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Rare-Earth Cobalticyanides $Ln\mathrm{Co(CN)_6}\cdot n\mathrm{H_2O}$

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

Laboratorium für Festkörperphysik ETH, CH-8093 Zürich, Switzerland

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Crystalline cobalticyanides $Ln\mathrm{Co^{III}(CN)_6}\cdot n\mathrm{H_2O}$ with Ln = La,..., Lu, Y have been synthesized by a double-infusion technique. In analogy to the Cr and Fe compounds, the large rare-earth ions form a hexagonal modification while the smaller ions lead to the orthorhombic structure with $4\mathrm{H_2O}$. Experiments show that no magnetic ordering occurs down to 1°K. The Stark splitting of the *J* ground state due to the crystalline field is analyzed for the Ce and Sm compounds.

Introduction

Rare-earth cobalticyanides were investigated at the beginning of the century by James and Willand (*1*). People were interested in the solubility of these salts in view of their applicability to the separation of the rare-earth ions. As in the case of the iron salts (and probably also of the chromium salts), thermal dissociation of the $Ln\mathrm{Co(CN)_6}\cdot n\mathrm{H_2O}$ complexes in oxidizing atmosphere leads to stoichiometric $Ln\mathrm{CoO_3}$ (*2*). Recently, Bonnet and Pâris (*3*) reported on infrared and X-ray studies. They ascribed these phases to the hexagonal $\mathrm{LaFe(CN)_6\cdot 5H_2O}$ structure although they gave the chemical formulas with only $4\mathrm{H_2O}$. We prepared the cobalticyanides in the hope of gaining some insight into the magnetic coupling effective in the $\mathrm{Cr^{III}}$ and $\mathrm{Fe^{III}}$ cyanides (*4*).

Preparation and Structures

The $Ln\mathrm{Co(CN)_6}\cdot n\mathrm{H_2O}$ salts were synthesized in crystalline form by means of the double-infusion technique as described for the iron salts (*4*). $\mathrm{K_3Co(CN)_6}$ and high-purity rare-earth oxides were used as starting materials. Crystals with dimensions of 1–3 mm were obtained only with the lighter rare-earth ions La,...,Nd whereas with the heavier *Ln* ions the crystallites had edge lengths that were at best some tenths of a millimeter. This different behavior is the consequence of the decreasing solubilities of the resulting cobalticyanides. As $\mathrm{Co^{III}}$ has no strong optical transition in the visible range, the color of these salts is determined by the rare-earth ion and thus is the same as in the rare-earth oxides $Ln_2\mathrm{O_3}$. Since the effective radii of $\mathrm{Fe^{III}}$ and $\mathrm{Co^{III}}$ do not differ greatly ($\mathrm{Fe^{III}}$, 0.69 Å; $\mathrm{Co^{III}}$, 0.665 Å (*5*, *6*)), it was to be expected that essentially the same phases and crystal structures would occur. This was confirmed by the experiment. Chemical analyses, Guinier patterns, and specific heat data served to identify the different modifications. As with Fe and Cr, we obtained the La salt only with $5\mathrm{H_2O}$ crystallizing in the hexagonal $\mathrm{LaFe(CN)_6\cdot 5H_2O}$ structure (*7*). The Ce, Pr, and Nd salts also crystallized in the hexagonal form but on standing they lost water and transformed gradually into the orthorhombic form with $4\mathrm{H_2O}$ (*8*). The loss of $1\mathrm{H_2O}$ per formula is accompanied by a reduction of the cell volume of ~15 Å^3 per formula unit. From the cell volumes we deduce that Bonnet and Pâris (*3*) were dealing with hexagonal $\mathrm{LaCo(CN)_6\cdot 5H_2O}$ but with orthorhombic $Ln\mathrm{Co(CN)_6}\cdot 4\mathrm{H_2O}$ in the case of all the other rare-earth ions. Figure 1 illustrates the dependence of the cell volume on the size of the rare-

