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Spin-polarized energy-band structure of YCo_5, $SmCo_5$, and $GdCo_5$

S. K. Malik*
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

F. J. Arlinghaus
Physics Department, General Motors Technical Center, Warren, Michigan 48090

W. E. Wallace
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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The spin-polarized electronic energy bands, densities of states, and magnetic moments of the intermetallic compounds YCo_5, $SmCo_5$, and $GdCo_5$ are calculated by a self-consistent augmented-plane-wave method. The results are similar in the three cases, with the computed magnetic moments in reasonable agreement with experiment. Only about one electron (of a possible three) is transferred from the rare earth to cobalt, leaving the minority-spin cobalt $3d$ band unfilled, and the moment high. There is evidence of d-d coupling between cobalt and the rare earth, providing information as to why experiments designed to reverse the antiparallel spin coupling between the two sublattices by manipulation of the electron concentration have been unsuccessful.

I. INTRODUCTION

Over the past few years a new class of magnetic materials has come into prominence—intermetallic compounds of the general formula RCo_5, where R is a rare-earth metal or yttrium.[1,2] These materials are ferromagnetic, with high Curie temperatures and remarkably large magnetocrystalline anisotropy.[3] They have great technical importance in the fabrication of permanent magnets. Magnets made from $SmCo_5$ have high coercivity and therefore have very considerable potential for use in the fabrication of electric motors.

One important property of these materials is not well understood. The coupling between the electron spins on the cobalt sublattice and those on the rare-earth sublattice is always antiferromagnetic (i.e., antiparallel). This prevents the heavier rare-earth homologs from being useful materials, the net moment being small. The persistence of this coupling scheme, moreover, cannot be understood in terms of the rather weak Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction; since the RKKY interaction is quite electron-concentration and structure sensitive, variations and exceptions would be expected. Numerous experimental attempts have been made to achieve reversal in coupling between rare-earth and transition-element moments, either by varying electron concentration or by structure changes, but none have been successful.[4] This paper addresses the fundamental electronic structure of RCo_5-type intermetallics through a study of their band structure. We calculate by a spin-polarized augmented-plane-wave (APW) technique the spin-up and spin-down electronic energy bands, the density of states and the magnetic moments of three representatives of their class of materials—YCo_5, $SmCo_5$, and $GdCo_5$.

Each of the three compounds studied exhibits a particular feature of interest. YCo_5 is the simplest to study because yttrium has no $4f$ electrons (configuration $4d^1 5s^2$). Since $4f$ levels are tightly bound core levels, they do not form energy bands; details of their electronic structure are due to their multiplet structure. They do not fit into the energy-band scheme, so their wave functions and charge densities are taken over from atomic calculations, and the number of occupied $4f$ levels is postulated *a priori*. Since YCo_5 has no $4f$ levels this problem for it does not arise, and a possible source of uncertainty is eliminated. YCo_5 is interesting for more fundamental reasons as well. Its existence as a typical RCo_5 material with large moment implies that $4f$ electrons are not the only source of the magnetic moment, as will prove to be the case. Of course, yttrium has many properties in common with the rare earths. Its outer electron configuration is $4d^1 5s^2$ compared to the usual $5d^1 6s^2$ of the rare earths, and its size is comparable.

We study $SmCo_5$ because it is a typical light rare-earth homolog, with large moment, as well as because it has by far the greatest technical interest. One of us (F.J.A.) has, in fact, previously calculated[5] the spin-polarized band structure of $SmCo_5$. We repeat that work here in order to have all three compounds treated exactly alike for comparison purposes. We believe further that the present work is more accurate and reliable; the results are better converged, and the $SmCo_5$ portion completely supersedes the older work.

