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An Analysis of the Rare Earth Contribution to the Magnetic Anisotropy in RCo_5 and R_2Co_{17} Compounds*

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An attempt has been made to treat the rare earth contribution to the magnetocrystalline anisotropy in RCo_5 and R_2Co_{17} compounds with a single ion model using a Hamiltonian of the form:

$$\mathscr{H} = B_2^0 O_2^0 + g\mu_B \mathbf{J}\cdot\mathbf{H}_{ex}$$

$\mathbf{H}_{ex}$ is regarded as arising mainly from the cobalt sublattice. Eigenvalues and eigenfunctions for the above Hamiltonian were obtained when the exchange field is perpendicular to the c-axis and compared with those when it is parallel to the c-axis. For values of H_{ex} estimated from experiment it is found that the sign of B_2^0 determines the direction preference of the rare earth sublattice magnetization. Comparison of theory with experiment shows that the correct sign of B_2^0 can be predicted on the point charge model considering only the effect of rare earth nearest neighbors. The calculations also predict that the quantity $|K_{1R}(0) + K_{2R}(0)|$ is nearly equal to the crystal field overall splitting (CFOAS) determined in the absence of exchange and is independent of the magnitude of the exchange field, provided that the exchange field is sufficiently large. The temperature dependence of $|K_{1R} + K_{2R}|$ has also been calculated and found to agree semiquantitatively with available experimental results.

Introduction

Compounds of the rare earth elements with cobalt constitute a comparatively new class of ferrimagnetic materials. The cobalt-rich compositions RCo_3, R_2Co_7, RCo_5, and R_2Co_{17}, where R is a lanthanide element, all crystallize with essentially hexagonal structures. The crystal chemistry of these materials is such that the structures of all of the other compounds can be derived from that of RCo_5 ($CaCu_5$) by systematic substitutions (*1*). It is well known that certain of these compounds have properties which make them attractive candidates for consideration as permanent magnet materials. In particular, the compositions RCo_5 and R_2Co_{17} are of interest because of their relatively high Curie temperatures (~1000 K), high room temperature saturation moments ($4\pi M_s \approx 10^4$ G), and, in certain cases, unusually large uniaxial magnetocrystalline anisotropies (*2*). For example, for YCo_5 and $SmCo_5$ room temperature values of K_1, the anisotropy constant, have been found to be $+5 \times 10^7$ erg cm^{-3} and $+13 \times 10^7$ erg cm^{-3}, respectively, which are among the highest yet reported (*3*, *4*).

It is found experimentally that the sign and magnitude of K_1, and hence the magnetic easy direction of the RCo_5 and R_2Co_{17} compounds, shows a strong and somewhat systematic dependence on the identity of the rare earth element. The existing information on the variation of the magnetic easy direction with temperature for the RCo_5 compounds is collected in Fig. 1. For YCo_5 and $CeCo_5$, in which the rare earth is nonmagnetic, an easy c-axis prevails throughout the temperature range from somewhat above room temperature to about 4 K. Among the compounds with a magnetic rare earth element, $SmCo_5$ maintains an easy axis but those with

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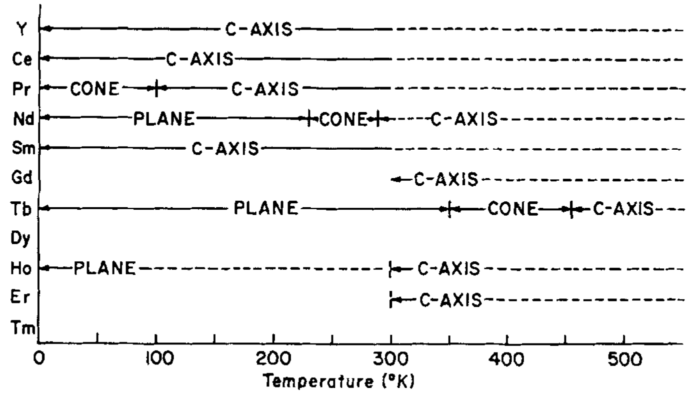

FIG. 1. Temperature dependence of the easy direction of magnetization for RCo_5 compounds. References used to compile this figure are (*3*), (*4*), (*5*) and (*6*).

Pr, Nd, Tb and Ho show a change from an easy axis to an easy plane (except for Pr, which has an easy cone) over some part of the temperature range. For $TbCo_5$ the easy plane exists even above room temperature.

Similar information for the R_2Co_{17} materials is available, mostly at room temperature, and is shown in Table I. In this case, those compounds with a nonmagnetic rare earth atom show an easy plane and among those with magnetic rare earth atoms only Sm, Er, Tm and Yb have an easy axis.

