Individual Co site contributions to the magnetic anisotropy of $R\,Co_5$ compounds and related structures

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(Received 8 November 1978)

NMR results are used to evaluate the spin-orbit contribution to the magnetic anisotropy of Co atoms at individual Co sites in $R\,Co_5$ compounds. The easy c-axis Co anisotropy of $R\,Co_5$ compounds is found to arise from the $(2c)$ sites, while the $(3g)$ sites make a smaller opposing contribution. The anisotropy parameters of the individual sites are used to calculate the variation of anisotropy with composition in mixed $R(Co_{1-x}Fe_x)_5$ compounds and also to estimate anisotropy parameters at individual sites in some structures related to the $R\,Co_5$ phase.

I. INTRODUCTION

The rare-earth cobalt intermetallic compounds such as $R\,Co_5$ and R_2Co_{17} have attracted considerable attention in recent years because of the large magnetic anisotropy which these compounds possess. The work reported here is directed toward understanding the origin of this large anisotropy and is part of an ongoing effort in our laboratory to develop high-energy-product permanent magnet materials for use in advanced millimeter-wave/microwave systems.

Within the single-ion approximation the anisotropy can be divided into rare-earth and cobalt parts and by comparing related compounds the relative importance of the two contributions can be assessed. In $SmCo_5$, for example, the uniaxial anisotropy field is about 550 kG at 4.2 °K and arises from Co and Sm contributions each of which favor a c-axis alignment of the magnetization. In YCo_5, where the rare-earth-like Y atom has a closed shell and therefore makes no contribution to the anisotropy, the measured uniaxial anisotropy field is about 150 kG at 4.2 °K and is due entirely to the Co atoms. While the basic features of the rare-earth contribution to the anisotropy can be fairly well understood in terms of the crystal fields acting on the R atoms,[1] a detailed understanding of the large Co contribution of the anisotropy has been, to a large extent, lacking.

In an illuminating paper on the subject, Déportes et al.[2] pointed out that the large Co anisotropy might arise from the large orbital magnetic moments of the Co atoms which could provide an anisotropy mechanism through spin-orbit coupling. As shown in Fig. 1, there are two Co sites in the $R\,Co_5$ structure. Polarized neutron studies[3] show that the Co_I atoms at $(2c)$ sites have large orbital moments with the $3d$ orbitals and magnetization density extended in the basal

plane perpendicular to the hexagonal c axis. Consequently, because of this orbital anisotropy, these Co atoms would be expected to make the larger spin-orbit contribution to the magnetic anisotropy. The magnetization densities of Co_{II} atoms at $(3g)$ sites, by contrast, are found to be more isotropic and these atoms would be expected to make a smaller contribution to the magnetic anisotropy.

Recent Co NMR studies by this author[4] support this model and show the Co atoms at $(2c)$ sites to have a large positive anisotropy contribution (favoring an easy c-axis alignment of the Co moments). The Co atoms at $(3g)$ sites by contrast are found to have a smaller negative contribution (favoring an alignment of the moments in the basal plane).

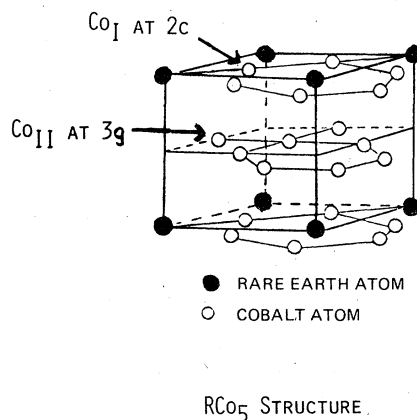Most of the Co sites in the other rare-earth cobalt compounds are related to the $(2c)$ and $(3g)$ sites of

● RARE EARTH ATOM
○ COBALT ATOM

RCo_5 STRUCTURE

FIG. 1. $R\,Co_5$ unit cell.

the $R\,Co_5$ compounds. Consequently, the quantitative evaluation of the anisotropy parameters of these sites and particularly the negative contribution from site ($3g$) has some interesting consequences in terms of understanding anisotropy in the related rare-earth cobalt compounds. The purpose of this paper is first to discuss in Sec. II the Co anisotropy in the $R\,Co_5$ compounds as determined[4] by NMR and then to show in subsequent sections how these results can be used to understand the anisotropy of related rare-earth cobalt structures.

II. Co ANISOTROPY IN THE $R\,Co_5$ COMPOUNDS

A. Spin-orbit contribution to the Co anisotropy

As already mentioned the spin-orbit coupling can provide an important contribution to the Co anisotropy in the $R\,Co_5$ compounds due to the large orbital moments. The spin-orbit coupling SO energy will be given by the usual expression

$$E_{SO} = \lambda \vec{L} \cdot \vec{S} = \tfrac{1}{2}\lambda\,(\vec{\mu}_L \cdot \vec{\mu}_S)\,(\mu_B)^{-2} . \tag{1}$$

