

## Magnetocrystalline anisotropy of $\text{SmCo}_5$ and its interpretation on a crystal-field model\*

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Results of magnetization measurements on carefully prepared single crystals of  $\text{SmCo}_5$  are presented over the temperature range 4–970 K. The contribution of the rare-earth sublattice magnetocrystalline anisotropy was evaluated using the data on  $\text{YCo}_5$  as “a blank.” These results are interpreted on the basis of a single-ion model. The following Hamiltonians were employed to obtain eigenvalues:  $\mathcal{H}$ (parallel to  $c$  axis) =  $\lambda \vec{L} \cdot \vec{S} + \mathcal{H}_{\text{CF}} + 2\mu_B S_z H_{\text{ex}}$ ,  $\mathcal{H}$ (perpendicular to  $c$  axis) =  $\lambda \vec{L} \cdot \vec{S} + \mathcal{H}_{\text{CF}} + 2\mu_B S_x H_{\text{ex}}$ .  $H_{\text{ex}}$  was regarded as arising mainly from the cobalt sublattice. Contributions arising from the multiplets  ${}^6H_{7/2}$  and  ${}^6H_{9/2}$  to the ground multiplet  ${}^6H_{5/2}$  were included. The crystal field was evaluated in terms of Racah’s tensor-operator technique employing  $3-j$  and  $6-j$  symbols. With the two sets of eigenvalues obtained from the above expressions, the anisotropy energy to rotate the magnetization direction from the axis to the plane was calculated and compared with experimental results on single crystals of  $\text{SmCo}_5$ . It is shown that the sign of the crystal-field parameter predicts the correct easy direction of magnetization and that the free-energy values calculated from 4 to 970 K are in reasonable agreement with experiment.

### INTRODUCTION

The large magnetocrystalline anisotropies, high Curie temperatures and high saturation moments at room temperature in the  $R\text{Co}_5$  systems ( $R$  = rare earth) have made some of them attractive candidates for permanent magnet applications.<sup>1</sup> All these properties can be derived from magnetization measurements on single crystals. During the last few years attempts have been made by several workers<sup>2–4</sup> to study the magnetic properties of  $R\text{Co}_5$  compounds. However, these experiments were performed on “pseudo single crystals” or were confined only to a limited temperature interval. This is obviously because of the difficulties entailed in preparing single crystals of  $R\text{Co}_5$  which have incongruent melting points.

In 1967 Hoffer and Strnat<sup>2</sup> measured the anisotropy constants of  $\text{YCo}_5$  single crystals. Tatsumoto *et al.*<sup>4</sup> reported the magnetocrystalline anisotropy constants by measuring the magnetization of single crystals of  $R\text{Co}_5$ . Their measurements, however, covered only a short temperature range. We have therefore made measurement of magnetization on single crystals of  $\text{SmCo}_5$  over a wider temperature range (4–970 K) and derived the anisotropy constants. Further, it was desirable to examine the general features of these systems in terms of the influence of the crystalline electric fields acting on the rare-earth sites. In a recent communication Greedan and Rao<sup>5</sup> have established the relationship between the basic parameters in crystal-field theory to the magnetocrystalline anisotropy in most of the rare-earth-cobalt intermetallic compounds. Their treatment, however, was confined to the cases where the ground manifold alone adequately de-

scribes the magnetic behavior of the rare-earth sublattice. They excluded a detailed analysis of the alloys of samarium in which the energy separation between the ground ( ${}^6H_{5/2}$ ) and first-excited ( ${}^6H_{7/2}$ ) multiplets of  $\text{Sm}^{3+}$  is only 1400 K and hence the influence of the excited terms has to be considered. In view of the wide application of  $\text{SmCo}_5$  as a permanent magnet, it was thought desirable to extend the earlier work to treat the special case of  $\text{Sm}^{3+}$ .