It seems clear then that the magnetocrystalline anisotropy of the RCo_5 and R_2Co_{17} compounds is determined by a contribution from the cobalt sublattice and by a contribution from the rare earth sublattice. In the RCo_5 case the cobalt sublattice favors large, positive values of K_1 and hence an easy axis. Its contribution to the anisotropy generally predominates at and above room temperature. The rare earth sublattice apparently favors an easy plane for Pr, Nd, Tb and Ho, but an easy axis for Sm. The crucial work of Tatsumoto et al. (*3*) on single crystals of $PrCo_5$, $SmCo_5$ and $NdCo_5$, and earlier work by Bartholin et al. (*6*) on oriented powders, show that the values for K_1 and K_2 contributed by the rare earth sublattice overwhelm the cobalt contribution at lower temperatures. In the case of the R_2Co_{17} compounds, K_1 for the cobalt sublattice is smaller by about an order of magnitude than in RCo_5 and negative, hence favoring an easy plane. (*4*) The rare earth sublattice anisotropy is apparently dominant, even at room temperature, and this is qualitatively manifest in an easy axis for Sm, Er, Tm and Yb.

TABLE I

EASY DIRECTION OF MAGNETIZATION FOR R_2Co_{17} COMPOUNDS AT ROOM TEMPERATURE

R	Easy direction	R	Easy direction
Y[a]	Plane (4, 7, 8)	Tb	Plane (9, 10)
Ce	Plane (7, 8)	Dr	Plane (9, 10)
Th	Plane (8)	Ho	Plane (9, 10)
Pr	Plane (7, 8)	Er	*c*-Axis (9, 10)
Nd	Plane (7, 8)	Tm	*c*-Axis (9, 10)
Sm	*c*-Axis (7)	Yb	*c*-Axis (10)
Gd	Plane (9, 10)	Lu	Plane (11)

[a] The easy plane for Y_2Co_{17} persists to 20 K.

In view of the important, sometimes dominant, role played by the rare earth sublattice anisotropy in RCo_5 and R_2Co_{17} compounds it seemed desirable to obtain a more detailed understanding of the factors which determine this contribution. To treat this problem we have adopted a modified single ion model. Support for such an approach is given by Tatsumoto et al. (*3*) who found that for $Y_xNd_{1-x}Co_5$ the anisotropy constants varied linearly with Nd-concentration. In our analysis, the rare earth ion is simultaneously subjected to a crystalline electric field and an effective exchange field. The details of this model are described below.

Description of the Method

We choose for our Hamiltonian the following:

$$\mathscr{H} = \sum_{n=0}^{\infty} \sum_{m=+n}^{-n} B_n^m O_n^m + g\mu_B \mathbf{J}\cdot\mathbf{H}_{ex}, \qquad (1)$$

where the first term on the RHS is a generalized formulation of the crystal field interaction and the second term represents the interaction of the rare earth moment with the exchange field.

Estimation of the Crystal Field Interaction

Let us first consider the crystal field part of the interaction. The O_n^m are the well-known Stevens operator equivalents and the B_n^m are coefficients, the sign and magnitude of which are determined by the environment of the rare earth site as well as by the ground state configuration of the RE^{3+} ion. The point symmetry at the rare earth site drastically limits the number of nonzero terms in the above expansion. We shall now discuss the point symmetries relevant to the $\mathrm{RCo_5}$ and $\mathrm{R_2Co_{17}}$ structures. All $\mathrm{RCo_5}$ compounds have the $\mathrm{CaCu_5}$ structure in which the point symmetry at the rare earth site is D_{6h}. The crystal field interaction for $\mathrm{RCo_5}$ compounds can then be described by:

$$(\mathrm{RCo_5})\mathscr{H}_{\mathrm{CF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6. \quad (2)$$

In the case of the $\mathrm{R_2Co_{17}}$ compounds two different structure types are exhibited. For R = Pr through Tb, the $\mathrm{Th_2Zn_{17}}$ structure exists and for R = Ho through Lu, the $\mathrm{Th_2Ni_{17}}$ structure is found (*12*). For R = Ce and Dy, both structures coexist (*12*). In the $\mathrm{Th_2Zn_{17}}$ structure type there is a single rare earth site with C_{3v} symmetry. For the $\mathrm{Th_2Ni_{17}}$ structure there are two rare earth sites of equal population and D_{3h} point symmetries. The appropriate Hamiltonians for the $\mathrm{Th_2Ni_{17}}$ and $\mathrm{Th_2Zn_{17}}$ structures are given by Eqs. (2) and (3), respectively.

$$(\mathrm{R_2Co_{17}})\mathscr{H}_{\mathrm{CF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6, \quad (3)$$

which differs from that for $\mathrm{RCo_5}$ only by inclusion of $B_4^3 O_4^3$ and $B_6^3 O_6^3$ terms. Bleaney (*16*), in his treatment of $\mathrm{RNi_5}$ compounds which are isostructural with $\mathrm{RCo_5}$, and Elliott (*20*), in his treatment of the hexagonal rare earth elements, have attempted to assess the relative contributions of each crystal field term using a point charge calculation and have concluded that the $B_2^0 O_2^0$ term is dominant. As a first order attempt and a working hypothesis we henceforth ignore all terms in the crystal field Hamiltonian except $B_2^0 O_2^0$. We shall reexamine this assumption at a later time.

