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Theory of ferromagnetism in $CeCo_5$

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Electronic-structure calculations for $CeCo_5$ in the hexagonal $CaCu_5$ structure and, for comparison, for the isostructural compounds YCo_5 and $LaCo_5$ are reported. It is shown that the anomalous properties of $CeCo_5$ can be understood as due to itinerant $4f$ states, in particular its reduced magnetic moment relative to YCo_5 and $LaCo_5$. An important concept in the electronic structure of $CeCo_5$ is the hybridization between the $3d$ states of cobalt and the $4f$ states of cerium. With spin-orbit coupling included in the calculation, good agreement with experiment for the total magnetic moment is achieved. A non-negligible $4f$ magnetic moment composed of both spin and orbital contributions is found on the cerium site. This manifests the existence of itinerant $4f$ magnetism in this compound. Common to all three compounds are the quite large orbital moments on the cobalt sites.

I. INTRODUCTION

The intermetallic compounds between rare-earth elements (R) and cobalt that form in the hexagonal $CaCu_5$ structure have received a lot of attention in the past 20 years. This interest derives mainly from their extremely favorable properties for technological applications as permanent magnets.[1,2] Practically all the rare-earth elements can together with cobalt form the $CaCu_5$ structure.[3] It is only for the radioactive element promethium, the two divalent elements europium and ytterbium, and for lutetium that the $CaCu_5$ structure has not been reported.

Among the RCo_5 compounds $CeCo_5$ stands out as anomalous in several respects. First, there are clear anomalies in the lattice constants for $CeCo_5$ (Fig. 1). In contrast to the expected smooth decrease through the series, the so-called lanthanide contraction, there is a pronounced deviation for $CeCo_5$. The normal smooth behavior is, for instance, shown by the isostructural RCu_5 series which have been included in Fig. 1 for comparison. Second, the magnetic properties, as for example reflected in the Curie temperature, deviate significantly from the values obtained from a simple interpolation between $LaCo_5$ and $PrCo_5$. Thus the transition temperature from paramagnetism to ferromagnetism is considerably depressed for $CeCo_5$ relative to its neighbor compounds (Fig. 2). Also the magnetic moment for $CeCo_5$ is anomalously low when compared to $LaCo_5$ and $PrCo_5$ (Fig. 6). These anomalies have been interpreted as evidence for a mixed-valence behavior of the cerium ion; i.e., the effective occupation number of the $4f$ shell is somewhere

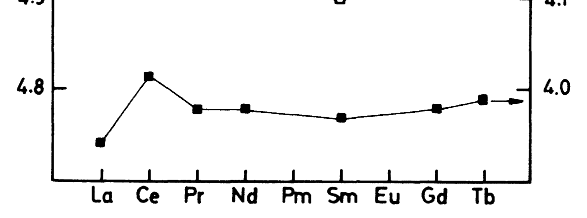

FIG. 1. The experimental hexagonal lattice constants, a (circle) and c (squares), through the RCo_5 (closed circles and squares) and RCu_5 (open circles and squares) series, with R from lanthanum to terbium in the Periodic Table.

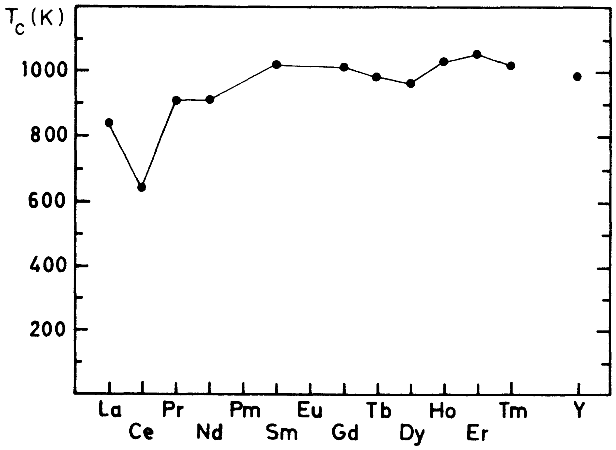

FIG. 2. The experimental Curie temperatures for the RCo_5 series (R=La–Tm) and YCo_5.

between zero and one.[4,5]

The nature of the $4f$ states in cerium and cerium compounds is a controversial subject.[6,7] There are on one hand theoretical models dealing with localized $4f$ configurations with occupation one or zero,[8] or a fluctuation between the two.[6] On the other hand, there have been arguments[9] that for some cerium systems the $4f$ states are itinerant, similar to the d states in transition metals or the $5f$ states in the early actinides. Quite a few *ab initio* electronic structure calculations on cerium systems have been performed;[10] for instance, good results have been obtained for the cohesive properties of the intermetallic cubic Laves-phase compounds $CeFe_2$, $CeCo_2$, and $CeNi_2$,[11] which support the itinerant model. However, it is far from generally accepted that the local approximation to the density-functional theory is able to treat the Ce $4f$ states within a band-theoretical approach correctly.