Here $\vec{L}$ and $\vec{S}$ are the unquenched orbital and spin angular momentum vectors of the Co atom and the orbital and spin moments are given by

$$\vec{\mu}_L = -\vec{L}\,\mu_B, \text{ and } \vec{\mu}_S = -2\vec{S}\,\mu_B .$$

Since λ is negative for the $3d$ ions with more than half-filled shells, the spin moment will align itself parallel to the orbital moment. If, in addition, the $3d$ orbitals are anisotropic then the spin will tend to align along the direction of largest orbital moment in order to achieve the lowest energy. For example in the case of the ($2c$) site the spin will align itself along the hexagonal c axis because of the larger orbital moment along the c axis due to the extension of the Co orbitals in the basal plane (see Fig. 2). The situation is similar to that which occurs in the case of ferrites.[5]

We can define a stabilization energy or local anisotropy energy per atom E_s, where *positive* E_s favors a moment alignment along the hexagonal c axis, by the expression

$$E_s = E_{SO}(\perp) - E_{SO}(\|)$$

$$= \tfrac{1}{2}|\lambda|\Big[\langle\mu_L\rangle_\| \langle\mu_S\rangle_\| - \langle\mu_L\rangle_\perp \langle\mu_S\rangle_\perp\Big]\mu_B^{-2} . \tag{2}$$

Here $\langle\mu_L\rangle_\|$ or $\langle\mu_L\rangle_\perp$ refer to the expectation values of $\vec{\mu}_L$ measured with the moments aligned and quantized parallel or perpendicular to the hexagonal c axis, respectively. The corresponding spin quantities are similarly defined. If we define

$$\Delta\mu_L = (\langle\mu_L\rangle_\| - \langle\mu_L\rangle_\perp) , \tag{3}$$

then for the case where $\langle\mu_L\rangle$ is small (of the order

of $\Delta\mu_L$) and where

$$\Big[(\langle\mu_S\rangle_\| - \langle\mu_S\rangle_\perp)/\langle\mu_S\rangle_\|\Big] \ll 1 ,$$

Eq. (2) reduces to the simpler expression

$$E_s = \tfrac{1}{2}|\lambda|(\langle\mu_L\rangle_\| - \langle\mu_L\rangle_\perp)\,\langle\mu_S\rangle_\|\mu_B^{-2}$$

$$= \tfrac{1}{2}|\lambda|\left(\frac{\Delta\mu_L}{\mu_B}\right)\left(\frac{\langle\mu_S\rangle_\|}{\mu_B}\right) . \tag{4}$$

As was shown in a previous note,[4] NMR studies allow a rather direct way of determining the moment difference $\Delta\mu_L$ which is a measure of the anisotropy in the orbital angular momentum. The value of $\Delta\mu_L$ can then be used in Eq. (4) to determine E_s, the local spin-orbit anisotropy energy of a Co atom at a given Co site. In the following subsections we will discuss briefly hyperfine fields at the Co atom and show how the $\Delta\mu_L$ values can be extracted from the NMR data.

B. Hyperfine fields at the Co atom in $R\,Co_5$ compounds

As in the case of Co in pure Co metal, the Co hyperfine field has an isotropic part arising from core polarization, localized and delocalized conduction-electron polarizations and the isotropic part of the orbital hyperfine field. Also, there is an anisotropic component arising from the dipolar fields and the anisotropic component of the orbital hyperfine field.
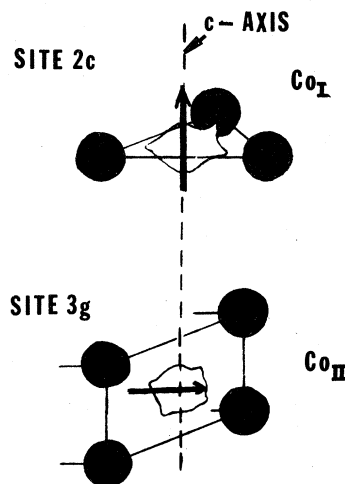

FIG. 2. Local environment around the two types of Co sites in the $R\,Co_5$ structure. The arrows indicate the symmetry axes established by the R neighbors.

From results in pure Co metal,[6] the major part of the anisotropic component should come from anisotropy in the orbital hyperfine field. The orbital hyperfine field is often expressed as[6]

$$H_L = \langle \mu_S \rangle (g - 2) \langle r^{-3} \rangle , \qquad (5)$$

here g is the Lande g factor. As already mentioned, for $3d$ atoms the unquenched orbital moment will add to the spin moment so that $g > 2$. Consequently, the *isotropic* orbital-hyperfine-field contribution is *positive* when referred to the direction of the total magnetic moment. Since we have

$$(g - 2) = \langle L \rangle / \langle S \rangle = 2 \langle \mu_L \rangle / \langle \mu_S \rangle , \qquad (6)$$

Eq. (5) can be written in the following equivalent form:

$$H_L = 2 \langle \mu_L \rangle \langle r^{-3} \rangle . \qquad (7a)$$

The anisotropic component of H_L is then given by

$$(H_\parallel - H_\perp)_L = 2(\Delta \mu_L) \langle r^{-3} \rangle , \qquad (7b)$$

where $H_\parallel$ and $H_\perp$ refer to the Co hyperfine field in a direction parallel and perpendicular to the hexagonal c axis.