In this paper, results on the magnetization measurements on single crystals of  $\text{SmCo}_5$  in the hard direction are presented over the temperature range 4–970 K. Using these results the anisotropy constants have been evaluated as a function of temperature. The stabilization energy involved in orienting the system from parallel to perpendicular directions (with reference to the crystallographic  $c$  axis) has been evaluated for the samarium sublattice. The results of magnetic anisotropy associated with the samarium sublattice have been interpreted theoretically using a single-ion model. The samarium ions were regarded as subjected to the combined influence of the crystalline electric field and an effective exchange field. The influence of the three lowest  $J$  multiplets ( ${}^6H_{5/2}$ ,  ${}^6H_{7/2}$ ,  ${}^6H_{9/2}$ ) has been considered in performing these calculations.

### EXPERIMENTAL

The samples used in this study were obtained from the Battelle Columbus Laboratories.<sup>6</sup> The single crystallinity was verified by x-ray Laue diffraction on polished surfaces of the crystals and selected crystals were ground into spheres approx-

imately 2 mm in diameter. All magnetic measurements were made using a variable-temperature Princeton Applied Research vibrating-sample magnetometer.

#### Measurement of anisotropy constants

The magnetocrystalline anisotropy constants  $K_1$  and  $K_2$  in a hexagonal system are related to the anisotropy energy

$$E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta, \quad (1)$$

where  $\theta$  is the polar angle made by the magnetization vector with the  $c$  axis and  $E_a$  is the anisotropy energy. These constants may be evaluated accurately from a knowledge of the magnetization as a function of field at a given temperature. From the above expression the following relation may be established<sup>7</sup>:

$$\frac{H}{M_1} = \frac{2K_1}{M_s^2} + \left( \frac{4K_2}{M_s^4} \right) M_1^2, \quad (2)$$

where  $H$  is the applied field strength,  $M_1$  the magnetization along the direction perpendicular to the crystallographic  $c$  axis, and  $M_s$  the spontaneous magnetization.

In our experiments the magnetizations  $M_1$  (along the  $c$  axis) and  $M_s$  were measured at various field strengths from 0 to 19.3 kOe at constant temperature. A least-squares procedure was employed to fit the plot of  $H/M_1$  vs  $M_1^2$  to obtain a straight-line relationship. (Approximately 20 data points were used for this fit.) The magnetocrystalline anisotropy constants  $K_1$  and  $K_2$  were calculated from the intercept and slope, respectively, of the straight-line fit to the data at a fixed temperature. It may be noted that  $K_2$  is very small in comparison with  $K_1$ .

In Fig. 1 the anisotropy constant  $K_1$  of  $\text{SmCo}_5$  from 4 to  $\sim 970$  K is displayed and compared with those published by Benz and Martin<sup>3</sup> and Tatsumoto *et al.*<sup>4</sup> It is interesting to note that these values are sensitive to the purity (especially the oxide content) of the sample. For instance, the samples prepared by Tatsumoto *et al.* were grown by prolonged annealing of the button ingots, while in our study they were grown under more carefully controlled conditions. The details of the conditions of the growth of these crystals and experimental techniques are described elsewhere.<sup>6,8</sup>

#### GENERAL DESCRIPTION OF THE CALCULATIONS

The  $\text{Sm}^{3+}$  ion in  $\text{SmCo}_5$  is subjected simultaneously to a crystalline electric field and an exchange field. The general Hamiltonian may be written

$$\mathcal{H} = \lambda \vec{L} \cdot \vec{S} + \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{ex}}. \quad (3)$$

The first term represents the spin-orbit coupling, and the matrix elements are given by

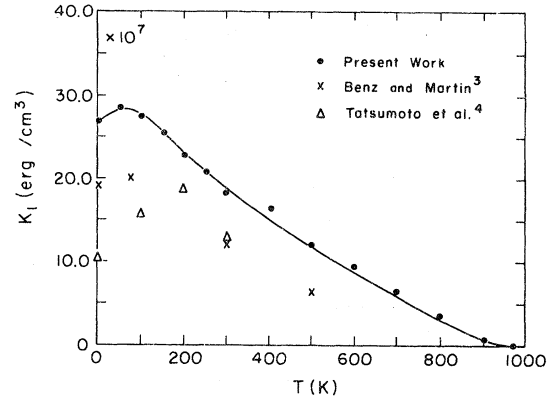


FIG. 1. Temperature dependence of the anisotropy constant  $K_1$  for  $\text{SmCo}_5$ .

$$\langle LSJM | \lambda \vec{L} \cdot \vec{S} | LSJM \rangle = \frac{1}{2} \lambda [J(J+1) - L(L+1) - S(S+1)], \quad (4)$$

where the symbols have their usual significance.

