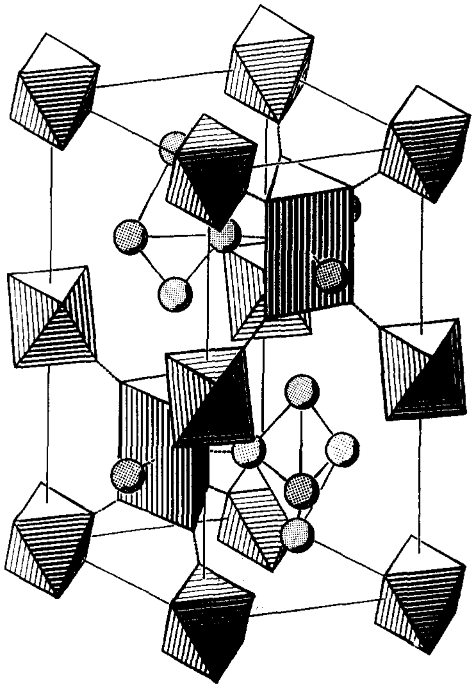

FIG. 1. View of the hexagonal $LaFe(CN)_6 \cdot 5H_2O$ structure, emphasizing the octahedral coordination of the transition element $[FeC_6]$ and the trigonal-prismatic coordination of the rare-earth ion $[LaN_6]$, as well as the trigonal bipyramids formed by the water molecules.

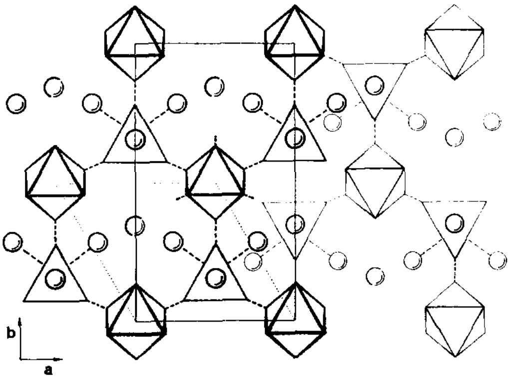

FIG. 2. Projection of the orthorhombic $SmFe(CN)_6 \cdot 4H_2O$ structure, symbolized by $[FeC_6]$ octahedra, $[LnN_6]$ trigonal prisms, and water molecules.

which contains only $4H_2O$. Its structure has been determined on our $SmFe(CN)_6 \cdot 4H_2O$ single crystals by Kietaibl and Petter (*13*, *14*). The two structures are closely related. Removal of $1H_2O$ per formula unit reduces the hexagonal symmetry to orthorhombic. The structures are reproduced in Figs. 1 and 2.

The transition elements, located along screw axes, are octahedrally coordinated by six carbon atoms. The CN units point radially away from the central metal atom. The rare-earth ions are surrounded by six nitrogen atoms at the apices of a trigonal prism and by additional H_2O molecules lying in the mirror plane opposite to the square prism faces: three in the hexagonal structure, but only two in the orthorhombic structure. Two more H_2O molecules occupy holes in the structure above and below the trigonal prism faces and are obviously less strongly bonded.

The adherence of the remaining *Ln* ferricyanides to the hexagonal or orthorhombic type was deduced from Guinier photographs taken with FeK_α radiation and silicon as calibration standard. The agreement between observed intensities and those calculated with the atomic parameters of the La and Sm salt was found to be satisfactory.

We have checked the hexagonal symmetry of our $LnFe(CN)_6 \cdot 5H_2O$ crystals as well as the orthorhombic symmetry of the nearly pseudohexagonal $LnFe(CN)_6 \cdot 4H_2O$ crystals by conoscopical studies which confirmed their optically uniaxial and biaxial characters, respectively.

Figure 3 presents the lattice constants *a* and *c* of the rare-earth ferri- and chromicyanides versus the ionic radii of the Ln^{3+} ions. We have used the radii of Shannon and Prewitt (*15*) except for La. The radius given for La^{3+} appears to be too large for the cyanides. Thus, we assumed $r = 1.027$ Å to be a more appropriate value. Figure 3 demonstrates that we obtained hexagonal ferricyanide crystals with $5H_2O$ per formula unit in the case of La. With *Ln* = Sm, Eu, . . ., Lu and Y our samples turned out to be purely orthorhombic and of composition $LnFe(CN)_6 \cdot 4H_2O$. The Ce, Pr, and Nd salts, however, were obtained in both modifications. Hexagonal $NdFe(CN)_6 \cdot 5H_2O$ is rather unstable, converting within a few days to the orthorhombic $NdFe(CN)_6 \cdot 4H_2O$. The loss