Last, we study $GdCo_5$ as a typical heavy rare earth homolog, with a small total moment. The half-filled $4f^7$ shell of gadolinium contributes a large spin moment opposed to that of the cobalt. $GdCo_5$ is preferred to heavier homologs because the $4f^7$ shell is spherical; the APW technique spherically averages the charge density and is thus less reliable in the case of strongly aspherical charge distributions. Furthermore, the compounds with the heavier rare earths do not have the exact stoichiometric composition RCo_5 but contain excess cobalt; this would cloud any comparison of theory and experiment.

II. DETAILS OF THE CALCULATION

All three compounds exhibit the $CaCu_5$ structure. This structure is hexagonal, with one rare-earth and five cobalt atoms per unit cell, and has the space group D_{6h}^1; the Brillouin zone is the hexagonal prism shown in Fig. 1. The primitive direct-lattice vectors are given by

$$\vec{t}_1 = a\vec{i}, \quad \vec{t}_2 = -\tfrac{1}{2}a\vec{i} + \tfrac{1}{2}a\sqrt{3}\,\vec{j}, \quad \vec{t}_3 = c\vec{k},$$

and the reciprocal-lattice vectors are given by

$$\vec{b}_1 = \frac{2\pi}{a}\vec{i} + \frac{2\pi}{a\sqrt{3}}\vec{j}, \quad \vec{b}_2 = \frac{4\pi}{a\sqrt{3}}\vec{j}, \quad \vec{b}_3 = \frac{2\pi}{c}\vec{k}.$$

The lattice constants are given in Table I.

The APW method uses a crystal potential which is spherical within nonoverlapping spheres centered on each atom in the unit cell, and constant in the remaining region outside the spheres. The cobalt sphere radius was chosen to be half the Co-Co nearest-neighbor distance in each case; the R sphere radius was chosen to be equal to the Co-R nearest-neighbor distance minus the cobalt radius.

The starting trial potential in each case was derived by superposition of free-atom charge densities as computed from a spin-polarized (different orbitals for different spin) modification of the Herman-Skillman atomic structure program.[6] The cobalt configuration used was

$$\text{Co: } 3d{\uparrow}^3\, 3d{\downarrow}^5\, 4s{\uparrow}^{0.5}\, 4s{\downarrow}^{0.5},$$

and the rare-earth configurations were

$$\text{Y: } 4d{\uparrow}^{0.5}\, 4d{\downarrow}^{0.5}\, 5s{\uparrow}^1\, 5s{\downarrow}^1,$$

$$\text{Sm: } 4f{\uparrow}^5\, 5d{\uparrow}^{0.5}\, 5d{\downarrow}^{0.5}\, 6s{\uparrow}^1\, 6s{\downarrow}^1,$$

$$\text{Gd: } 4f{\uparrow}^7\, 5d{\uparrow}^{0.5}\, 5d{\downarrow}^{0.5}\, 6s{\uparrow}^1\, 6s{\downarrow}^1.$$

Results are not sensitive to the starting configuration, but a reasonable choice speeds convergence. An exchange potential of the Slater $X\alpha$ type[7] is used, with the exchange for each spin given by

$$V_x^s = 6\alpha(3\rho_s/4\pi)^{1/3}.$$

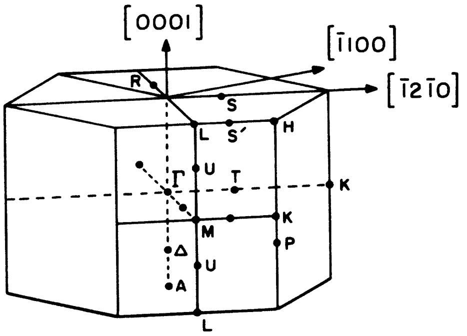

FIG. 1. Brillouin zone for $CaCu_5$ structure.

Preliminary calculations suggested that $\alpha = 1$ is the most reasonable choice, and all the results shown here use it.

The calculation presented here is a self-consistent, spin-polarized APW technique, in which the results of one iteration are used to modify the trial potential and the new potential used to repeat the process until initial and final potentials agree. In addition, spin-up and spin-down electrons see different potentials. The electrostatic part of the potential is the same for both, but the exchange part depends on the density of occupied states of that spin. The potential affects the occupied states and they in turn affect the potential, thus, another self-consistency requirement is imposed: that the magnetic moment (which is the net difference between occupied spin-up and spin-down states) has a stable value.