C. Determination of $\Delta \mu_L$ from the hyperfine fields in YCo₅ and SmCo₅

Values of the Co hyperfine field at the two Co sites of SmCo₅ were obtained in our earlier paper[4] from the Co^{59} NMR spectrum. The spectrum from nuclei in domain walls allowed a determination of $H_\parallel$ and $H_\perp$ at the two sites. The values obtained are summarized in Table I. By comparing the NMR spectra of Co^{59} in SmCo₅ with that for Co^{59} in YCo₅ obtained by Searle *et al.*,[7] hyperfine field values could be estimated for YCo₅ as well and these are also included in the Table.

Zero-field NMR permits a determination of the magnitude but not the sign of the hyperfine field and in listing the hyperfine fields in Table I we assumed them to be negative. This should be a reasonable assumption as the core-polarization contribution which is negative and the delocalized conduction-electron contribution which is also negative should dominate the hyperfine field.

In Co metal the orbital contribution to the hyperfine field anisotropy is roughly a factor of three times larger than the dipolar one. Since in these compounds the orbital anisotropy is quite large relative to Co metal, it should be a good approximation to neglect the dipolar contribution compared to the orbital one. Then the measured values of $(H_\parallel - H_\perp)$ from Table I can be used in Eq. (7b) to calculate the values of $\Delta \mu_L$. Values of $\Delta \mu_L$ calculated this way are listed in Table I where we have taken $\langle r^{-3} \rangle$ to have a

value of 0.35×10^{26} cm^{-3} the same as in Co metal.[6] Corresponding values of E_s expressed in wave numbers obtained by using Eq. (4) with $|\lambda| = 300$ cm^{-1} and $\langle \mu_S \rangle_\parallel = 1.7$ μ_B are also listed.[8]

As can be seen from Table I, for site ($2c$) the quantity $\Delta \mu_L$ is positive indicating a larger orbital moment along the hexagonal c axis in agreement with the preceding discussion. For site ($3g$), by contrast, $\Delta \mu_L$ is negative indicating a larger orbital moment in a direction perpendicular to the c axis. The larger orbital moment along the perpendicular direction suggests an extension of the Co orbitals out toward the four neighboring R atoms as indicated in Fig. 2. Consequently, it appears that the different sign of the orbital anisotropy for the two Co sites arises from the different symmetry direction established by the plane of the neighboring R atoms.

We can make these arguments more quantitative by considering the electric field gradient (efg) at the Co site. Since the efg is a measure of the axial electric field at the site, it should be at least a crude measure of the axial character of the Co orbital charge and hence of the anisotropy.

We use a point-charge model which neglects the effects of the Co neighbors and assumes the rare-earth nearest neighbors to have a $+3$ charge. Then for site ($2c$) the efg arising from the three planar R neighbors (see Fig. 2) will have an axial component V_{zz} lying *along* the hexagonal c axis with a magnitude 0.62×10^{14} V/cm^2. For site ($3g$), V_{zz} arising from the four R neighbors will be directed *perpendicular* to the c axis and will have a magnitude 0.59×10^{14} V/cm^2. Consequently, the orientations, if not the precise magnitudes of the efg's correlate with the local anisotropies at the two sites.

D. Relation of the stabilization energy to the measured anisotropy

The anisotropy energy for a hexagonal system is just given by

$$E = K_1 \sin^2 \theta + K_2 \sin^4 \theta , \qquad (8)$$

where θ is the angle between the magnetic moment and the c axis. The difference $E_A = E_\perp - E_\parallel = K_1 + K_2$ can be identified with the stabilization energy per atom defined previously summed over all the different atoms. The total Co anisotropy energy E_A per unit cell is then given by

$$E_A(R Co_5) = 2E_s(2c) + 3E_s(3g) . \qquad (9)$$

Note that for the $R Co_5$ structure, one unit cell corresponds to one formula unit.

Using the values of E_s listed in Table I, the net Co anisotropy energy for YCo₅ can be calculated to be 27 cm^{-1} / formula unit (expressed in wave numbers) or about 6.4×10^7 ergs/cm^3. The measured[9] anisotropy

TABLE I. Values of Co hyperfine fields (parallel and perpendicular to the hexagonal c axis) for Co atoms at different sites of SmCo$_5$ and YCo$_5$. Values of $\Delta\mu_L$ and E_s at the different sites computed from Eqs. (7b) and (4) are also listed.

Compound	Site	$H_{\parallel}$ (kG)	$H_{\perp}$ (kG)	$(H_{\parallel}-H_{\perp})$ (kG)	$\Delta\mu_L$ (μ_B)	E_s cm^{-1}
SmCo$_5$	2c	−114	−176	+62	+0.095	+25
	3g	−159	−132	−27	−0.042	−10
YCo$_5$	2c	−99	−159	+60	+0.092	+24
	3g	−139	−121	−18	−0.028	−7

energy K_1 for YCo$_5$ is about 7.5×10^7 ergs/cm^3 and K_2 is thought to be relatively small compared to K_1. Consequently, it appears that the Co single-ion anisotropy can explain most of the anisotropy of the compound. In Secs. III−VI we extend the model to discuss anisotropy in several related rare-earth cobalt structures.