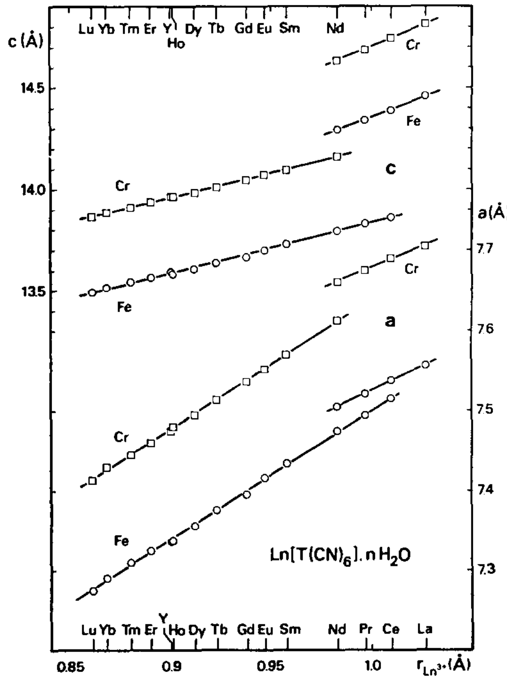

FIG. 3. Lattice constants *c* and *a* of the ferricyanides $LnFe(CN)_6 \cdot nH_2O$ and the chromicyanides $LnCr(CN)_6 \cdot nH_2O$ as functions of the radii of the rare-earth ions.

of 1H_2O is accompanied by a reduction of the volume per formula unit of ~15 Å^3. Comparison of our unit-cell volumes with those reported by Bonnet and Pâris (6) reveals that with the exception of the La compound these authors were in fact dealing with the orthorhombic modifications, which agrees with their chemical analyses that yielded 4H_2O.

The chromicyanides crystallize in the same structures (Table II). Although the complex anion is somewhat larger, the transition between the two modifications also takes place at the Nd salt. Hexagonal NdCr(CN)$_6$·5H_2O is very unstable, disintegrating at room temperature within a few days. The orthorhombic distortions ($a\sqrt{3}/b - 1$) versus ionic radii are illustrated in Fig. 4, where the data of the cobalticyanides (*16*) are added for comparison. It is rather surprising that the distortion can be positive or negative. It shifts to smaller absolute values on going from Cr to Fe and Co. For negative values the functions are nearly parallel straight lines which cross the zero line near Nd for the chromicyanides, near Sm for the ferricyanides, and between Tb and Gd for the cobalticyanides.

TABLE I

LATTICE PARAMETERS AT 22°C OF THE HEXAGONAL *Ln*Fe(CN)$_6$·5H_2O AND THE ORTHORHOMBIC *Ln*Fe(CN)$_6$·4H_2O COMPLEXES

Ln	*a* (Å)	*b* (Å)	*c* (Å)	*v*/*z* (Å^3)
La	7.557(2)		14.457(3)	357.5
Ce	7.538(2)		14.387(3)	354.0
	7.514(5)	13.03(2)	13.86(2)	339
Pr	7.521(2)		14.342(4)	351.3
	7.494(3)	12.971(8)	13.829(5)	336.0
Nd	7.505(3)		14.296(6)	348.6
	7.473(4)	12.919(5)	13.794(6)	332.9
Sm	7.433(3)	12.875(4)	13.730(5)	328.5
Eu	7.416(3)	12.856(5)	13.702(5)	326.6
Gd	7.396(4)	12.839(6)	13.673(6)	324.6
Tb	7.377(3)	12.816(5)	13.643(5)	322.4
Dy	7.356(3)	12.797(5)	13.610(6)	320.3
Ho	7.337(3)	12.777(5)	13.586(6)	318.4
Er	7.324(3)	12.762(4)	13.568(5)	317.1
Tm	7.310(2)	12.742(4)	13.545(6)	315.4
Yb	7.290(3)	12.722(6)	13.517(6)	313.4
Lu	7.274(2)	12.708(4)	13.494(5)	311.9
Y	7.336(2)	12.778(4)	13.596(5)	318.6