For simplicity we ignore the fact that the cobalt atoms occupy two crystallographically distinct sites and assume all cobalt potentials are the same. In each iteration the energy bands for each spin direction were computed at a number of points in the Brillouin zone—eight for the first few iterations and then 144 for the remainder. At the end of one pass, the eigenvectors for each state are used to compute the corresponding charge densities. The Fermi energy is determined simply

TABLE I. Lattice constants, number of iterations to achieve self-consistency, and the resulting spin moments for YCo_5, $SmCo_5$, and $GdCo_5$.

	a (Å)	c (Å)	Number of iterations	Spin moment
YCo_5	4.928	3.992	30	$7.31\mu_B$
$SmCo_5$	4.989	3.981	23	$6.49\mu_B$
$GdCo_5$	4.976	3.973	23	$6.49\mu_B$

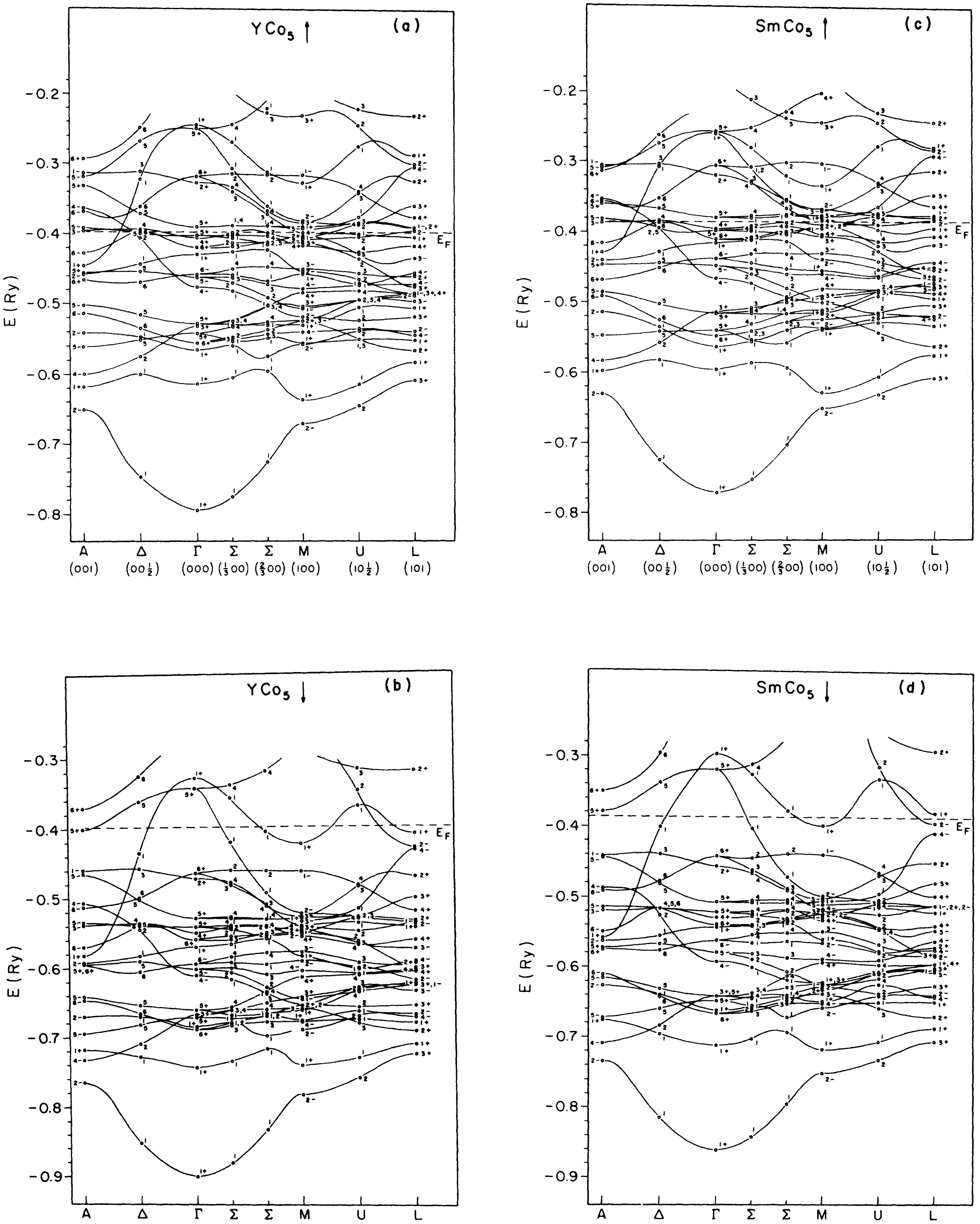

FIG. 2. (a) Energy bands for YCo_5, spin up (↑); (b) energy bands for YCo_5, spin down (↓); (c) energy bands for $SmCo_5$, spin up (↑); (d) energy bands for $SmCo_5$, spin down (↓); (e) energy bands for $GdCo_5$, spin up (↑); (f) energy bands for $GdCo_5$, spin down (↓).

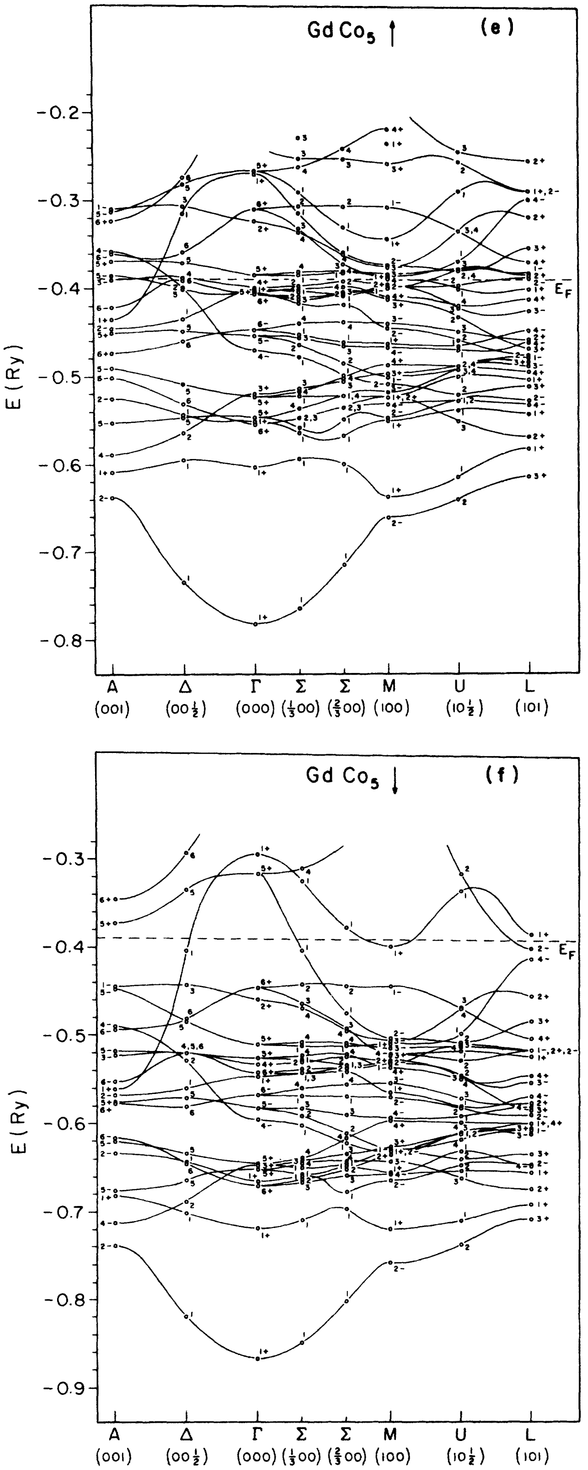

Figure 2 (*continued*)