In order to investigate to what an extent an *ab initio* calculation can be used to describe the properties of the ferromagnetic compound $CeCo_5$, self-consistent electronic-structure calculations have been performed. To be able to make comparisons and to facilitate the analysis of the calculated results the same type of calculations have also been performed for the isostructural compounds $LaCo_5$ and YCo_5. These compounds are excellent reference compounds because they have properties representative of the normal members of the RCo_5 series while, at the same time, they have an empty $4f$ shell. Thereby the problems associated with the treatment of localized $4f$ electrons do not appear in the calculations.

Although $LaCo_5$ and YCo_5 are here primarily used as reference compounds they are of great interest as relatives to the technologically important permanent magnet $SmCo_5$. The reason for this is that those properties of $SmCo_5$ that originate from the cobalt sublattice are also present in these compounds. In fact, for the contributions to the anisotropy energy, where the effect of the Sm^{3+} ion is largest, a substantial fraction nevertheless seems to stem from the Co sublattice at room temperature. This can be seen in the anisotropy constant K_1, which at room temperature is 6.3 and 5.5 MJ/m^3 for $LaCo_5$ and YCo_5, respectively, which should be compared with 11.2 MJ/m^3 for $SmCo_5$.[1]

The main purpose of the present report is to show that a treatment of the cerium $4f$ states as itinerant gives results that describe very well the ground-state properties of $CeCo_5$. At the same time as a byproduct of these electronic structure studies some important aspects of the RCo_5 magnetism can be derived. This holds in particular for the presence of large orbital moments on the cobalt sites.

In Sec. II details of the calculations will be given. Section III contains the results of non-spin-polarized calculations, which also are used to introduce the concept of hybridization. Thereafter results are given from calculations where spin polarization is allowed for. Finally the spin-orbit coupling is included in the calculations and the results are discussed and compared with experiment. A summary is given in Sec. IV.

II. DETAILS OF THE CALCULATIONS

The $CaCu_5$ structure (space group $P6/mmm$) is a hexagonal Bravais lattice with six atoms per unit cell (Fig. 3). One important property of this structure is the existence of two inequivalent types of Cu sites. Thus there are two atomic sites of type I with the point group $\bar{6}m2$ and three atomic sites of type II with the point group mmm. As is expected for an intermetallic compound the structure is quite close-packed. If the space is filled up by touching spheres the packing fraction is 67%. This can be compared with the packing fraction of 74% for fcc and 71% for the cubic Laves phase. The construction of touching spheres defines an ideal hexagonal c/a ratio of 0.816 and an ideal ratio of the radii for the two different atom types of 0.764, i.e., the radius ratio between Cu and Ca.

The electronic structure was calculated with the linear-muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA) (Refs. 12 and 13) with the so-called combined corrections to the ASA included. The parametrization of von Barth and Hedin[14] was used for the exchange and correlation part of the effective one-electron potential, obtained within the local-spin-density approximation to the density-functional theory.

To include important relativistic effects the Dirac equation without the spin-orbit term is solved to get the wave functions within the atomic spheres. In some of the calculations the spin-orbit term is reintroduced into the Hamiltonian matrix, which is set up to calculate the eigenvalues in the band-structure part of the self-consistent loop. Convergence of the charge density was achieved within one part in 10^4, and was obtained with 225 **k** points sampled in the irreducible part of the Brillouin zone.

All calculations were performed at the experimental lattice constants[15] (Table I). Since the experimental c/a ratios are all close to the ideal value, the geometrical ideal ratio of sphere radii was adopted for the atomic spheres for the rare-earth and the cobalt atoms. The actual radii of the atomic spheres used in the calculations are all listed in Table I.

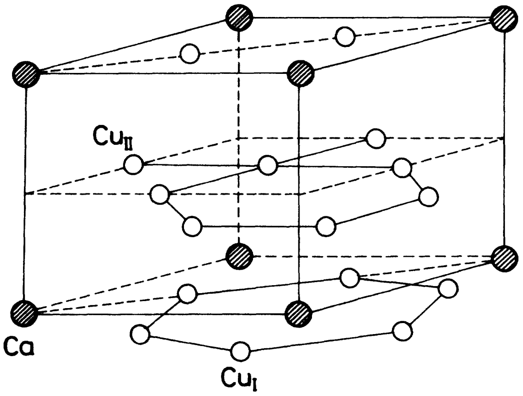

FIG. 3. The $CaCu_5$ crystal structure. The closed circles are the positions of the Ca sites. The open circles in the basal plane are the positions of the Cu_I sites and the open circles in the intermediate plane are those of the the Cu_{II} sites.