FIG. 3. Comparison of the anisotropy constant K_1 calculated for the R (Co$_{1-x}$Fe$_x$)$_5$ system with the experimental values of K_1 measured by Rothwarf et al. (Ref. 10) for the systems where R = Th or Y. In computing the calculated curve the values of E_s given in Table I for YCo$_5$ were used along with the site occupancy factors corresponding to the smoothed curves of Fig. 4 (see text).

III. MAGNETIC ANISOTROPY IN THE MIXED SYSTEM Y (Co$_{1-x}$Fe$_x$)$_5$

A knowledge of the anisotropy contribution from the individual Co sites is of particular interest for understanding the variation of anisotropy with composition in the mixed systems like Y (Co$_{1-x}$Fe$_x$)$_5$ where preferential site substitutions can occur.

The anisotropy constants (K_1) at room temperature as a function of composition for the compounds Th (Co$_{1-x}$Fe$_x$)$_5$ and Y (Co$_{1-x}$Fe$_x$)$_5$ have been measured by Rothwarf and coworkers[10] and are shown in Fig. 3. The anisotropy is relatively low near the Fe-rich end of the system so that the Fe anisotropy may not be very important in these systems. Assuming only the Co contributes to the anisotropy, we can express the anisotropy of the compound per unit cell by the following expression:

$$E_A = 2E_c(1-f_1) + 3E_g(1-f_2) . \tag{10}$$

Here in order to shorten the notation we have denoted the value of E_s for the $(2c)$ site of the RCo$_5$ compound by E_c and the value of E_s for the $(3g)$ site by E_g. The quantity f_1 is the fractional occupancy of the $(2c)$ site by Fe [the probability of an Fe atom occupying the $(2c)$ site] and f_2 is the corresponding fraction for the $(3g)$ site.

The values of f_1 have been determined for the Th (Co$_{1-x}$Fe$_x$)$_5$ system by neutron-diffraction measurements of Laforest and Shaw.[11] Since $2f_1 + 3f_2 = 5x$, f_2 is fixed by the value of f_1. Values of f_1 and f_2 obtained from the data of Ref. 11 are plotted in Fig. 4. We see that there is a partial preference of Fe for the $(3g)$ site at low concentrations of Fe as discussed in Ref. 11.

Using these site occupancy factors in Eq. (10) along with the previously determined values of E_c and E_g for YCo$_5$, we can evaluate E_A at each concentration of Fe and the results are shown in Fig. 3. The experimental and calculated values of K_1 cannot
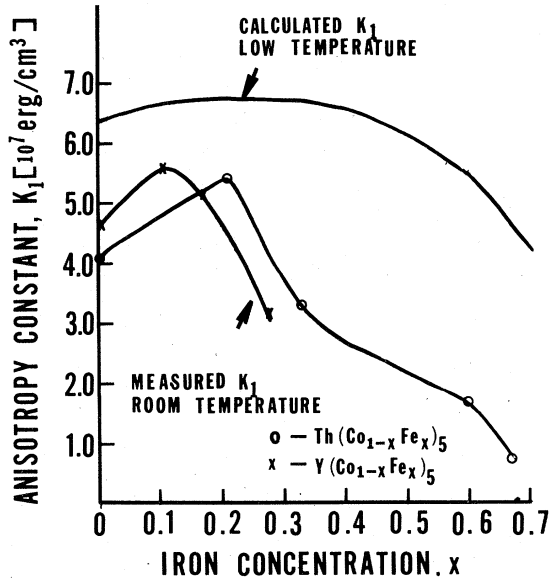
be compared directly because the calculated values are at low temperatures while the experimental values are at room temperature. Nevertheless, the variation of the calculated and measured K_1 with Fe concentration shows an overall similarity.

IV. COBALT ANISOTROPY IN THE R_2Co_{17} COMPOUNDS

A. Anisotropy of Y_2Co_{17}

The R_2Co_{17} structure is derived from the more basic RCo_5 structure by ordered substitutions of R atoms by pairs of Co atoms.[12] The unit cell of the rhombohedral R_2Co_{17} structure is shown in Fig. 5. In this section we try to estimate the anisotropy of the Co atoms at the different Co sites of Y_2Co_{17} by extending the YCo_5 results.

The $18f$ site of the rhombohedral R_2Co_{17} structure derives from the $2c$ site of RCo_5 by replacing one of the R neighbors by a pair of Co atoms. Also, distortions in the ideal structure move the Co_I atoms at these sites toward the substitutional Co pair. As discussed in Ref. 1, these factors should reduce the anisotropy associated with the Co_I atoms. In Table II we assign these atoms a stabilization energy αE_c where α should be less than unity because of the an-

TABLE II. Values of E_s for atoms at different Co sites of YCo_5 and Y_2Co_{17}. The numerical values in the last column expressed in wave numbers correspond to $\alpha = 0.5$ (see text).

Compound	Co Ions and Sites	E_s	E_s cm^{-1}
YCo_5	$Co_I(2c)$	E_c	24
	$Co_{II}(3g)$	E_g	-7
Y_2Co_{17} (rhombohedral)	$Co_I(18f)$	αE_c	12
($R\bar{3}m$)	$Co_{II}(18h)$	$(\frac{3}{4})E_g$	-5.2
	$Co_{III}(6c)$	E_d	-18
	$Co_{IV}(9d)$	$(\frac{1}{2})E_g$	-3.5

isotropy reduction.