Let us now examine the $B_2^0 O_2^0$ term more closely. The operator equivalent $O_2^0 = 3\tilde{J}_z^2 - J(J+1)$. The coefficient B_2^0 is the product of several factors as shown below (*13*):

$$B_2^0 = \alpha_J \langle r^2 \rangle (1 - \sigma_2) K_2^0 A_2^0,$$

α_J	the Stevens multiplicative factor which is listed for the various elements in Tables II to V
$\langle r^2 \rangle$	taken from the *H–F* calculations of Freeman and Watson (*14*)
σ_2	a constant which takes into account the shielding of the 4*f* wave functions from the environment by the outer, filled 5*s*, 5*p* shells. Burns (*15*) has estimated $\sigma_2 \sim 0.5$
K_2^0	a constant equal to $1/4\,(5/\pi)^{1/2}$
A_2^0	which is determined by the electrostatic potential due to the environment, is given in the point charge approximation by (*13*):

$$A_2^0 = (-1)^{+1} \frac{4\pi}{5} e^2 \sum_k \frac{Z_k}{R_k^3} Y_2^0(\theta_k)$$

Z_k, R_k	the charge and the distance to the *k*th ion in the environment of the reference rare earth atom
Y_2^0	the spherical harmonic given by $1/4\,(5/\pi)^{1/2}\,(3\cos^2\theta_k - 1)$, where θ_k is the angle between the $\mathbf{R}_k$ and the *Z* axis which we identify with the crystallographic *c*-axis.

A number of problems now arise in trying to determine A_2^0 within the point charge model. First it is difficult to assess the Z_k for the various surrounding ions. Secondly it is unclear how far from the reference ion one must go to evaluate the lattice sum. Both of these problems arise from the metallic nature of the systems under consideration. For example, the shielding of surrounding point charges by the conduction electrons is expected to increase very rapidly with distance. For this reason it is normally assumed that only nearest and next nearest neighbors contribute significantly to A_2^0. For purposes of obtaining an order of magnitude estimate of A_2^0 it is reasonable to assign a +3 charge to the rare earth ions, however, there exists considerable uncertainty regarding the effective charge on the transition metal atoms. Bleaney (*16*), in his treatment of crystal fields in $\mathrm{RNi_5}$, where the nickel atoms appear to have the nonmagnetic $3d^{10}$ configuration, has reasoned that a near zero charge resides on Ni. Rossat-Mignod and Yakinthos (*17*) have made a similar assumption in their treatment of the crystal field in $\mathrm{RNi_3}$, where nickel is also nonmagnetic. In the case of magnetic cobalt atoms in RCo_5 there are certainly holes in the d-band which might at first sight lead one to expect an effective positive charge on cobalt. However, this effect of removing d electrons may be substantially offset by the lower nuclear charge on cobalt than on nickel. Then, to an order of magnitude in A_2^0 it may be reasonable to assume that the effective Z_k at cobalt is not much different from that on nickel atoms in isostructural compounds, and that either is substantially smaller than the charge on the rare earth ions. Again we shall return to examine this assumption at an appropriate time in a following section.

In Fig. 2 is shown the crystal environment of the rare earth sites in RCo_5, and the two different R_2Co_{17} structures considering only the nearest and next nearest rare earth neighbors which all lie within a 5 Å radius from the central atom. For purposes of evaluating the contributions to A_2^0 it is convenient to recognize two types of neighbors—those which lie in the equatorial plane, usually next neighbors, and those which lie on the c-axis, usually nearest neighbors. A cursory examination of Y_2^0 shows the contribution to A_2^0 from the axial neighbors is negative, while that from equatorial neighbors is positive. Values of A_2^0 calculated on the point charge model are shown for each type of rare earth site in Tables II to V. Note that for $CaCu_5$, Th_2Zn_{17} and Th_2Ni_{17}(I) A_2^0 is negative while for Th_2Ni_{17}(II), the only site having no axial neighbors, it is positive.