TABLE I. The experimental volume per unit cell and the hexagonal lattice constants, a and c, for LaCo$_5$, CeCo$_5$, and YCo$_5$. The atomic sphere radii for the different spheres, which were used in the calculations, are denoted as S_R and S_{Co}.

Compound:	LaCo$_5$	CeCo$_5$	YCo$_5$
V (Å^3)	88.31	84.45	83.98
a (Å)	5.086	4.928	4.928
c (Å)	3.942	4.015	3.993
c/a	0.775	0.815	0.810
S_R (Å)	1.870	1.842	1.838
S_{Co} (Å)	1.428	1.407	1.404

III. RESULTS AND DISCUSSIONS

A. Non-spin-polarized calculation

First, the reference compounds YCo$_5$ and LaCo$_5$ will be discussed. The hybridization between the cobalt d states and the d states of the rare-earth element is an important concept for the understanding of the electronic structure of these compounds. When proceeding from the individual metals to the intermetallic compound the hybridization produces bonding and antibonding states, in a similar way as for a diatomic molecule, although the states are here broadened into bands due to the translational symmetry. Since the Co $3d$ states are lower in energy than the rare-earth d states the dominating contribution to the bonding states are of Co $3d$ nature. However, due to the hybridization mechanism there is also spectral weight from the R d states in the bonding orbitals which causes the R d occupation to be about 1.6 (cf. Table II).

To clarify this picture the same analysis of the calculations as Brooks *et al.*[16] used for LuFe$_2$, which relies on the formalism of Andersen *et al.*,[17] will be adopted. Accordingly, an approximate form of the LMTO Hamiltonian matrix can be written

$$H_{QQ'}(\mathbf{k})=C_T\delta_{QQ'}+\Delta_T^{1/2}S_{QQ'}(\mathbf{k})\Delta_{T'}^{1/2}\ , \tag{1}$$

where $Q=(\mathbf{R}lm)$ labels the atomic site $\mathbf{R}$ and the azimuthal and magnetic quantum numbers l and m, and where $T=(\mathbf{R}l)$. C_T and Δ_T are the band center and the bandwidth potential parameters, respectively, which are obtained from a self-consistent calculation. $S_{QQ'}(\mathbf{k})$ are the potential-independent structure constants for the wave vector $\mathbf{k}$. In this simple model the hybridization arises from the off-diagonal blocks of the structure constants. If to a first approximation the hybridization is neglected and the sp conduction electrons are not considered at all, there will be 25 pure spin degenerate Co $3d$ bands and five pure spin degenerate R d bands. In the case where the density of states (DOS) for the cobalt and rare-earth d states are approximated by two rectangles an expression for the width of these are obtained as

$$W_T=\left[\frac{12M_{TT}^2}{(2l+1)N_t}\right]^{1/2}\Delta_T\ , \tag{2}$$

where M_{TT}^2 is the second moment of the block T of the structure constants and N_t is the number of atoms of type t per unit cell. Using the values from Table III one calculates the widths to be 0.255 and 0.244 Ry for the $3d$ states and 0.140 and 0.202 Ry for the R d states for YCo$_5$ and LaCo$_5$, respectively. With the rectangular DOS centered at the corresponding C_T one obtains that there are gaps of 0.156 Ry (YCo$_5$) and 0.169 Ry (LaCo$_5$) between the different type of states (bonding-antibonding separation). As the total number of electrons of interest is approximately 40 per unit cell (Co has about 7.6 d electrons and Y and La have about 1.6 d electrons, see Table II) and the $3d$ DOS can occupy 50 there is a zero occupation of R d states at this level of approximation.

First-order perturbation theory gives in the limit of weak hybridization a quantitative measure of the amount of transfer of T' character from what was originally pure T' bands into the originally pure T bands

$$N_{TT'}=gM_{TT'}^2\Delta_T\Delta_{T'}/(C_T-C_{T'})^2\ , \tag{3}$$

where $M_{TT'}^2$ is the off-diagonal second moment of the

TABLE II. The occupation numbers, for the $3d$ states of cobalt ($n_{\mathrm{Co_I}\text{-}3d}$ and $n_{\mathrm{Co_{II}}\text{-}3d}$), the $4d$ (yttrium) or $5d$ (lanthanum and cerium) ($n_{R\text{-}d}$) and the $4f$ states of the rare-earth atoms ($n_{R\text{-}4f}$), from the non-spin-polarized calculations. Also given are the Stoner product IN and the different local Stoner products [$(IN)_{\mathrm{Co_I}}$, $(IN)_{\mathrm{Co_{II}}}$, and $(IN)_R$] for the three compounds.