by counting states; the states of either spin being occupied up to a common Fermi level. The total charge density is then found as a sum of that for all occupied states plus a constant core charge density which was found at the outset from the Herman-Skillman atomic calculation. At this point one iteration is complete. In principle, one may now solve Poisson's equation using this total charge density to derive a potential, which for consistency ought to be the same as the starting potential, from which the charge density has just been computed. In fact, this will not be so; we must use this final potential as starting potential for a new iteration and repeat the process until self-consistency is achieved.

This straightforward process is very unstable and will fail to converge. To achieve stability (never guaranteed), we first average new and old charge densities, the usual choice being 0.75 times the old charge density plus 0.25 times the new. Where instability threatens (usually evident as oscillation of the results from iteration to iteration), we used 0.85 times the old plus 0.15 times the new, achieving stability at the price of slow approach to convergence. The averaged charge- density is now used in Poisson's equation, and the potential thus derived used in a new iteration. Along with convergence of the potential, we require convergence of the band energies and of the magnetic moment. The moment is the most sensitive, so we will use it as an indicator in the discussion of results; in all cases other convergence criteria were also checked and follow the same trend.

III. RESULTS AND DISCUSSION

The converged energy bands for YCo_5, $SmCo_5$, and $GdCo_5$ are presented in Fig. 2, and the corresponding density of states curves are presented in Fig. 3. The YCo_5 results required 30 iterations, while $GdCo_5$ and $SmCo_5$ required 23 each. Perhaps the most striking result is the similarity of all three sets of results. The following comments apply to all.

The width of the cobalt $3d$ band complex is ~4 eV in each case, for both spin up and spin down. The spin-up and spin-down density-of-states curves are very similar in shape; the results might be approximated by a rigid shift or "exchange splitting" of about 1.6 eV. This $3d$-band complex lies in the middle of a typical parabolic s-p band. No other obvious feature can be identified; in particular, no rare-earth band stands out separately. The rare-earth contribution is found hybridized into the cobalt bands, and because there are 45 cobalt electrons to only three rare-earth electrons, the rare earth dominates nowhere . Examination of the separate contributions to the charge density shows a rare-earth contribution almost everywhere, however, and this is important in the aggregate. In