Estimation of the Exchange Field

The exchange field at the rare earth ion can be considered to be composed of two contributions, the R–R exchange interaction and the R–Co exchange interaction. As the latter is by far the larger of the two for RCo_5 and R_2Co_{17} compounds, we shall neglect the R–R interaction. Information on the magnitude of the R–Co exchange can be obtained from experiment. Nowik and Wernick (*18*) from Mössbauer data have analyzed the temperature dependence of the Dy sublattice magnetization in $DyCo_5$ using a molecular field for the R–Co exchange interaction and obtain a value of $g\mu_B H_{ex}(0)/k = 142$ K, which yields $H_{ex} = 1570$ kOe. Using this value as a basis we can generate effective R–Co exchange fields for the remaining rare earth elements by assuming that $H_{ex} \sim (g-1)/gAM_{Co}$ as suggested by Buschow and Van Stapele (*19*) where A is nearly constant and M_{Co} is the cobalt magnetization which is also constant for RCo_5 and R_2Co_{17} compounds. The cobalt moment is not only constant from compound to compound but is also, due to the large Curie temperatures of these materials, essentially constant with temperature over the range of interest. The values of the exchange fields estimated on the manner described are listed in Tables II to V. Probably, values for H_{ex} determined in this manner are good only to 30%.

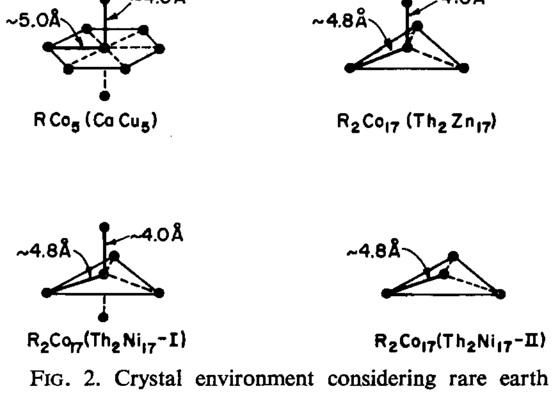

FIG. 2. Crystal environment considering rare earth nearest neighbors only for RCo_5 and R_2Co_{17} structures.

In order to determine the orientation preferred by the rare earth sublattice it seems necessary to take explicit account of the collinear ferrimagnetic structures of the RCo_5 and R_2Co_{17} materials. That is, we have calculated the energy of the rare earth system under the influence of the crystal field and the two physically important orientations of the exchange field as indicated in Eqs (4) and (5).

$$(a) \quad \mathscr{H} = B_2^0[3J_z^2 - J(J+1)] + g\mu_B J_z H_{ex}, \qquad (4)$$

$$(p) \quad \mathscr{H} = B_2^0[3J_z^2 - J(J+1)] + g\mu_B J_x H_{ex}. \qquad (5)$$

The Hamiltonian of (a) applies when the exchange field and hence the cobalt moment lie along the c-axis and that of (p) when the exchange field and hence the cobalt moment lie perpendicular to the c-axis. The procedure is then to obtain the eigenvectors and eigenenergies of the two Hamiltonians. One then compares energies of the ground states for the two cases. At 0 K, the rare earth system will be found in that state which has the lower energy. The preferred direction for the rare earth sublattice moment is determined by examination of this ground state eigenfunction.

We illustrate this procedure by the example of the Nd sublattice ($J = 9/2$) in $NdCo_5$. The Hamil-

TABLE II

RESULTS FOR RCo_5 COMPOUNDS–$CaCu_5$ STRUCTURE

R	$g\mu_B H_{ex}$(K)	$\alpha_J(\times 10^3)$	$A_2^0\langle r^2\rangle$(K)	B_2^0(K)	CFOAS (K)	Rare earth sublattice preferred direction		Stabilization energy (K)
						Theory	Expt	
Pr	84	−21.0	−1110	+4.5	215	Plane	Cone	180
Nd	115	−6.4	−1030	+1.3	82	Plane	Plane	80
Sm	—	+41.2	−970	−7.9	144	Axis	Axis	—
Tb	210	−10.1	−775	+1.4	160	Plane	Plane	150
Dy	140	−6.3	−745	+0.9	160	Plane		150
Ho	104	−2.1	−720	+0.3	55	Plane	Plane	45
Er	84	+2.69	−680	−0.4	70	Axis		65

tonian for case (a) is already in diagonal form and readily yields the following characteristics for the ground state, using the values of B_2^0 and H_{ex} in Table II:

$$E(a) = -456\,\mathrm{K},$$

$$|a\rangle = |-9/2\rangle.$$

The ground state wave function indicates that the Nd^{3+} moment is along the c-axis. The Hamiltonian for case (p) is clearly not in diagonal form as the J_x operator can admix states differing by $\Delta M = \pm 1$. Standard computer techniques were used to diagonalize this energy matrix and the following ground energy and eigenfunction were obtained for Nd^{3+} in $NdCo_5$:

$$E_g(p) = -547\,\mathrm{K}$$

$$\begin{aligned} |p\rangle = -.03[|-9/2\rangle - |+9/2\rangle] + {} & \\ & .11[|-7/2\rangle - |+7/2\rangle] \\ -.24[|-5/2\rangle - |+5/2\rangle] + {} & \\ & .40[|-3/2\rangle - |+3/2\rangle] \\ -.51[|-1/2\rangle - |+1/2\rangle]. & \end{aligned}$$