The $18h$ and $9d$ sites of R_2Co_{17} derive from the $3g$ site of RCo_5 by replacing one or two of the R neighbors, respectively, by pairs of Co atoms. Using the crude point-charge model discussed in Sec. II we can assign the Co atoms at these sites stabilization energies of $\frac{3}{4}E_g$ and $\frac{1}{2}E_g$ in view of the reduction in R neighbors from 4 to 3 and from 4 to 2 in the two
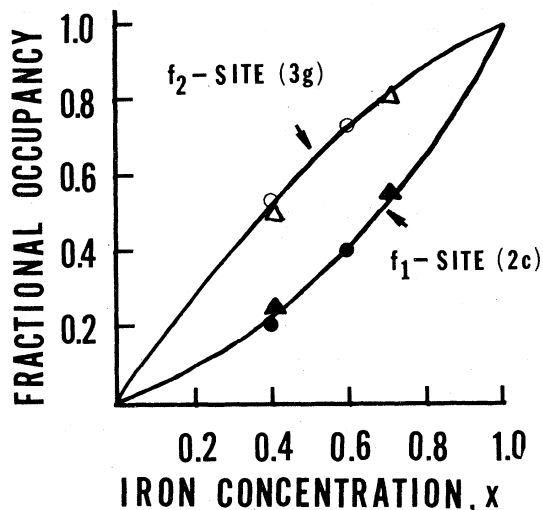

FIG. 4. f_1 the fractional occupancy of the $2c$ site by Fe and f_2 the fractional occupancy of the $3g$ site by Fe plotted as a function of iron concentration x in the compound Th $(Co_{1-x}Fe_x)_5$. The data is from Laforest and Shaw (Ref. 11). The triangles or circles correspond to two different heat treatments I and II described in their paper.
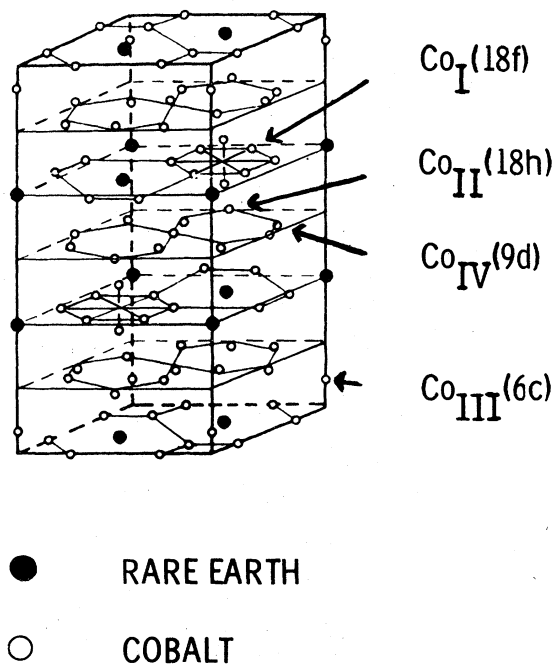

FIG. 5. Unit cell of the rhombohedral R_2Co_{17} structure.

cases. Finally, we leave the stabilization energy of
Co_{III} atoms which form a substitutional dumb-bell
pair in terms of an undetermined parameter E_d.

The total anisotropy energy per unit cell (of 3 for-
mula units) can then be written

$$E_A = 18\alpha E_c + 9(\tfrac{1}{2}E_g) + 18(\tfrac{3}{4}E_g) + 6E_d \ . \tag{11}$$

Assuming E_c and E_g to have the same value in
Y_2Co_{17} as in YCo_5, only E_d and α remain undeter-
mined. The measured E_A of the compound further
fixes these parameters.

For Y_2Co_{17} the measured[13] K_1 is about -0.55×10^7
ergs/cm^3. This corresponds to an anisotropy energy
E_A of about -20 cm^{-1}/unit cell. Using this value in
Eq. (11) and taking $E_d=0$ would give a value for α
of 0.25. Taking $\alpha=0.5$ would, however, give a value
for E_d of -18 cm^{-1}/atom. The latter set of parame-
ters are likely to be closer to the correct ones. First,
a value of α of about 0.5 is obtained using the point-
charge model discussed previously which assumed
the stabilization energy to be proportional to electric
field gradient at the site. Secondly, an unusually
large contribution to the anisotropy from Fe atoms
on the dumb-bell site is indicated by Mössbauer stu-
dies[14] which show a large hyperfine field anisotropy
for these atoms.

The sign of the hyperfine field anisotropy observed
in the Mössbauer studies[14] of Fe atoms on the
dumb-bell sites corresponds to a *more negative*
hyperfine field when the magnetization is parallel to
the c axis of the compound. From our previous con-
siderations then this corresponds to a negative or
planar anisotropy contribution. In view of this large
negative Fe-anisotropy contribution at the dumb-bell
site, a large negative Co anisotropy might be expect-
ed as well.

Finally, a rather large negative value of E_d can ex-
plain the variation of anisotropy with composition in
the mixed system $R_2(Co_{1-x}Fe_x)_{17}$ as has been point-
ed out by Gubbens *et al.*[15] and as will be discussed in
more detail in Sec. IV B.