TABLE II

LATTICE PARAMETERS AT 22°C OF THE HEXAGONAL *Ln*Cr(CN)$_6$·5H_2O AND THE ORTHORHOMBIC *Ln*Cr(CN)$_6$·5H_2O COMPLEXES

Ln	*a* (Å)	*b* (Å)	*c* (Å)	*v*/*z* (Å^3)
La	7.706(2)		14.815(4)	380.9
Ce	7.690(3)		14.742(5)	377.5
Pr	7.675(3)		14.684(6)	374.5
Nd	7.661(5)		14.631(8)	371.8
	7.613(5)	13.199(8)	14.165(7)	355.8
Sm	7.571(2)	13.146(4)	14.097(4)	350.8
Eu	7.553(4)	13.131(7)	14.076(8)	349.0
Gd	7.536(3)	13.117(5)	14.047(6)	347.2
Tb	7.514(2)	13.090(3)	14.012(4)	344.6
Dy	7.494(2)	13.075(5)	13.984(6)	342.6
Ho	7.479(3)	13.057(5)	13.967(7)	341.0
Er	7.458(3)	13.037(7)	13.939(7)	338.9
Tm	7.445(2)	13.021(3)	13.911(5)	337.2
Yb	7.427(2)	13.007(4)	13.887(5)	335.4
Lu	7.413(2)	12.995(4)	13.864(5)	333.9
Y	7.474(2)	13.055(8)	13.967(6)	340.7

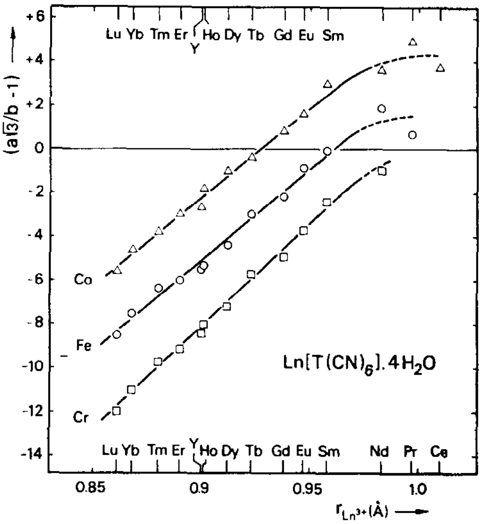

FIG. 4. Comparison of the orthorhombic distortions ($a\sqrt{3}/b - 1$) in the chromi- and ferricyanides with those in the corresponding cobalticyanides (*16*).

The two structures differ markedly in their Debye temperatures. Therefore it is possible to confirm the adherence to one of the two structures by means of low-temperature specific-heat measurements.

We wonder whether an additional proton might be incorporated within the trigonal bipyramid formed by the $5H_2O$ molecules of the hexagonal structure, thus reducing one of the two cations. Isomorphous compounds such as $HLn[Fe^{II}(CN)_6]\cdot 5H_2O$ (e.g., $HEuFe(CN)_6\cdot 5H_2O$, $Eu^{2+}Fe^{III} \rightleftarrows Eu^{3+}Fe^{II}$?) or $HBa[Cr^{III}(CN)_6]\cdot 5H_2O$ appear to be feasible.

Magnetic Properties

The magnetic properties have been investigated by measuring the following quantities:

(a) the initial susceptibility $\chi_0(T)$ between 1.3 and 40°K by means of a mutual-induction method using a field of 5 Oe at 21 cps;

(b) the magnetic susceptibility $\chi(T)$ between 4 and 300°K on a Faraday balance in fields of 3 to 13 kOe;

(c) the magnetization $M(H)$ at 1.3°K in pulsed fields up to 120 kOe with a pulse duration of 20 msec; and

(d) the specific heat $c_p(T)$ between 1.6 and 22°K or between 18 and 80°K (only on some selected compounds).

Ferricyanides

Our magnetic data of the ferricyanides are summarized in Table III. Ordering temperatures lying below 1.3°K have been estimated from extrapolations of $\chi_0(T)$ and $c_p(T)$. From the temperature dependence of the specific heat we deduce that the magnetic phase transitions are of second order. In the case of the Gd salt, the $c_p(T)$ curve points to another anomaly below 1.6°K (*8*).