The energy of case (p) is clearly the lower of the two and by inspection of $|p\rangle$ it is clear that the rare earth moment lies in a direction perpendicular to the c-axis, i.e., in the basal plane. Moreover, the component of the moment in x direction is given by $g\mu_B \langle p|J_x|p\rangle$, which upon evaluation is found to be within 0.1 % of the maximum moment for Nd^{3+}. Therefore, the Nd^{3+} moment is indeed collinear with the cobalt moment. This nearly maximum value for the Nd^{3+} moment is a consequence of the fact that the influence of the exchange field is much greater than that of the crystal field. Nevertheless, it is the crystal field interaction which determines the direction preference of the rare earth sublattice.

Results and Discussion

The result of applying the above procedure to all four sites of interest is shown in the Tables II to V. It quickly becomes clear that the direction preference of rare earth sublattice is determined by the sign of B_2^0, which is in turn determined by the product of the signs of α_J and A_2^0. Indeed, as the sign for A_2^0 remains constant for a given site the variation in the sign of B_2^0 from element to element is determined by the variation in the sign of α_J from element to element. We have also carried out calculations using a wide variation of values for $|B_2^0|$, but holding constant the sign of B_2^0 and the magnitude of H_{ex}, and there is no change in the qualitative prediction concerning the rare earth direction preference.

In the final column of the tables we have tabulated values for a quantity which we call the stabilization energy. At 0 K this is simply $|E_{gr}(a) - E_{gr}(p)|$. The stabilization energy is a particularly useful quantity in those cases in which the rare earth direction preference is perpendicular to that of the cobalt sublattice.

This quantity can be very simply related to the single ion anisotropy constants of the rare earth atoms at 0 K, $K_{1R}(0)$ and $K_{2R}(0)$. The anisotropy energy of the rare earth system in a hexagonal crystal can be written in the usual manner as $E_A(0) = K_{1R}\sin^2\theta + K_{2R}\sin^4\theta$ where θ is the angle between the rare earth magnetic moment and the c-axis. Evaluating the expression for E_A with first the moment along the c-axis and then the moment in the plane and subtracting gives just the stabilization energy as we have defined it, which is:

$$E_{stab}(0) = |E_A(0°) - E_A(90°)| = |K_{1R}(0) + K_{2R}(0)|.$$

TABLE III

RESULTS FOR R_2Co_{17} COMPOUNDS–Th_2Zn_{17} STRUCTURE

						Rare earth sublattice preferred direction		
R	$g\mu_BH_{ex}$(K)	$\alpha_J(\times 10^3)$	$A_2^0\langle r^2\rangle$(K)	B_2^0(K)	CFOAS (K)	Theory	Expt	Stabilization energy (K)
Pr	84	−21.0	−325	+1.3	65	Plane	(Plane)	55
Nd	115	−6.4	−300	+0.40	25	Plane	(Plane)	20
Sm	—	+41.2	−280	−2.40	—	Axis	Axis	
Tb	210	−10.1	−225	+0.43	45	Plane	(Plane)	40

It should be emphasized that this stabilization energy is merely a parameter which permits a somewhat crude, but quantitative estimate of the relative stability of the rare earth sublattice in its preferred direction and does not take into account the anisotropy energy changes associated with the cobalt sublattice.

At this time it is pertinent to compare these predictions with the experimental results which are also listed in the tables. For the RCo_5 series (Table II), good agreement is seen with the available data, an exception being $PrCo_5$, which has only an easy cone at low temperatures (3). We also predict an easy plane for $DyCo_5$ and an easy axis for $ErCo_5$ at low temperatures but no experimental results exist. It should be noted here that we have not attempted detailed calculations for Sm^{3+} in either RCo_5 or R_2Co_{17} because of the complexities involved in accounting for the admixture of the $J = 7/2$ state into the $J = 5/2$ ground state due to the action of the exchange field. The values of α_J and B_2^0 given in Table II are those for the $J = 5/2$ manifold only. However, the previously mentioned strong correlation between the sign of B_2^0 and the rare earth easy direction permits a qualitative prediction in this case, which is in agreement with experiment.