#### Crystal-field interaction

The second term in Eq. (3) describes the crystal-field Hamiltonian. Usually when one is dealing with only the ground multiplet, the operator equivalent technique is employed<sup>9</sup> to obtain the eigenvalues and the eigenfunctions. However, in the case of  $\text{Sm}^{3+}$ , the  ${}^6H_{7/2}$  and  ${}^6H_{9/2}$  multiplets lie only 1400 and 3200 K, respectively, above the ground multiplet.

Therefore, we employed the more general approach using the tensor-operator technique developed by Racah.<sup>10</sup> In this method the crystal-field interaction may be written<sup>11</sup>

$$\mathcal{H}_{\text{CF}} = \sum_{k,q} N_k^q A_k^q \langle r^{-k} \rangle U_q^k, \quad (5)$$

where  $N_k^q$  are the normalization factors tabulated by Weber and Bierig.<sup>11</sup>  $A_k^q$  are related to the strength of the crystal field.  $U_q^k$  are defined by

$$U_q^k = \left( \frac{4\pi}{2k+1} \right)^{1/2} Y_k^q. \quad (6)$$

The expression for the matrix elements of  $U_q^k$  can be written in terms of the 3- $j$  and 6- $j$  symbols as follows<sup>11</sup>:

$$\langle \alpha SLJ J_z | U_q^k | \alpha SLJ' J'_z \rangle = (-1)^{J_z + S + L} [(2J+1)(2J'+1)]^{1/2} \times \begin{pmatrix} J & k & J' \\ -J_z & q & J'_z \end{pmatrix} \begin{Bmatrix} L & J & S \\ J' & L & k \end{Bmatrix} \langle \alpha SL || U^k || \alpha SL \rangle, \quad (7)$$

where  $\alpha$  is used to describe the quantum states completely, the large parentheses represent the 3- $j$  symbol, the large curly parentheses represent the 6- $j$  symbol, and the last term is the reduced matrix element.

$\text{SmCo}_5$  has the  $\text{CaCu}_5$  structure in which the point symmetry at the rare-earth site is  $D_{6h}$ . Considering the relevant terms for the above symmetry, expression (5) may be written

$$\mathcal{H}_{\text{CF}} = N_2^0 A_2^0 \langle r^2 \rangle U_0^2 + N_4^0 A_4^0 \langle r^4 \rangle U_0^4 + N_6^0 A_6^0 \langle r^6 \rangle U_0^6 + N_6^6 A_6^6 \langle r^6 \rangle U_6^6, \quad (8)$$

Point-charge model calculations were performed to assess relative contributions of these terms in expression (8) based on the approximation used by Bleaney,<sup>12</sup> Rossat-Mignod and Yakinthos,<sup>13</sup> and Greedan and Rao.<sup>5</sup> Briefly, the calculations involve the effect of the six rare-earth neighbors in the plane of the reference atom and the two neighbors along the axis as shown in Fig. 2. Following the arguments given in the earlier works<sup>5,12,13</sup> the effect of the cobalt atoms was ignored. These calculations indicated that the second-order term is dominant compared to those of higher order. However, the latter were also retained in the actual calculations.