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

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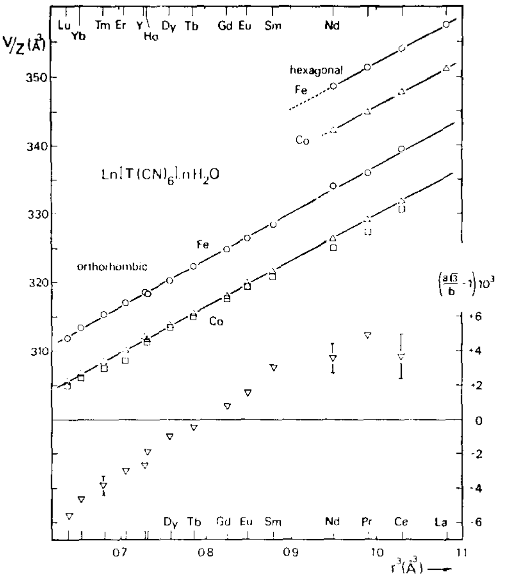

FIG. 1. Volumes per formula unit versus ionic radii of the Ln^{3+} ions: triangles, our own data for LnCo(CN)$_6$·nH$_2$O; squares, data for LnCo(CN)$_6$·nH$_2$O according to (3); circles, our own data for LnFe(CN)$_6$·nH$_2$O (4) for comparison; lowest curve, orthorhombic distortion $(a\sqrt{3}/b - 1)$ for the LnCo(CN)$_6$·4H$_2$O phases.

earth ion. In this graph we have used the revised radii of Shannon and Prewitt (6) with the exception of La. The radius given for La^{3+} appears to be too large. Thus we have determined an appropriate radius for La^{3+} from the corresponding graph of the LnFe(CN)$_6$·5H$_2$O compounds (4). The volumes of the orthorhombic unit cells of the Co salts differ by ~27 Å^3 from those of the corresponding Fe salts. The curve $(a\sqrt{3}/b - 1)$ versus ionic radii, which describes the orthorhombic distortion, covers positive and negative values. Tb- and Gd-cobalticyanides are nearly pseudohexagonal.

Magnetic Properties

The compounds MCo^{III}(CN)$_6$·nH$_2$O with M = La, Lu, and Y are diamagnetic. In these structures the transition element is octahedrally coordinated by six carbon atoms. In this surrounding the triplet t_{2g} is filled with the six excess d electrons while the energetically higher e_g level is completely empty. The paramagnetism of the remaining Ln salts thus is entirely due to the f electrons localized on the rare-earth cations. Figure 2 shows the low-temperature reciprocal initial susceptibilities

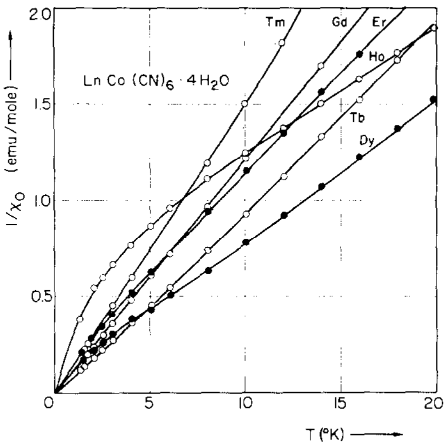

FIG. 2. Reciprocal molar initial susceptibility of some LnCo(CN)$_6$·4H$_2$O complexes.

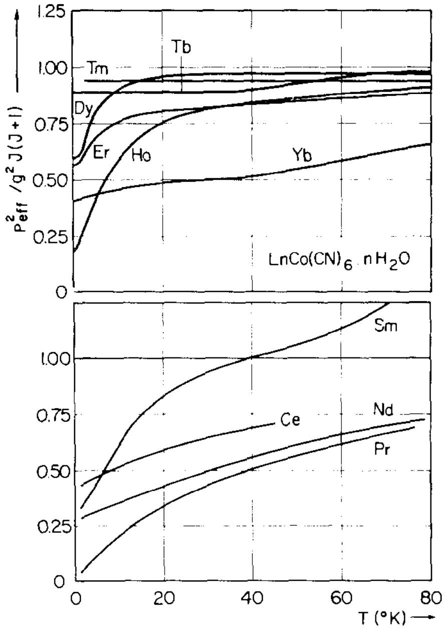

FIG. 3. Temperature dependence of the effective magnetic moments p^2_{eff} of LnCo(CN)$_6$·nH$_2$O complexes relative to the theoretical values for the J ground state of the Ln^{3+} ions.