For the R_2Co_{17} compounds, Table III [Th_2Zn_{17}-type], experimental information is rather inconclusive regarding the rare earth direction preference as the cobalt sublattice itself favors an easy plane which is also the theoretical rare earth preference for most of the elements which form this structure. Data at low temperatures are necessary in order to assess the extent of agreement with theory. However, we are able to predict that Sm_2Co_{17} will have an easy axis and we note that the room temperature data for the other compounds are not in variance with theory.

For the R_2Co_{17} compounds, Tables IV and V, of the Th_2Ni_{17}-type it is necessary to consider the two crystallographic sites separately.

For the Th_2Ni_{17}(I) sites, our predictions for the rare earth direction are in agreement with experiment at room temperature. However, for Th_2Ni_{17}(II) sites we find just the opposite. This ambiguity for the Th_2Ni_{17} structure-type compounds arises because of a difference in the sign of A_2^0 between the two sites. This difference in sign occurs because site (II) has no axial rare earth neighbors. However, the stabilization energies of the site (I) rare earth ions is greater than that of the site (II) ions. Since the strong

TABLE IV

RESULTS FOR R_2Co_{17} COMPOUNDS–Th_2Ni_{17} STRUCTURE (I)

						Rare earth sublattice preferred direction		
R	$g\mu_BH_{ex}$(K)	$\alpha_J(\times 10^3)$	$A_2^0\langle r^2\rangle$(K)	B_2^0(K)	CFOAS (K)	Theory	Expt	Stabilization energy (K)
Ho	104	−2.1	−1730	+0.70	130	Plane	(Plane)	125
Er	84	+2.69	−1690	−0.90	150	Axis	Axis	135
Tm	70	+10.1	−1575	−3.20	340	Axis	Axis	270
Yb	60	+31.8	−1520	−9.5	345	Axis	Axis	170

TABLE V

RESULTS FOR R_2Co_{17} COMPOUNDS–Th_2Ni_{17} STRUCTURE (II)

R	$g\mu_B H_{ex}$(K)	α_J($\times 10^3$)	$A_2^0\langle r^2\rangle$(K)	B_2^0(K)	CFOAS (K)	Rare earth sublattice preferred direction: Theory	Expt	Stabilization energy (K)
Ho	104	−2.1	+1315	−0.52	100	Axis	(Plane)	90
Er	84	+2.69	+1250	+0.65	110	Plane	Axis	100
Tm	70	+10.1	+1200	+2.4	260	Plane	Axis	220
Yb	60	+31.8	+1160	+7.2	260	Plane	Axis	145

exchange field constrains the rare earth moments on sites (I) and (II) to be collinear with the cobalt sublattice moments and hence with each other, the direction preference of the total rare earth moment will be determined by the net stabilization energy between sites (I) and (II). This net stabilization energy clearly favors the direction preference of the site (I) atoms. For the most part the greater stabilization energy of site (I) atoms is due to the greater crystal field at this site than at the other. The presence of axial neighbors at relatively short distances for site (I) and the lack of such neighbors at site (II) is responsible for the difference in magnitude.

We would like to point out an interesting aspect of the results, namely the close correspondence in most cases between the stabilization energies at 0 K and the crystal field overall splitting of the rare earth manifold (CFOAS), as is evident from Tables II to V. To understand this situation let us consider the case of Nd^{3+} in $NdCo_5$, which has been mentioned earlier. The influence of the crystal field alone is to split the $J = 9/2$ level into five doublets, the lowest state being $|\pm 1/2\rangle$ and the highest level $|\pm 9/2\rangle$. If one then applies an exchange field along the z direction the effect is to shift the energy of each state by an amount given by $M_J(g\mu_B H_{ex})$. If the exchange field is sufficiently large, the $|9/2\rangle$ state will be lowest. This is to be expected since this state has the largest component of moment in the direction of the field. On the other hand when an exchange field of equal magnitude is applied in the basal plane the resulting lowest state is derived largely from the $|\pm 1/2\rangle$ doublet, which was the lowest state according to the crystal field only scheme. Again, this can be understood by noting that the $|\pm 1/2\rangle$ doublet has the largest component of magnetic moment in the direction of the field. Thus the difference in energy between the ground state of the two cases in the limit of large exchange fields nearly corresponds to the energy separation of the two states before the exchange field was applied. This is just the CFOAS.

From a perusal of the results of our calculations it appears that the essential equality of CFOAS and E_{stab} holds down to a critical value of the quantity $2Jg\mu_B H_{ex}/\text{CFOAS} \approx 4$. This quantity is just the ratio of the total magnetic splitting (in the absence of CF) to the total crystal field splitting (in the absence of an exchange field). We note that small values of the ratio E_{stab}/CFOAS occur for Tm^{3+} and Yb^{3+} in the Th_2Ni_{17} structure type. For Tm^{3+} and Yb^{3+} the exchange fields are the lowest in the rare earth series due to small values of $(g-1)/g$ and the CFOAS are the greatest due to large values of α_J.