An explicit expression for  $A_k^q$  in the point-charge model is given by

$$A_k^q = (-1)^{q+1} (4\pi/2k+1) e^2 K_k^q \sum_i \frac{Z_i}{R_i^{k+1}} Y_k^{-q}(\theta_i, \varphi_i), \quad (9)$$

where  $Z_i$  and  $R_i$  are the charge and the distance to the  $i$ th ion in the environment of the reference rare-earth atom,  $K_k^q$  are constants tabulated elsewhere,<sup>1</sup>  $Y_k^q$  are the spherical harmonics, and  $\theta_i$  and  $\varphi_i$  are the polar angles for  $\vec{R}_i$ . The  $z$  axis is identified with the crystallographic  $c$  axis. Further, to account for the shielding of the  $4f$  electrons from the crystalline environment, additional factors of  $1 - \sigma_k$  were incorporated into expression (9). We used  $\sigma_2 \sim 0.5$ ,  $\sigma_4 \sim 0.1$  and  $\sigma_6 \sim 0.05$  as estimated by Burns.<sup>14</sup> This procedure yielded the values  $A_2^0 \langle r^2 \rangle = -420$  K,  $A_4^0 \langle r^4 \rangle = -25$  K,  $A_6^0 \langle r^6 \rangle = 1$  K, and  $A_6^6 \langle r^6 \rangle = 6$  K.

#### Estimation of exchange field

The third term in expression (3) describes the effect of the exchange field and may be written

$$f(J, M) = \left( \frac{(J+L+S+2)(-J+S+L)(J+S-L+1)(J+L-S+1)(J+M+1)(J-M+1)}{4(J+1)^2(2J+1)(2J+3)} \right)^{1/2}. \quad (13)$$

The value of  $H_{\text{ex}}$  was estimated from the temperature variation of the rare-earth sublattice magnetization in  $\text{RCO}_5$  compounds. The procedure is described in detail in the earlier paper.<sup>5</sup>  $H_{\text{ex}}$  thus obtained for  $\text{SmCo}_5$  is  $3 \times 10^6$  Oe near 0 K and corresponds to  $|H_{\text{ex}} \mu_B / k_B| \sim 200$  K.

At this point it is interesting to note that an alternate approach using the Curie temperatures of

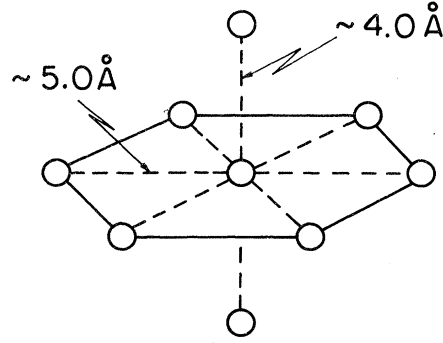


FIG. 2. Structure of  $\text{SmCo}_5$  showing only the nearest samarium neighbors of the reference rare-earth ion.

$$\mathcal{H}_{\text{ex}} = 2 \mu_B \vec{S} \cdot \vec{H}_{\text{ex}}, \quad (10)$$

where  $H_{\text{ex}}$  is the exchange field acting on the spin.<sup>15</sup>

We recognize that to a reasonable approximation the exchange field on the  $\text{Sm}^{3+}$  ion arises mainly from the Sm-Co exchange interaction.  $H_{\text{ex}}$  therefore may be considered proportional to the cobalt sublattice magnetization as pointed out by Buschow and van Stapele.<sup>16</sup>

When  $H_{\text{ex}}$  is along the  $c$  axis we have

$$\mathcal{H}_{\text{ex}} = 2 \mu_B S_z H_{\text{ex}}, \quad (11a)$$

and when  $H_{\text{ex}}$  is along the basal plane we can write

$$\mathcal{H}_{\text{ex}} = 2 \mu_B S_x H_{\text{ex}}. \quad (11b)$$

The relevant matrix elements for the two cases are<sup>17</sup>

$$\langle JM | S_z | JM \rangle = (g_J - 1)M, \quad (12a)$$

$$\langle JM | S_z | J+1, M \rangle = f(J, M), \quad (12b)$$

$$\langle JM | S_x | J, M+1 \rangle = \frac{1}{2}(g_J - 1)[(J-M)(J+M+1)]^{1/2}, \quad (12c)$$