of some heavy rare-earth salts. It follows from these measurements that the magnetic interactions are weak. Assuming a crystal-field splitting of the order of ~100°K for the J ground state of the Ln^{3+} ions it is permitted at $T < 2°\text{K}$ to fit a Curie–Weiss law for the Ln^{3+} ions with a magnetic ground state. The order of magnitude of the magnetic interactions then can be estimated from the paramagnetic Curie temperature. For the Co^{III} complexes we find $|\theta_p| < 0.3°\text{K}$.

The compound $\text{EuCo(CN)}_6 \cdot 4\text{H}_2\text{O}$ exhibits at low temperatures a Van Vleck paramagnetism $\chi_0 = 6.2 \times 10^{-3}$ emu/mole, which compares well with other Eu^{3+} compounds.

Figure 3 illustrates the effective magnetic moments $p^2_{\text{eff}}(T)$. After correcting for the diamagnetic part, this moment was calculated from χT relative to the free-ion value $g^2J(J+1)$. These curves demonstrate the decisive influence of the crystal field. For the simplest cases, those with Ce and Sm, the crystal-field splitting is discussed later on in some detail. It is evident that Pr^{3+} has a nonmagnetic ground state. The ground state of Pr^{3+}, $J = 9/2$, is split by the hexagonal crystal field into three doublets and three singlets with one singlet obviously lying lowest.

The Crystal Field in the Ce and Sm Salts

Since in $4f$ electron systems the spin–orbit coupling (order of 10^4°K) is much larger than the crystal-field interaction (order of 100°K) the electrostatic crystal field can be treated as a perturbation that lifts in part the degeneracy of the J ground state as given by Hund's rule. For hexagonal symmetry with quantization parallel to the c-axis, Segal and Wallace (*9*) calculated the eigenvalues and eigenfunctions, treating the influence of a magnetic field simultaneously with the perturbation due to the crystal field.

In the hexagonal structure of $\text{CeCo(CN)}_6 \cdot 5\text{H}_2\text{O}$, the Ce^{3+} ion is located on a threefold axis in a mirror plane. For this symmetry the perturbing operator of the electrostatic crystal field is reduced to the following expression (*14*):

$$\mathscr{H}_{CF} = B_2{}^0\,O_2{}^0 + B_4{}^0\,O_4{}^0 + B_6{}^0\,O_6{}^0 + B_6{}^6\,O_6{}^6$$

where $\text{O}_n{}^m$ are linear combinations of the angular-momentum operators as introduced by Stevens (*10*). $B_n{}^m$ are crystal-field parameters reflecting the surrounding ions and the radial distribution of the $4f$ electrons:

$$B_n{}^m = \alpha_J \langle r^n \rangle A_n{}^m,$$

where α_J are the Stevens multiplicators determined by l, J, and the number of $4f$ electrons, $\langle r^n \rangle$ is the r-dependent part of the matrix element which can be separated (calculated by Freeman and Watson (*11*)), and $A_n{}^m$ are the geometrical factors taking into account the charge distribution of the surroundings. The values of these factors $A_n{}^m$ thus are strongly influenced by the character of the bonds effective between the rare-earth ions and their ligands. The ionic point-charge model is usually a bad approximation in strongly covalent crystals and the crystal-field parameters $A_n{}^m\langle r^n \rangle$ therefore are derived from experimental data.