It is also pertinent to compare the predictions of the point charge model for $K_{1R}(0) + K_{2R}(0)$ with the few existing experimental results. Tatsumoto et al. (*3*) have determined values of $|K_{1R}(0) + K_{2R}(0)|$ for $NdCo_5$ and $PrCo_5$ to be 160 and 25 K, respectively. Comparing with our predictions from Table II of 82 and 215 K, respectively, we find fair agreement in the case of $NdCo_5$ but the point charge model prediction deviates from the experimental value by nearly an order of magnitude for $PrCo_5$.

Finally, we turn to a discussion of the temperature dependence of the stabilization energy. To do so we must take into account the population of excited states according to the Boltzmann distribution. We have computed in the usual manner for various temperatures up to about 600 K the thermal average of energy for the RE system for both orientations of the exchange field. The stabilization energy at a given temperature is then the difference between the thermal

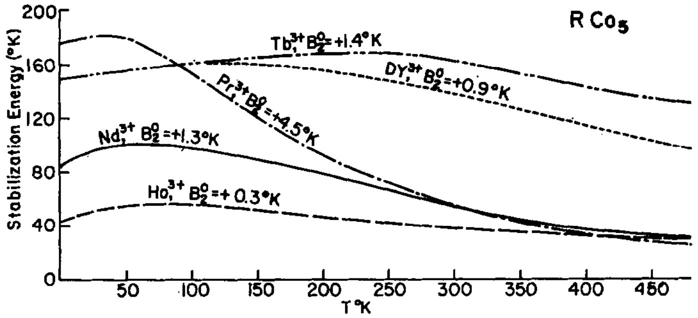

FIG. 3. Temperature dependence of the stabilization energy for various RCo_5 compounds.

averages $|\langle E(a)\rangle_{th} - \langle E(p)\rangle_{th}|$. Figure 3 shows the temperature dependence of the rare earth stabilization energy for the five RCo_5 compounds for which our calculations predict a change in easy direction as the temperature is lowered, from the cobalt-favored c-axis to the rare earth-favored basal plane. The large and weakly temperature dependent stabilization energies for Tb^{3+} and Dy^{3+} are immediately apparent and are in contrast to the relatively strong temperature dependence for Nd^{3+} and Pr^{3+}. If the cobalt anisotropy energy is assumed to be nearly constant within the RCo_5 series and also nearly constant with temperature within the range of interest (*3*) we then have a crude understanding of why the easy plane for $TbCo_5$ persists at a temperature which is substantially higher than that for other RCo_5 systems. Our results also predict that $DyCo_5$ should change to an easy plane in a temperature range similar to that for $TbCo_5$. It should be noted, again, that our calculation overestimates the relative stabilization energy for the easy plane in $PrCo_5$.

Turning to the case of the R_2Co_{17} compounds, Fig. 4 shows the temperature dependence of the net stabilization energy for those cases in which we predict a change in the easy direction from the cobalt-favored basal plane to the rare earth-favored c-axis. Unfortunately, data regarding the magnetic easy direction for these materials are available only at room temperature, and there are no data on anisotropy constants at any temperature. Our calculations predict that the easy axis will become manifest at lower temperatures for Yb_2Co_{17} than for Er_2Co_{17} and Tm_2Co_{17}.

Summary and Conclusions

Our predictions of the directional preference for the rare earth sublattice magnetic moment in RCo_5 and R_2Co_{17} compounds obtained by means of a simple model are in reasonable agreement with available experimental results. This model involves only two parameters, a dominant exchange field term and a smaller crystal field term. Values for the exchange field are estimated from experiment. Values for the crystal field part were obtained with the aid of some assumptions, the most crucial of which is that only the $B_2{}^0 O_2{}^0$ term is important in the

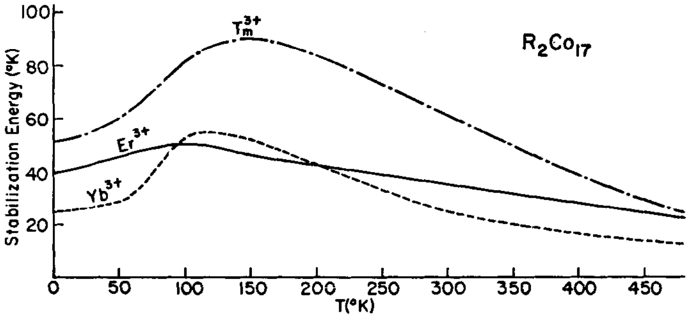

FIG. 4. Temperature dependence of the net stabilization energy for various R_2Co_{17} compounds with the Th_2Ni_{17} structure.