For convenience we have summarized in Table II
numerical values of the stabilization energy for the
different sites based on a value of α of 0.5 and values
of E_c and E_g obtained previously for YCo_5.

B. Anisotropy in the mixed system $Y_2(Co_{1-x}Fe_x)_{17}$

The anisotropy in the system $Y_2(Co_{1-x}Fe_x)_{17}$ has
been measured by Perkins and Nagel[16] and by Per-
kins and Strässler[17] and shows an interesting variation
with composition. The measured anisotropy as a
function of x is shown in Fig. 6. In this section we
try to model the experimental variation by using the
anisotropy parameters obtained in Sec. III.

Generalizing Eq. (11), the Co anisotropy as a func-
tion of Fe concentration can be expressed

$$E_A = 18\alpha E_c(1-f_1) + 9(\tfrac{1}{2}E_g)(1-f_2)$$
$$+ 18(\tfrac{3}{4}E_g)(1-f_3) + 6E_d(1-f_4) \ , \tag{12}$$

here f_1, f_2, f_3 and f_4 are the Fe occupancy factors
for the sites 18f, 9d, 18h, and 6c, respectively. Since
the total number of Fe ions per unit cell is just 51x,
the following relation is obtained:

$$18f_1 + 9f_2 + 18f_3 + 6f_4 = 51x \ . \tag{13}$$

The occupancy factors f are not known very accu-
rately but neutron diffraction studies[18] indicate that
Fe atoms show a preference for the 6c (dumb-bell)
sites at low substitutions and also a relative prefer-
ence for the 9d and 18h sites over the 18f sites.
Mössbauer studies[15] also show a preference of Fe
atoms for the dumb-bell sites which is about 2.5
times the statistical one. This preference of Fe for
the dumb-bell site is further indicated by the NMR
studies of Inomata.[19]

As has been discussed qualitatively,[15] such a site
preference could explain the variation of anisotropy
with composition. We see from Table II that the Co_I
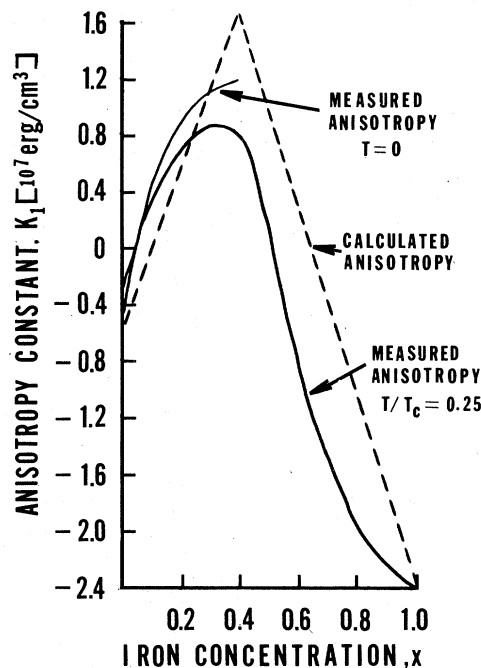atoms at 18f sites are the only ones with a positive

FIG. 6. Comparison of the anisotropy constant K_1 calculat-
ed for the $Y_2(Co_{1-x}Fe_x)_{17}$ system with the smoothed exper-
imental anisotropy constants measured at $T/T_C=0.25$ by
Perkins and Nagel (Ref. 16) and at $T=0$ by Perkins and
Strässler (Ref. 17). T_C is the Curie temperature.

anisotropy contribution. Consequently, preferential iron substitutions on the other sites should cause the anisotropy initially to go from negative to positive as is observed. Similar arguments have also been made by Inomata.[19]

In order to model the variation quantitatively, we have assumed reasonable values for the preferential substitution factors. We take f_4 to be $2.5x$ up to $x = 0.4$ at which point the site is filled and $f_4 = 1$ for $x > 0.4$. We assume a statistical substitution on $9d$ and $18h$ sites, that is $f_2 = f_3 = x$. The value of f_1 is then determined by Eq. (8) and will have a value less than x since the Fe atoms occupy the dumb-bell sites at the expense of the $18f$ sites.

Using these site occupancy factors and the aniso-tropy energies listed in the last column of Table II we have calculated the Co contribution to the anisotropy as a function of x for the $Y_2(Co_{1-x}Fe_x)_{17}$ system. We assume the net Fe anisotropy to vary linearly from zero up to the value of -2.4×10^7 erg/cm^3 found for the Y_2Fe_{17}-end member. The net calculated anisotro-py is shown in Fig. 6 and compares favorably with the experimental anisotropy variation suggesting the correctness of the anisotropy parameters obtained in Sec. III. While the assumption of a linear variation of the Fe anisotropy is rather artificial it seems to be a necessary one. In a more detailed model it would be necessary to assign anisotropy parameters to both Fe and Co atoms at the different sites.

V. ANISOTROPY IN $R\,Co_3$ and R_2Co_7 COMPOUNDS

Finally, we can consider the anisotropy in the $R\,Co_3$ and R_2Co_7 structures. The structures can be derived from the $R\,Co_5$ structure by replacing certain of the Co atoms by R atoms.[20] The $R\,Co_3$ structure is shown in Fig. 7. A model of the R_2Co_7 structure can be found in Ref. 21. Values of the stabilization energies can be estimated by comparing the environ-

ment of various sites with that of the basic sites in the $R\,Co_5$ compounds. The different types of Co sites in these structures are indicated in Table III.