In our examples, Ce^{3+} and Sm^{3+}, the number of parameters reduces to two, since for a $J = \frac{5}{2}$ ground state the matrix elements of $O_6{}^m$ vanish. In the nearly pseudohexagonal Sm compound we neglect the orthorhombic part of the crystal field due to the H_2O molecules. The crystal-field operator then is

$$\mathscr{H}_{CF} = W[(1-|y|)\,O_2{}^0/F(2) + yO_4{}^0/F(4)]$$

in terms of the crystal-field parameters W and y (*12*). The factors $F(n)$ depend only on J and are common to all matrix elements of $O_n{}^m$. They have been calculated by Hutchings (*13*).

Under the action of the crystal field the $J = \frac{5}{2}$ ground state splits into three doublets which are all pure M states: $|\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and $|\pm\frac{5}{2}\rangle$. Their energies have been calculated by Segal and Wallace (*9*) as functions of W and y.

The magnetic susceptibility can be calculated according to the Van Vleck formula,

$$\chi = N\frac{\sum\limits_i \{(E_i^{(1)})^2/kT - 2E_i^{(2)}\}\exp(-E_i{}^0/kT)}{\sum\limits_i \exp(-E_i{}^0/kT)},$$

provided that the magnetic field $H = H_{\text{ext}} + H_{\text{mol}}$ (external and molecular field) can be treated as a perturbation and that the ratio

H/T is such that the magnetic system is far from saturation. The terms E_i^0 are the energy eigenvalues of the unperturbed system, in our case the energies of the crystal-field states, and $E_i^{(k)}$ are perturbation energies of kth order in H. For the rare-earth ions the operator, taking account of the perturbation due to the magnetic field, has the form

$$\mathscr{H}_H = \mu_B g \mathbf{J}\mathbf{H}.$$

The Van Vleck formula can describe our measurements of the initial susceptibility above 1°K very well, since we apply a magnetic field $H_{\text{ext}} = 5$ Oe, and the molecular field H_{mol} is negligible in the cobalticyanides.

We have calculated the matrix elements of $\mathscr{H}_H$ for $\mathbf{H}$ parallel (H_z) and $\mathbf{H}$ perpendicular (H_x) to the quantization direction for different values of W and y. From these data we have derived the powder susceptibilities $\chi_p = \frac{1}{3}\chi_z + \frac{2}{3}\chi_x$. As J_z is diagonal in the crystal-field states (pure M states) $E_i^{(1)} = M_i$ and $E_i^{(2)} = 0$. On the other hand, J_x is not diagonal and for the matrix elements of J_x the following relations (*14*) hold.

$$\langle M_i | J_x | M_k \rangle = 0$$

except for

$$\langle M | J_x | M \pm 1 \rangle = \tfrac{1}{2}((J \mp M)(J \pm M + 1))^{1/2}.$$

If, however, in the doublet $|\pm\frac{1}{2}\rangle$, the two eigenfunctions are replaced by the linear combinations

$$\Psi_{1,2} = (1/\sqrt{2})| + 1/2\rangle \pm (1/\sqrt{2})| - 1/2\rangle$$

then J_x is diagonal within all the degenerate crystal-field states and the perturbation energies can be calculated according to the simple formulas valid for nondegeneracy. The values thus calculated are compared in Fig. 4 with powder susceptibilities measured on $CeCo(CN)_6 \cdot 5H_2O$. The best agreements with the experimental data are reached with those values of y for which $|\pm\frac{1}{2}\rangle$ is the ground state. Within this range χ_0 is not sensitive to variations in y, with an appropriate value for W. This is in contrast to the strong y-dependence of the magnetic specific heat. We have calculated the Schottky anomaly assuming termperature-independent crystal-field energies. A comparison with experimental values

$$c_{\text{mag}} = c_p[CeCo(CN)_6 \cdot 5H_2O] \\ - c_p[LaCo(CN)_6 \cdot 5H_2O]$$

is presented in Fig. 5. We find a fair agreement for a vanishing second-order term, $|y| = 1$. The difference between calculated and experimental curve may reflect the fact that taking the specific heat of the La compound for the lattice part of the Ce compound is an approximation. Moreover, c_{mag} represents a difference