The compounds with nonmagnetic rare-earth ions such as La, Lu, and Y, as well as those with Ce, Nd, and Yb are antiferromagnetic at low temperatures. The remaining complexes order in ferrimagnetic arrangements as can be deduced from the magnetization curves reproduced in Fig. 5. The Tb salt has the highest ordering temperature of all ferricyanides: $T_N = 5.7$°K. It is a metamagnet with a threshold field $H_c = 5$kOe at 1.3°K. Figure 6 illustrates the anisotropy

TABLE III

MAGNETIC DATA OF THE FERRICYANIDES $LnFe(CN)_6\cdot nH_2O$[a]

Ln	Magnetic order	$T_{N,C}$ (°K)	θ_p (°K)	p_{eff}^2 (experimental)	p_{eff}^2 (theoretical)
La	(afm)	(<1)	−1	3.1	3.0
Ce	afm	2.6	−8	9.6	9.4
Pr	(afm)	(<1)	*	*	
Nd	afm	1.9	*	*	
Sm	ferri	3.5	*	*	
Eu	(afm)	(≃1)	*	*	
Gd	ferri	3.2	−2	67	66.0
Tb	meta	5.7	+6	98	97.5
Dy	ferri	2.8	+1	114	116.3
Ho	ferri	1.3	−6	115	115.5
Er	(ferri)	(≃1)	−5	94	94.8
Tm	(ferri)	(1.1)	+2	63	60.2
Yb	afm	1.8	0	24	23.6
Lu	afm	2.2	−2	3.5	3.0
Y	afm	2.0	−2	3.2	3.0

[a] An asterisk indicates the invalidity of the Curie–Weiss law within $2 < T < 290$°K. The data in parentheses have been extrapolated.

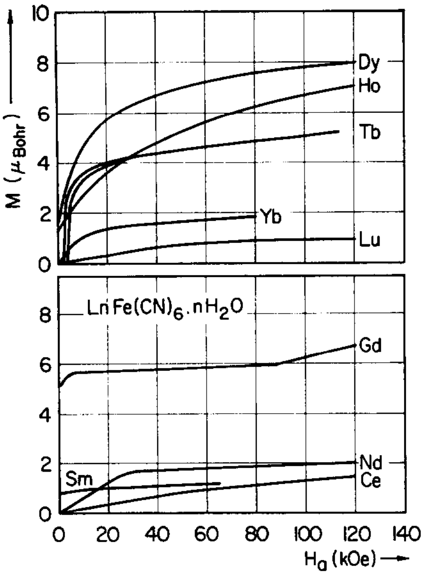

FIG. 5. Magnetizations of the ferricyanides LnFe-$(CN)_6 \cdot nH_2O$ at 1.3°K as functions of an external magnetic field.

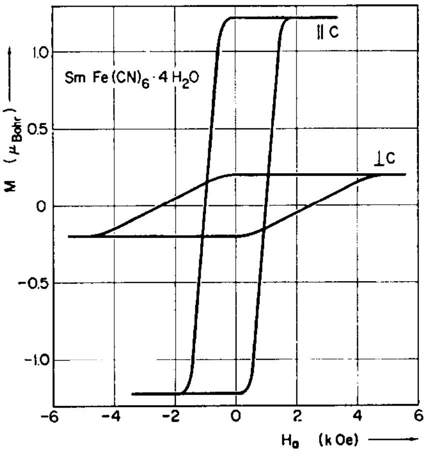

FIG. 6. Magnetic hystereses of $SmFe(CN)_6 \cdot 4H_2O$ single crystals measured at 1.3°K in an alternating magnetic field of 50 cps.

of the magnetic hysteresis measured on $SmFe(CN)_6 \cdot 4H_2O$ at 1.3°K.

The magnetic behavior of the La, Lu, and Y salts is similar to that of ordinary transition-element compounds obeying a Curie–Weiss law. For these compounds the paramagnetic data compiled in Table III were derived from measurements of the initial susceptibility in the temperature range 1.3–20°K. For the compounds which contain two different kinds of magnetic ions, the paramagnetic Curie temperatures and the effective magneton numbers were derived from susceptibility measurements in the range 200 to 300°K.

The octahedral CN surrounding induces a low-spin state of the d electrons localized on the transition-element cation. The five d electrons of Fe^{III} which occupy the t_{2g} triplet thus lead to an $S = \frac{1}{2}$ state, as is evident from the susceptibility of the complexes containing rare-earth ions which are nonmagnetic (La, Lu, Y) or which possess a nonmagnetic ground state (Pr in the actual crystal field (*16*), and Eu). If we neglect the magnetic interactions between Fe^{III} and rare-earth ions we obtain in a first approximation the magnetic susceptibility of the Fe^{III} sublattice from the difference of the susceptibilities of LnFe$(CN)_6 \cdot nH_2O$ and LnCo$(CN)_6 \cdot nH_2O$, since Co^{III} is nonmagnetic. Experimentally, this difference yields for Fe^{III} an effective Bohr magneton number of $p_{\mathrm{eff}}^2 = 3.0$ and 3.1 for the Pr and the Eu salts, respectively, in fair accord with the La, Lu, and Y salts and the theoretical value 3.