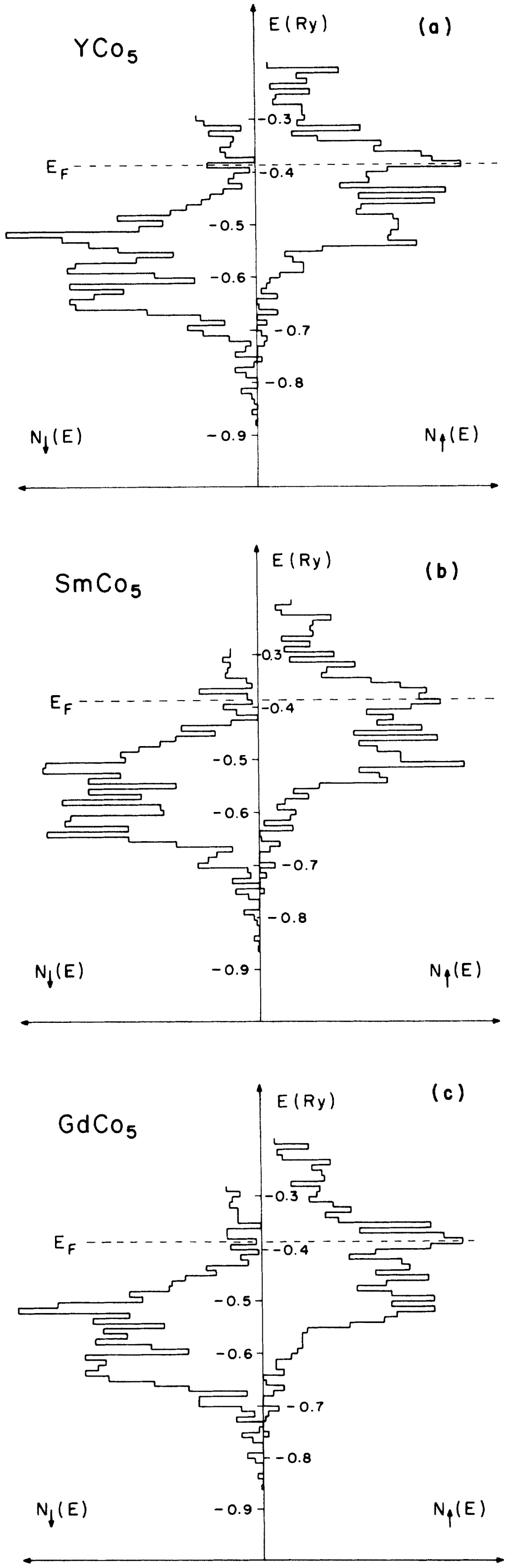

FIG. 3. (a) Density of states for YCo_5; (b) density of states for $SmCo_5$; (c) density of states for $GdCo_5$.

all three cases the energy-band curves reveal a completely filled majority-spin 3*d* subband. The Fermi energy falls in a region of very-low down-spin density of states, though also at a peak in the minority-spin density.

The calculated spin magnetic moments are $7.31\mu_B$ for YCo_5, $6.49\mu_B$ for $SmCo_5$, and $6.49\mu_B$ for $GdCo_5$. To compare these with experimental values we must add contributions for orbital moment and for localized 4*f* moment. Reck and Fry[8] show that cobalt metal has an extra magnetic moment (due to unquenched orbital angular momentum) of $0.147\mu_B$. According to recent polarized neutron scattering measurements[9] on single crystals, YCo_5 has a total orbital moment of $1.746\mu_B$. The band structures of all three compounds (YCo_5, $SmCo_5$, and $GdCo_5$) are quite similar, with their behavior dominated by the 3*d*-band complex. It is therefore reasonable to estimate the orbital moments of all three at this same $1.746\mu_B$ value. Adding this number to the spin moments, we get $9.06\mu_B$ for YCo_5, $8.24\mu_B$ for $SmCo_5$, and $8.24\mu_B$ for $GdCo_5$.

There are no 4*f* electrons on an yttrium atom, but gadolinium has the maximum seven unpaired 4*f* electrons in a half-filled shell, giving a 4*f* moment of $7.0\mu_B$, which is not affected by the crystal fields. The magnetic moment of a free Sm^{3+} ion is $0.71\mu_B$. However, it has been shown that the crystal-field interaction considerably influences[10,11] the magnetic moment of the Sm^{3+} ion, and because of the strong J admixture, the Sm^{3+} ion, for some crystal-field strengths, may behave effectively like an $(L+S)$ ion rather than an $(L-S)$ ion. This shows up in the coupling of the samarium and transition-element moments; the rare-earth moment couples antiparallel to the transistion-element moment for $(L+S)$ ions (Gd and above in the Periodic Table), while it couples parallel for $(L-S)$ ions (below Gd in the Periodic Table). Recent calculations[12] of the magnetic moment of Sm^{3+} ion in $SmCo_5$ using the crystal-field parameters[13, 14] which successfully explain the magnetocrystalline anisotropy behavior of $SmCo_5$, yield a value of about $0.4\mu_B$ which couples parallel to the cobalt moment. Thus, taking into account the 4*f* moment, we obtain $1.24\mu_B$ as the total moment of $GdCo_5$, $8.64\mu_B$ that of $SmCo_5$, while the magnetic moment of YCo_5 remains $9.06\mu_B$. These numbers compare well with the experimental values[13, 15, 16] of 8.1 for YCo_5 (neutron diffraction measurements[9] on single crystal YCo_5 yield 8.7 for the same), 8.9 for $SmCo_5$ and 1.2 for $GdCo_5$. We see, therefore, that the spin-polarized APW technique is capable of giving reliable answers for magnetic moments, even in such a complex structure as this.