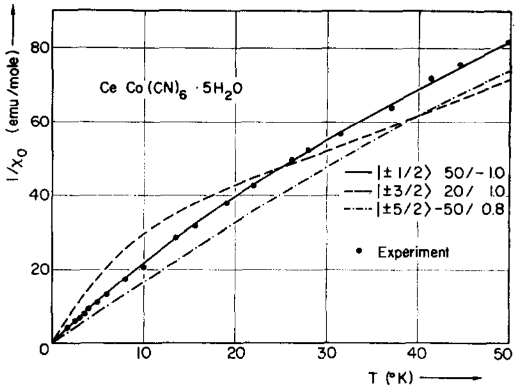

FIG. 4. Comparison of the reciprocal susceptibility of $CeCo(CN)_6 \cdot 5H_2O$ with theoretical values calculated for different fields. The given parameters mean: ground state, W/y.

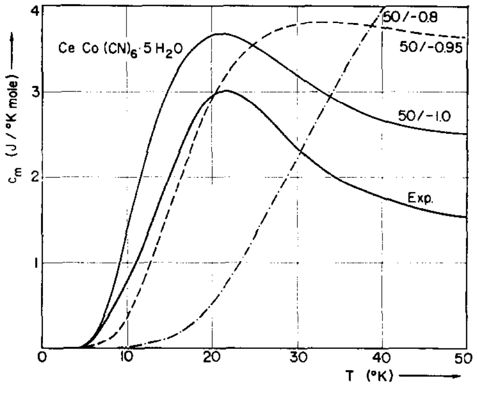

FIG. 5. Fit of magnetic specific heat curves c_{mag} calculated for different crystal fields with the experimental approximation for the Schottky anomaly: $c_{\text{exp}} = c_p[CeCo(CN)_6 \cdot 5H_2O] - c_p[LaCo(CN)_6 \cdot 5H_2O]$. The given parameters are W/y.

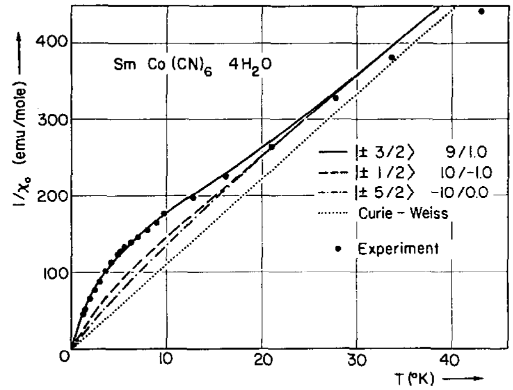

FIG. 6. Comparison of the reciprocal susceptibility of $SmCo(CN)_6 \cdot 4H_2O$ with theoretical curves calculated for various crystal fields. Higher J states are neglected. Parameters are: ground state, W/y.

of two rather large quantities, especially toward higher temperatures.

In Fig. 6 we compare the powder susceptibilities measured on $SmCo(CN)_6 \cdot 4H_2O$ with curves calculated for various values of W and y. Unequivocally the doublet $|\pm\frac{3}{2}\rangle$ lies lowest and the best fit to the experimental values is reached with $y \approx 0.9$. Thus the influence of the second-order term is weak. At temperatures above 30°K the influence of higher J states is visible and χ can no longer be described with the J ground state only.

The crystal-field parameters derived from this fit are compiled in Table II and the corresponding energy schemes are shown in Fig. 7. For both ions we thus find that the fourth-order term dominates. Surprisingly, this term changes sign from Ce^{3+} to Sm^{3+}. This implies a change in the charge distribution on going from the hexagonal ($5H_2O$) to the orthorhombic (~pseudohexagonal $4H_2O$) structure although the axial ratio changes by only ~3%.

The influence of the orthorhombic part of the crystal field in $SmCo(CN)_6 \cdot 4H_2O$ is presumably not pronounced since its susceptibility at $T \to 0$ corresponds to a pure $M = \frac{3}{2}$ ground state, whereas the operators $O_n^m (m \neq 0)$ of the orthorhombic field would mix the states.