In the remaining rare-earth complexes the experimental values for the magnetic moments agree well with the calculated $p_{\mathrm{eff}}^2 = g^2J(J+1) + 3$. With Pr and Nd the crystal-field splitting of the J ground state is obviously large enough to make the Curie–Weiss law invalid below 300°K. In the complexes with Sm and Eu the deviation from the Curie–Weiss is caused by mixing in higher J states since the splitting of the J multiplet due to spin–orbit coupling is much lower than in the other rare-earth ions.

Chromicyanides

The magnetic properties of the rare-earth chromicyanides are analogous to those of the ferricyanides. The three d electrons of Cr^{III} are in an $S = \frac{3}{2}$ state and the higher magnetic moment of Cr^{III} thus leads to higher ordering temperatures, as is experimentally confirmed (Table IV). The com-

TABLE IV

MAGNETIC DATA OF THE CHROMICYANIDES *Ln*$Cr(CN)_6 \cdot nH_2O$[a]

Ln	Magnetic order	$T_{N,C}$ (°K)	θ_p (°K)	p^2_{eff} (experimental)	p^2_{eff} (theoretical)
La	afm	1.6	−2	15.2	15.0
Ce	meta	4.2	−4	20.4	21.4
Pr	(afm)	(<1.4)	−3	26.4	27.8
Nd	ferri	6.2	−6	27.5	28.1
Sm	ferri	10.5	*	*	
Eu	afm	2.0	*	*	
Gd	ferri	10.2	−12	76	78.0
Tb	ferri	11.7	−5	106	109.4
Dy	ferri	5.0	−4	124	128.3
Ho	ferri	1.7	−12	123	127.5
Er	ferri	2.3	−8	104	106.8
Tm	ferri	2.2	−5	70	72.2
Lu	afm	2.8	−6	14.2	15.0
Y	afm	2.4	−4	14.8	15.0

[a] An asterisk indicates the invalidity of the Curie–Weiss law in the temperature range 2–290°K. The data in parentheses have been obtained by extrapolation.

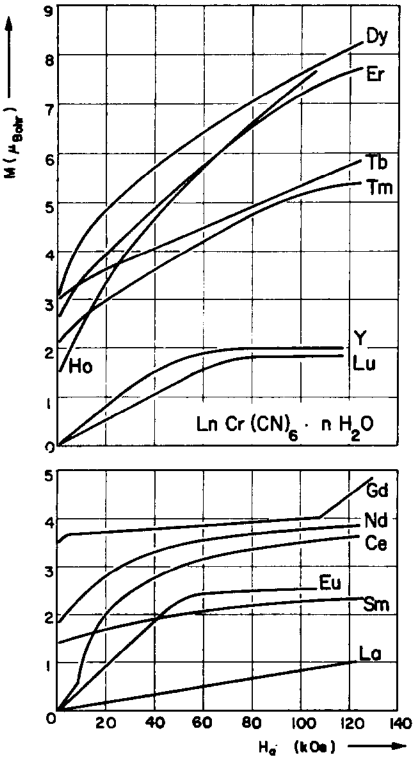

FIG. 7. Magnetizations of the chromicyanides *Ln*$Cr(CN)_6 \cdot nH_2O$ as functions of an external magnetic field, measured at 1.3°K with pulsed fields.

pounds with La, Lu, and Y, in which the low-temperature magnetic coupling is determined by the transition element, are again antiferromagnetic. In this group it is the Ce salts that exhibits a metamagnetic transition at 10 kOe (Fig. 7) whereas no metamagnetic behavior is displayed by the Tb salt. The behavior of the remaining chromium complexes is analogous to that of the iron complexes. Again the Tb compound exhibits the highest ordering temperature. The paramagnetic effective moments agree rather well with the theoretical values $p^2_{eff} = g^2J(J+1) + 15$.