$$\langle J+1, M \pm 1 | S_x | J, M \rangle = \mp f(J, M) \frac{1}{2} \sqrt{(J \pm M + 1)(J \pm M + 2) / (J + M + 1)(J - M + 1)}, \quad (12d)$$

where

$\text{RFe}_2$  and  $\text{RNi}_2$  compounds to estimate the effective exchange field has been described recently by de Wijn *et al.*<sup>18</sup> for the case of cubic  $\text{SmFe}_2$ . This procedure yields a value of  $|H_{\text{ex}} \mu_B / k_B| = 135$  K at low temperatures. Considering that the two estimates of  $H_{\text{ex}}$  at Sm sites are in two different systems it is reassuring to note that they are of comparable magnitude.

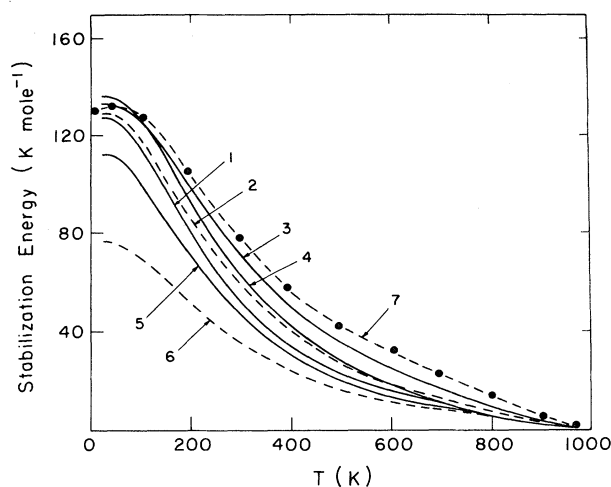


FIG. 3. Experimental (curve 7) and calculated curves of stabilization energy vs temperature. The parameters relating to the various curves are indicated in Table I.

#### Free-energy calculations

In this manner all the terms in the Hamiltonian (1) were evaluated to form the  $24 \times 24$  matrix using as the basis kets the  $|JM\rangle$  states of the  $J = \frac{5}{2}, \frac{7}{2},$  and  $\frac{9}{2}$  multiplets. This matrix was diagonalized separately for the two directions of the exchange field mentioned in Eqs. (11a) and (11b). In addition to the parameters obtained from the point-charge model, a variety of combinations of  $A_k^q$  and a few selected values of  $H_{ex}$  in the neighborhood of the estimated value mentioned earlier were tried. From the energy levels thus obtained, the Helmholtz free energy  $A = -RT \ln Q$ , where  $Q$  is the partition function, was calculated for the two orientations of the exchange field. For a chosen set of  $A_k^q$  and  $H_{ex}$ , the direction for which  $A$  is lower will be preferred by the samarium sublattice. At any temperature the difference between the free energies for the two orientations is the stabilization energy associated with the samarium sublattice. This has been calculated as a function of temperature from 4 to 970 K and is shown in Figs. 3 and 4.

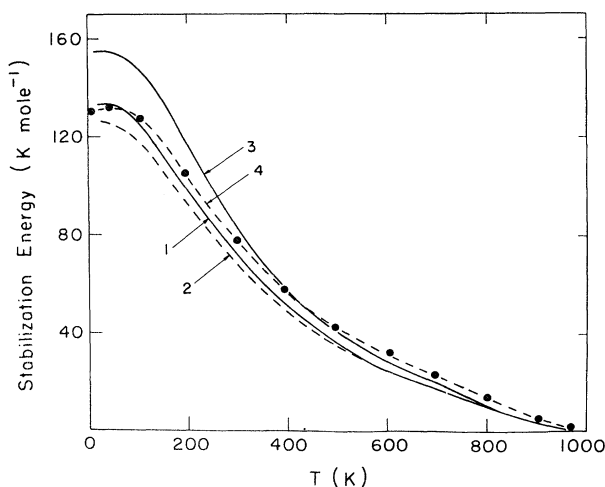


FIG. 4. Experimental (curve 4) and calculated curves of stabilization energy vs temperature. The parameters are listed in Table II.