TABLE I

LATTICE CONSTANTS OF THE COBALTICYANIDES, HEXAGONAL $LnCo(CN)_6 \cdot 5H_2O$, AND ORTHORHOMBIC $LnCo(CN)_6 \cdot 4H_2O$[a]

Ln	$r_{Ln^{3+}}$ (Å)	a (Å)	b (Å)	c (Å)	V/Z (Å^3)	$((a\sqrt{3})/b - 1)\,10^3$
La	1.027	7.516 (2)		14.357 (6)	351.2	
Ce	1.01	7.495 (3)		14.301 (8)	347.9	
		7.460 (3)	12.873 (9)	13.821 (6)	331.8	+3.7
Pr	0.997	7.477 (3)		14.234 (7)	344.6	
		7.448 (2)	12.836 (3)	13.769 (3)	329.1	+4.9
Nd	0.983	7.464 (3)		14.192 (7)	342.4	
		7.421 (2)	12.808 (4)	13.732 (3)	326.3	+3.6
Sm	0.958	7.386 (2)	12.754 (3)	13.660 (3)	321.7	+3.0
Eu	0.947	7.367 (2)	12.739 (3)	13.628 (3)	319.7	+1.6
Gd	0.938	7.350 (2)	12.720 (3)	13.604 (4)	318.0	+0.8
Tb	0.923	7.327 (2)	12.696 (3)	13.568 (3)	315.5	−0.4
Dy	0.912	7.311 (2)	12.675 (3)	13.538 (3)	313.7	−1.0
Ho	0.901	7.293 (2)	12.655 (3)	13.515 (4)	311.9	−1.8
Er	0.890	7.276 (2)	12.641 (3)	13.489 (3)	310.2	−3.0
Tm	0.880	7.261 (2)	12.624 (3)	13.458 (3)	308.4	−3.8
Yb	0.868	7.244 (2)	12.606 (3)	13.434 (3)	306.7	−4.6
Lu	0.861	7.232 (2)	12.597 (3)	13.415 (3)	305.5	−5.6
Y	0.900	7.293 (2)	12.665 (3)	13.521 (3)	312.2	−2.7

[a] The listed radii for the rare-earth ions stem from Shannon and Prewitt (*6*) except the value for La^{3+}, which we derived from the volume–radius dependence of the $LnFe(CN)_6 \cdot 5H_2O$ series (*4*).

TABLE II

THE CRYSTAL-FIELD PARAMETERS FOR Ce^{3+} AND Sm^{3+} IN $CeCo(CN)_6 \cdot 5H_2O$ AND $SmCo(CN)_6 \cdot 4H_2O$, RESPECTIVELY, AS DEDUCED FROM MEASUREMENTS OF THE INITIAL SUSCEPTIBILITY AND THE SPECIFIC HEAT

	Ce^{3+}	Sm^{3+}
W (°K)	50 ± 10	9 ± 2
y	-1.0 ± 0.02	0.9 ± 0.2
$A_2 \langle r^2 \rangle$ (°K)	0 ± 10	10 ± 20
$A_4 \langle r^4 \rangle$ (°K)	-120 ± 30	52 ± 12

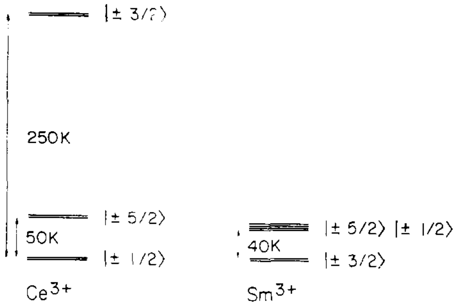

FIG. 7. Energy level diagram for the J ground states of Ce^{3+} and Sm^{3+} in $CeCo(CN)_6 \cdot 5H_2O$ and $SmCo(CN)_6 \cdot 4H_2O$, respectively, as deduced from susceptibility and specific heat measurements.

For a determination of the crystal-field parameters of the remaining rare-earth cobalticyanides we need both χ_z and χ_x measured on single crystals since three free parameters have to be determined. These parameters are of interest since they contain information about the charge distribution and thus the chemical bonds.

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