crystal field potential. We have also assumed that the simple, electrostatic point charge model can be used to determine B_2^0 to at least an order of magnitude and that in particular the sign and to a lesser extent the magnitude of B_2^0 are dominated by the rare earth near neighbors. We have explicitly tested these assumptions by first considering fourth order and sixth order contributions to the crystal field potential and have found them to have negligible influence on the results when evaluated in the point charge model. We have also considered the possible contribution to B_2^0 from the near neighbor cobalt atoms within the point charge model. If the effective charge on cobalt is assumed to be positive, the contribution from the cobalt atoms to B_2^0 opposes that due to the rare earth ions because the nearest neighbor cobalt atoms are located in the equatorial plane. Further, it is found that if the effective charge on cobalt is greater than about $+0.2e$ the resultant B_2^0 is dominated by the cobalt nearest neighbors and has a sign which is the opposite of that necessary to obtain agreement with experiment. Thus, the contributions from the effective charge (if positive) on the cobalt atoms seem to be small enough to be ignored, at least for the determination of the sign of B_2^0. Regarding the magnitude of the crystal field, we have performed calculations by varying $|B_2^0|$ by almost two orders of magnitude while holding H_{ex} constant and have also varied H_{ex} by about 40% holding $|B_2^0|$ constant. The general result is that the stabilization energy per rare earth atom is roughly equal to the CFOAS whenever the overall magnetic splitting, roughly $2g\mu_B J H_{ex}$, is greater than about four times the CFOAS but that the stabilization energy can be much smaller than the CFOAS whenever these two quantities are closer in magnitude.

Also we have calculated the temperature dependence of the sum of the single ion anisotropy constants $|K_{1R} + K_{2R}|$ as a function of temperature and can draw some general conclusions. In particular given our choice of values for B_2^0 and H_{ex} we find that the quantity $|K_{1R} + K_{2R}|$ is a relatively strong function of temperature for Pr^{3+}, Nd^{3+}, Tm^{3+}, and Yb^{3+} and a relatively weak function of temperature in the range studied for Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+}. This behavior appears to be directly related to the magnitude of the overall magnetic splitting which is relatively large for elements with large values of J and large exchange fields and relatively small for elements with smaller J and smaller exchange fields.

Finally, we believe that the approach adopted here represents a reasonable first effort directed toward the fuller understanding of the origins of the magnetocrystalline anisotropy in materials which are of great practical interest.

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References

1. D. Cromer and A. Larsen, *Acta Crystallogr.* **12**, 855 (1959).
2. J. J. Becker, *IEEE Trans. Magn.* **MAG-4**, 239 (1968); J. J. Becker, *J. Appl. Phys.* **41**, 1055 (1970).
3. E. Tatsumoto, T. Okamoto, H. Fujii, and C. Inoue, *J. Phys. (Paris)* **32**, Cl-550 (1971).
4. G. Hoffer and K. Strnat, *J. Appl. Phys.* **38**, 1377 (1967).
5. R. Lemaire, *Cobalt* **32**, 132 (1966).
6. H. Bartholin, B. VanLaar, R. Lemaire, and J. Schweizer, *J. Phys. Chem. Solids* **27**, 1287 (1966).
7. A. E. Ray and K. J. Strnat, *U.S. Air Force Rep.*, AFML-TR-71-210 Oct. 1971 p. 27.
8. H. J. Schaller, R. S. Craig, and W. E. Wallace, *J. Appl. Phys.* **43**, 3161 (1972).
9. K. J. Strnat, *AIP Conf. Proc., No. 5, Magnetism Magnetic Materials, 1971*, 1047 (1971).
10. J. E. Greedan, unpublished data.
11. F. Givord and R. Lemaire, *Solid State Commun.* **9**, 341 (1971).
12. W. Ostertag and K. J. Strnat, *Acta Crystallogr.* **21**, 560 (1966).
13. W. E. Wallace, "Rare Earth Intermetallic," Chap. 3, Academic Press, New York, in press.
14. A. J. Freeman and R. E. Watson, *Phys. Rev.* **127**, 2058 (1962).
15. G. Burns, *J. Chem. Phys.* **42**, 377 (1965).
16. B. Bleaney, *Proc. Phys. Soc.* **82**, 469 (1963).
17. J. Rossat-Mignod and J. Yakinthos, *Phys. Status Solidi (B)* **47**, 239 (1971).
18. I. Nowik and J. H. Wernick, *Phys. Rev.* **140**, 131A (1965).
19. K. H. J. Buschow and R. P. Van Stapele, *J. Appl. Phys.* **41**, 4066 (1970).
20. R. J. Elliott, *in* "Magnetism" (G. T. Rado and H. Suhl, Eds.), Vol. 2A, p. 404, Academic Press, New York (1965).