The $3b$ site in these structures is surrounded by six R atoms, with three lying above the plane of the Co and three below. We assign this site a stabilization energy βE_c. A point-charge model which takes into account the neighboring R atoms and which assumes the stabilization energy to be proportional to the elec-tric field gradient would give a value for β of about 1.7. The $6c$ sites in these structures have the same environment as the $2c$ site of $R\,Co_5$ and we assign

TABLE III. Values of E_s for atoms at different Co sites of YCo_3 and Y_2Co_7 given in terms of the stabilization ener-gies E_c and E_g.

Compound	Co Ions and Sites	E_s
YCo_3	$Co_I(3b)$	βE_c
(rhombohedral)	$Co_{II}(6c)$	E_c
$(R\bar{3}m)$	$Co_{III}(18h)$	γE_g
Y_2Co_7	$Co_I(3b)$	βE_c
(rhombohedral)	$Co_{II}(6c)$	E_c
$(R\bar{3}m)$	$Co_{III}(6c)$	E_c
	$Co_{IV}(9e)$	E_g
	$Co_V(18h)$	γE_g

$Co_I(3b)$

$Co_{II}(6c)$
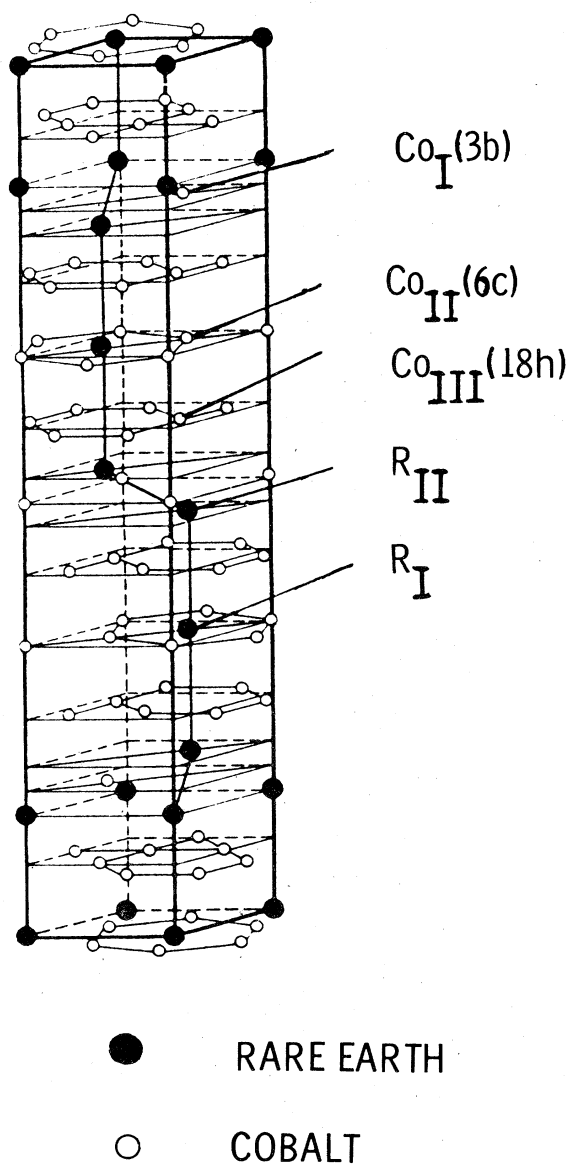
$Co_{III}(18h)$

R_{II}

R_I

● RARE EARTH

○ COBALT

FIG. 7. Rhombohedral $R\,Co_3$ crystal structure.

them an energy E_c. The $18h$ sites in the two structures have five R neighbors. With the exception of the fifth neighbor the environment is similar to that of the $3g$ site of $R\mathrm{Co}_5$. Consequently, we can assign this site an energy γE_g where γ might be expected to be of the order of unity. Finally, the $9e$ site has the same environment as the $3g$ site of $R\mathrm{Co}_5$ and we assign it an energy E_g. These assignments are summarized in Table III.

The anisotropy of the $R\mathrm{Co}_3$ and $R_2\mathrm{Co}_7$ compounds have not been measured in as much detail as for the $R_2\mathrm{Co}_{17}$ and $R\mathrm{Co}_5$ compounds. LuCo$_3$ like YCo$_3$ exhibits a high magnetocrystalline anisotropy[21] with the magnetization lying along the c axis at 20 °K. The anisotropy field is about 100 kG corresponding to a K_1 of about $+1.4 \times 10^7$ erg/cm^3. Since Lu has a filled $4f$ shell, all of the anisotropy originates from the Co atoms. This value of K_1 corresponds to an E_A of about $+38$ cm^{-1}/unit cell where one unit cell corresponds to nine formula units. Taking $\beta = 1.7$ would require a value for γ of about 1.8 in order for the calculated value of E_A to agree with the experimental one. The large value of γ may arise from the fact that the $18h$-site Co atom has two R neighbors which lie relatively close compared to the $3g$ site of the $R\mathrm{Co}_5$ structure.