The Magnetic Interactions

The magnetic behavior at low temperatures depends on both the rare-earth and the transitions elements. Obviously, the transition element is decisive for the magnetic interactions since only the complexes with magnetic transition-element cations like Cr^{III} and Fe^{III} show magnetic ordering, and not with nonmagnetic Co^{III} (*16*). The magnetic interaction in these insulators is the result of superexchange and dipole–dipole interactions. The distances between the magnetic moments are rather large. The shortest *Ln*–T

TABLE V

COMPARISON OF ESTIMATED ORDERING TEMPERATURES T_d DUE TO THE DIPOLE ENERGIES WITH OBSERVED NÉEL TEMPERATURES T_N FOR SOME CYANIDES *Ln*T-$(CN)_6 \cdot nH_2O$ WITH NONMAGNETIC RARE-EARTH IONS

Ln-T	T_d (°K)	T_N (°K)
Lu-Fe	0.01	2.2
Y-Fe	0.01	2.0
La-Cr	0.09	1.6
Lu-Cr	0.09	2.8
Y-Cr	0.09	2.4

distance is ~5.5 Å, while the *Ln*-*Ln* and T-T distances are larger than 7 Å. The Cr^{III} and Fe^{III} complexes with nonmagnetic rare-earth ions are of particular interest since the Cr-Cr and Fe-Fe distances are so large that the dipole energy can be neglected safely, at least in the iron compound.

Table V presents ordering temperatures T_d which result only from the dipole energy estimated in order of magnitude according to the formula

$$kT_d \approx \mu_1 \sum_i z_i \mu_i / r_i^3,$$

where μ_i, z_i, r_i = magnetic moment, number, and distance of the *i*th (up to the next-nearest) neighbors, respectively.

Since the observed ordering temperature is higher than T_d, it is obvious that the superexchange interaction is important in these compounds. This indirect interaction takes place via extremely long paths, as illustrated in Fig. 8. Between two localized moments we meet five diamagnetic atoms such as Cr-C-N-Lu-N-C-Cr in $LuCr(CN)_6 \cdot 4H_2O$ and it is rather nontrivial that an antiferromagnetic coupling with $T_N = 2.8$°K is mediated by such a long exchange path. The bonding of the rare-earth ion with the trigonal-prismatic coordination presumably has a considerable covalent part, which is necessary for the occurrence of superexchange interactions. There are three different bond angles: 77°, 88°, and 158°. Probably, both antiferromagnetic and ferromagnetic interactions are effective. This leads to complicated magnetic structures. The increase of the ordering temperatures in the compounds which contain magnetic ions on both the cation sites is partly due to the increased dipole interactions. The ordering temperatures cannot simply be correlated with *gJ*, since the magnetic moments of most rare-earth ions are strongly anisotropic and field dependent due to the splitting of the *J* ground state by the electrostatic crystal field.

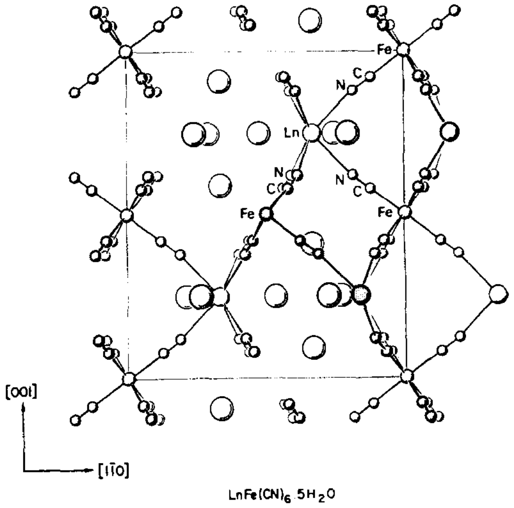

FIG. 8. (110) section of the hexagonal cell of $LnFe(CN)_6 \cdot 5H_2O$ emphasizing the superexchange paths.

The marked field dependence of the magnetization *M*(*H*), particularly of the Ho and Dy compounds (see Figs. 5 and 7) reflects the influence of the crystal field and prevents a simple interpretation of the magnetic structures. An exception is offered by Gd because of its *S* ground state. Its magnetic moment is virtually isotropic and field independent. The magnetization curves of the Gd ferri- and chromicyanide reveal a ferrimagnetic phase in $H < 100$ kOe. The absolute value of the magnetization suggests an antiparallel orientation of ferromagnetic Gd and Cr or Fe sublattices.

In conclusion, we would like to point out that the superexchange path in $LuCr(CN)_6 \cdot 4H_2O$ is the longest found up to now, leading to an ordering temperature >2°K. The influence of the chemical bonding of the rare-earth ion on the superexchange interaction is another problem of interest. More information might be gained from isomorphous compounds which contain Bi^{3+} instead of Ln^{3+}, since in the former the 5*d* orbitals are all filled. According to Bailey *et al.* (*5*) the Bi ferricyanide has the same structure as the rare-earth ferricyanides. From the ionic radii we expect that Tl^{3+} also forms isostructural ferri- and chromicyanides.

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