Compound:	LaCo$_5$	CeCo$_5$	YCo$_5$
$n_{\mathrm{Co}_I\text{-}3d}$	7.64	7.61	7.59
$n_{\mathrm{Co_{II}}\text{-}3d}$	7.61	7.58	7.56
$n_{R\text{-}d}$	1.59	1.86	1.60
$n_{R\text{-}4f}$	0.35	1.13	0.24
IN	1.42	0.94	1.21
$(IN)_{\mathrm{Co_I}}$	1.73	1.04	1.49
$(IN)_{\mathrm{CO_{II}}}$	1.20	0.99	0.99
$(IN)_R$	0.14	0.23	0.16

TABLE III. The self-consistently calculated potential parameters, Δ and C, for the $3d$ states of cobalt, $4d$ of yttrium, $5d$ of lanthanum, and $5d$ and $4f$ of cerium for the RCo$_5$ compounds. The different diagonal and nondiagonal second moments of the structure constants for the three compounds are denoted by M_{AB}^2.

Compound:	LaCo$_5$	CeCo$_5$	YCo$_5$
$\Delta_{\mathrm{Co}\text{-}3d}$ (Ry)	0.008 49	0.009 04	0.009 05
$\Delta_{R\text{-}d}$ (Ry)	0.116 0	0.111 6	0.089 0
$\Delta_{R\text{-}4f}$ (Ry)		0.013 6	
$C_{\mathrm{Co}\text{-}3d}$ (Ry)	−0.199 5	−0.196 5	−0.216 8
$C_{R\text{-}d}$ (Ry)	0.191 7	0.154 3	0.138 1
$C_{R\text{-}4f}$ (Ry)		−0.039 5	
$M_{3d\text{-}3d}^2$	1715	1665	1654
$M_{R\,d\text{-}R\,d}^2$	1.259	1.006	1.035
$M_{4f\text{-}4f}^2$		0.310 6	
$M_{3d\text{-}R\,d}^2$	104.7	114.4	112.9
$M_{3d\text{-}4f}^2$		122.8	

structure constants and where g is the spin degeneracy. Using the parameters of Table III one obtains that $N_{3d-R\,d}$ is equal to 1.44 and 1.35 for YCo_5 and $LaCo_5$, respectively. Thus when neglecting hybridization the occupation number for the R d states is zero because of their high-lying bands but when hybridization is reintroduced a number of about 1.4 d states per R atom are found in the bonding part of the DOS, i.e., the part that was made up from pure Co $3d$ states in the unhybridized case. Accounting for fact that the bonding d states are not filled—i.e, by multiplying with the fractional occupation number of about $\frac{40}{50}$—the model gives an occupation number of 1.15 and 1.08 for YCo_5 and $LaCo_5$, respectively, which is somewhat low in comparison with the self-consistently calculated values 1.60 and 1.59 (Table II).

The DOS from the self-consistent non-spin-polarized calculations are shown in Fig. 4. As can be seen the DOS for YCo_5 and $LaCo_5$ are very similar. Here the overall dominating feature is the bonding states, which are mainly of cobalt $3d$ character. The DOS at the Fermi level E_F is high in both systems which actually causes the Stoner products (SP) to be greater than one; i.e., the Stoner criterion for ferromagnetism is fulfilled. The calculated Stoner products are given in Table II.