Using these same values of β and γ, would give a Co-anisotropy energy per unit cell of about $+120$ cm^{-1} for the $R_2\mathrm{Co}_7$ structure. This corresponds to an anisotropy energy of about $+3.0 \times 10^7$ ergs/cm^3. Strnat and coworkers[22] have recently measured the anisotropy constants of some $R_2\mathrm{Co}_7$ compounds. For La$_2$Co$_7$ the anisotropy energy $K_1 + 2K_2$ is about $+3.5 \times 10^7$ erg/cm^3 while for Pr$_2$Co$_7$ the value is about $+3.7 \times 10^7$ ergs/cm^3. At least for these two

compounds the calculated Co anisotropy appears to be in good agreement with the measured anisotropy.

VI. SUMMARY

Most of the Co sites in the rare-earth cobalt compounds discussed here can be considered as modifications of the $2c$ and $3g$ sites of the $R\mathrm{Co}_5$ structure. Consequently, NMR determination of the anisotropy parameters for these sites allows one to estimate the parameters for the related sites in the other structures. Sites related to the $2c$ site of the $R\mathrm{Co}_5$ structure make positive contributions to the anisotropy while sites related to the $3g$ site make negative contributions. In order to explain the anisotropy of the $R_2\mathrm{Co}_{17}$ alloys a large additional negative contribution from the dumb-bell site appears to be needed.

The change in anisotropy with substitution of Fe for Co in these alloys appears to be due mainly to the preferential substitution of Fe on certain sites. For the $R\mathrm{Co}_3$ compounds, the positive and negative contributions to the anisotropy are more closely paired off than for the $R\mathrm{Co}_5$ alloys. Consequently, the variation of anisotropy with Fe concentration should be larger for these alloys. If the Fe substitution is similar to that in the $R\mathrm{Co}_5$ compounds, a marked increase in the uniaxial anisotropy should be observed with increasing Fe substitution.

Cobalt NMR studies in the $R_2\mathrm{Co}_{17}$, $R\mathrm{Co}_3$ and $R_2\mathrm{Co}_7$ compounds should allow a more precise determination of the Co anisotropy parameters and such studies are planned. Further Mössbauer studies might also be helpful for understanding the anisotropy contribution arising from individual Fe sites.

[1]J.E. Greedan and V.U.S. Rao, J. Solid State Chem. 6, 387 (1973).

[2]J. Deportes, D. Givord, J. Schweizer, and F. Tasset, IEEE Trans. Magn. 12, 1000 (1976).

[3]F. Tasset, Ph.D thesis (University of Grenoble, 1975) (unpublished).

[4]R.L. Streever, Phys. Lett. A 65, 360 (1978); Bull. Am. Phys. Soc. 23, 401 (1978).

[5]J. Smit, in Magnetic Properties of Materials, edited by J. Smit (McGraw-Hill, New York, 1971), p. 10.

[6]M. Kawakami, T. Hihara, Y. Koi, and T. Wakiyama, J. Phys. Soc. Jpn. 33, 1591 (1972).

[7]C.W. Searle, H.P. Kunkel, S. Kupca, and I. Maartense, Phys. Rev. B 15, 3305 (1977).

[8]The value of $|\lambda|$ used here is that obtained for hexagonal Co metal by N. Mori, T. Ukai, and H. Yoshida, J. Phys. Soc. Jpn. 37, 1272 (1974).

[9]W.G.D. Frederick and M. Hoch, IEEE Trans. Magn. 10, 733 (1974).

[10]F. Rothwarf, H.A. Leupold, J. Greedan, W.E. Wallace, and D.K. Das, Int. J. Magn. 4, 267 (1973).

[11]J. Laforest and J.S. Shah, IEEE Trans. Magn. 9, 217 (1973).

[12]G. Bouchet, J. Laforest, R. Lemaire, and J. Schweizer, C.R. Acad. Sci. Ser. B 262, 1227 (1966).

[13]G. Hoffer and K. Strnat, J. Appl. Phys. 38, 1377 (1967).

[14]P.C.M. Gubbens and K.H.J. Buschow, Phys. Status Solidi A 34, 729 (1976).

[15]P.C.M. Gubbens, A.M. van der Kraan, and K.H.J. Buschow, Solid State Commun. 19, 355 (1976).

[16]R.S. Perkins and H. Nagel, Physica (Utrecht) B 80, 143 (1975).

[17]R.S. Perkins and S. Strässler, Phys. Rev. B 15, 477 (1977).

[18]R.S. Perkins and P. Fischer, Solid State Commun. 20, 1031 (1976).

[19]K. Inomata, J. Phys. Soc. Jpn. 15, 821 (1976).

[20]R. Lemaire, Cobalt, 32, 132 (1966), and 33, 201 (1966); E.F. Bertant, R. Lemaire, and J. Schweizer, C.R. Acad. Sci. 260, 3595 (1965).

[21]F. Givord and R. Lemaire, Cobalt 50, 16 (1971).

[22]K.J. Strnat, A.E. Ray, and H.F. Mildrum, IEEE Trans. Magn. 13, 1323 (1977).