#### RESULTS AND DISCUSSION

It is evident that the stabilization energy calculated by us may be related to the absolute sum of the anisotropy constants  $|K_1 + K_2|$ . To obtain  $K_1$  associated with the samarium sublattice alone, the values of  $K_1$  for  $\text{YCo}_5$  from the measurements of Tatsumoto *et al.*<sup>4</sup> and Klein and Menth<sup>19</sup> have been subtracted from the  $K_1$  obtained in the present study. As pointed out earlier,  $K_2$  is negligibly small in comparison to  $K_1$  for  $\text{SmCo}_5$ . From the values of  $K_1$  thus obtained, stabilization energy was calculated. These results are shown in Figs. 3 and 4 along with the theoretically calculated stabilization energy.

It is interesting to note that the stabilization energy evaluated using the  $A_k^q$  corresponding to the point-charge model predicts that the preferred direction of the samarium sublattice is along the  $c$  axis over the entire temperature range, in agreement with experiment. Further, the stabilization energy versus temperature curve calculated on the basis of this model is in reasonable agreement with

TABLE I. Crystal-field and exchange-field parameters relating to Fig. 3.

Curve No.	$A_2^0 \langle r^2 \rangle$	$A_4^0 \langle r^4 \rangle$	$A_6^0 \langle r^6 \rangle$	$A_6^6 \langle r^6 \rangle$	$H_{ex} \mu_B / k_B$ (°K)
1	-420	-25	1	6	180
2	-420	-25	1	6	200
3	-420	-25	1	6	240
4	-420	-50	1	6	200
5	-370	-25	1	6	180
6	-260	0	0	0	200
7	Experimental				

TABLE II. Crystal-field and exchange-field parameters relating to Fig. 4.

Curve No.	$A_2^0 \langle r^2 \rangle$	$A_4^0 \langle r^4 \rangle$	$A_6^0 \langle r^6 \rangle$	$A_6^6 \langle r^6 \rangle$	$H_{\text{ex}} \mu_B / k_B$ (°K)
1	-420	-25	1	6	240
2	-420	0	0	0	240
3	-420	-100	1	6	240
4	Experimental				

the experimental curve, as shown in Fig. 3. However, it may be pointed out that the close agreement may be somewhat fortuitous. Nevertheless, as pointed out earlier<sup>5</sup> there exist certain systematic trends in the directional preferences of magnetic moments in  $\text{RCO}_5$  and other related compounds in which the second-order crystal-field term is dominant. Calculations based on the point-charge model do indicate the dominance of the second-order term. An examination of the sign of the reduced matrix element  $\langle ||U^2|| \rangle$  in expression (7) reveals that when this term is negative, the moments prefer the  $c$  axis while when its sign is positive, at low temperatures, the moments are either tilted with respect to the  $c$  axis or more commonly lie in the basal plane.

Calculations performed with various combinations of  $A_k^q$  and  $H_{\text{ex}}$  indicate the following: The mag-

nitude of the stabilization energy is significantly affected by relatively moderate changes in  $A_2^0 \langle r^2 \rangle$  and  $H_{\text{ex}}$ . The sixth-order terms have the least effect while the effect of the fourth-order terms is more significant. These trends can be observed in Figs. 3 and 4. The parameters  $A_2^0 \langle r^2 \rangle = -420$  K,  $A_4^0 \langle r^4 \rangle = -25$  K,  $A_6^0 \langle r^6 \rangle = 1$  K,  $A_6^6 \langle r^6 \rangle = 6$  K, and  $H_{\text{ex}} \mu_B / k_B = 240$  K seem to offer the best fit with the experimental results. In conclusion it seems clear that the contribution of the samarium sublattice to the magnetic anisotropy of  $\text{SmCo}_5$  can be reasonably accounted for on a crystal-field-with-exchange-field model.

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