A more difficult question is whether trends in the band structure are predictable as a function of the rare-earth component involved. In the present case, we have seen that the three band structures are essentially the same. It is hard to be sure that the small differences observed are not random, but an apparent trend is discernible. For discussion purposes, it is best to concentrate on the $3d$-band spin moments (i.e., the part actually calculated) which were $7.3\mu_B$ for YCo_5, $6.5\mu_B$ for $SmCo_5$, and $6.5\mu_B$ for $GdCo_5$.

The trend is, in fact, more regular than these numbers suggest. Careful study of the band curves shows a band moving relative to the Fermi level as we go from Y to Sm to Gd. This is obvious in looking at the respective spin-down bands near the Fermi level. The state A^{5+} is just barely occupied in YCo_5 (0.003 Ry below E_F), just unoccupied in $SmCo_5$ (0.007 Ry above E_F) and higher still in $GdCo_5$ (0.017 Ry above E_F). Similarly the state L^{1+} is 0.01 Ry below E_F in YCo_5, 0.007 above in $SmCo_5$, and 0.009 above in $GdCo_5$. The fact that these states pass above E_F as we go from Y to Sm causes the drop in magnetic moment, while the further rise of these states in going from Sm to Gd causes no further change in occupation of states.

We see, further, that the principal feature of all three compounds is the 4-eV wide $3d$-band complex, that in this respect all three are just cobalt metal. The rare-earth constituent serves principally to present the cobalt in a different crystal structure, giving rise to the large magnetocrystalline anisotropy which makes these materials so interesting in permanent-magnet applications. This provides a natural explanation for the fact that YCo_5 is quite similar to the other RCo_5's, while yttrium has no $4f$ electrons; these are not important. It does have a similar electronic configuration ($4d^15s^2$) to the rare earths ($5d^16s^2$), and about the same atomic size.

Lemaire *et al.*[17] first suggested a $3d$-band model, but assumed that the three extra electrons from the rare-earth constituent would fill up holes in the rigid minority-spin subband. This would reduce the moment to about $1.1\mu_B$ per cobalt atom, or $5.5\mu_B$ for any RCo_5, too small a value. The present calculations show that only about one electron per rare-earth atom is transferred to cobalt in each case. The slight differences among the three compounds arise from slight variations in the amount of charge transfer, the exchange splitting, and the hybridization of rare-earth-orbitals with cobalt. The most striking difference occurs between YCo_5, for which there is a moment of $\sim 0.3\mu_B$ induced on the yttrium site, and $SmCo_5$ and $GdCo_5$, for which the induced moment on the rare-earth site is $\sim 0.1\mu_B$, which is probably zero within the limits of accuracy of the calculation.

Finally, it has been suggested that the antiparallel coupling between rare-earth and cobalt sublattices arises from a RKKY-type mechanism, involving s-d and s-f exchange interactions. In this case, compounds with parallel coupling might be prepared by varying composition or conditions, since the sign of the RKKY interaction is sensitive to electronic concentration. This could lead to much larger magnetic moments. The present calculation casts a pall over such projections, however, by giving evidence of strong d-d coupling (rare earth $4d$ or $5d$ with cobalt $3d$). This is a much stronger coupling, and implies that the antiparallel spin coupling likely cannot be reversed.

In summary, these calculations provide considerable understanding of the RCo_5-type compounds. They show the origin of the moment, give good estimates of its magnitude, its variation, and the reasons for those variations. They show the important role of partial charge transfer (band-filling effects) and of d-d electronic coupling.

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*On leave of absence from Tata Institute of Fundamental Research, Bombay 400 005, India.

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