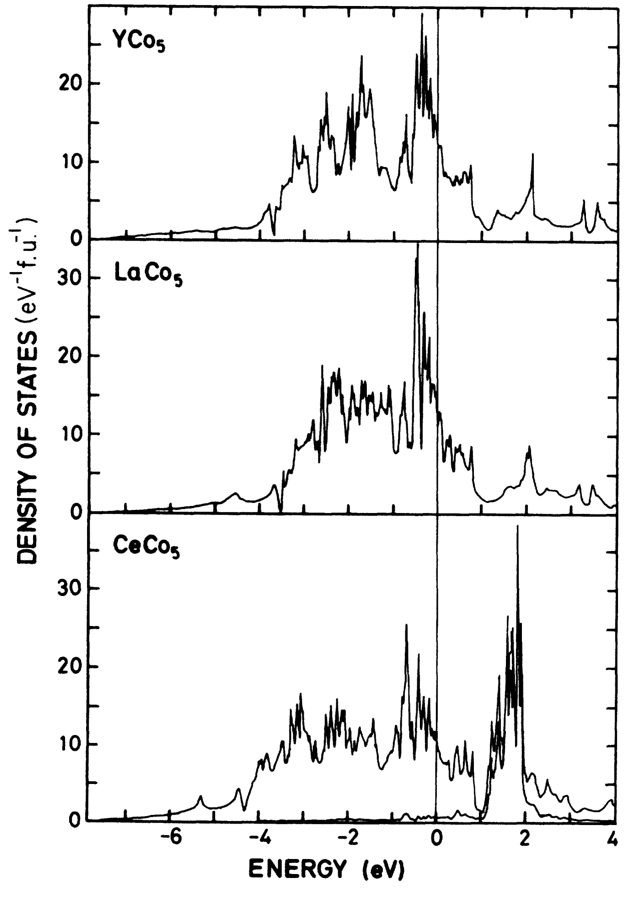

FIG. 4. The total density of states (DOS) for the non-spin-polarized calculations. For $CeCo_5$ the Ce-$4f$ partial DOS is also shown. The Fermi energy is at zero.

When proceeding from $LaCo_5$ to $CeCo_5$ the addition of an extra valence electron changes the picture dramatically. The extra electron is mainly of $4f$ character, which can be seen from the calculated occupation numbers given in Table II. Now, for cerium, both the $5d$ and $4f$ states hybridize with the cobalt $3d$ states, and the same perturbative model as above will be used for both the $5d$ and $4f$ bands to analyze the results from the full calculation.

For the widths of the pure unhybridized d bands similar values are obtained, using Eq. (2), as for the reference compounds, namely 0.255 and 0.173 Ry for Co $3d$ and Ce $5d$, respectively. The unhybridized Ce $4f$ bands are, however, very narrow, with a width of 0.010 Ry, reflecting the short spatial range of the $4f$ orbital and hence the small overlap. By centering the three different DOS at their respective C_T values one finds that they are all separated in energy, with the Ce $4f$ DOS in the gap between the Co $3d$ and Ce $5d$ DOS. With the extra electron of the cerium atom relative to the lanthanum there are now about 41 electrons of d or f character per unit cell. Thus all these will enter states of Co $3d$ character when hybridization is neglected. Taking hybridization into account by using Eq. (3) together with the self-consistent potential parameters, the result is 1.88 and 1.23 for $N_{3d\text{-}5d}$ and $N_{3d\text{-}4f}$, respectively, which with a fractional occupation number of $\frac{41}{50}$ correspond to occupation numbers of 1.54 and 1.01 for Ce $5d$ and Ce $4f$, respectively. This is in quite good correspondence with the self-consistently calculated values 1.86 and 1.13, respectively.

The self-consistently calculated DOS of $CeCo_5$ in Fig. 4 has similar features as the DOS of the two reference compounds but has in addition a narrow high peak made up of $4f$ states between 1.0 and 2.0 eV above the Fermi level, in accordance with the picture from the simplified model above. However, also the cobalt $3d$ states are influenced through the hybridization of these new states, especially the $3d$ states highest in energy are modified compared with the states in the compounds YCo_5 and $LaCo_5$. As mentioned above the hybridization mixes some cerium $4f$ character into the bonding part of the bands, which shows up as a long tail of $4f$ nature down from the main $4f$ peak in the DOS. So, this effect explains the fact that the self-consistently calculated occupation number for the Ce $4f$ states are 1.13 although the dominating part of the $4f$ peak is well above the Fermi level. In these calculations the Stoner parameters are calculated, which together with the DOS at the Fermi level can be used to investigate the Stoner criterion for magnetism. As already mentioned the criterion for magnetism is fulfilled for the cases of YCo_5 and $LaCo_5$, but the SP is less than one for $CeCo_5$, due to the lower DOS at E_F, indicating that the compound is locally stable towards ferromagnetism. This is very significant and contrary to simple intuitive ideas about Ce compounds where one certainly would expect that such a substantial f occupation as 1.13 would give rise to a high DOS at the Fermi level and accordingly an enhancement of the instability towards magnetism. Instead the opposite is obtained from the present calculation for $CeCo_5$. To a certain extent this is due to the fact that the $4f$ states "steal" Co $3d$ spectral weight in the upper part of the bonding band. Therefore the Co $3d$ density of states near the Fermi level is decreased and the driving force towards magnetism on the cobalt atoms is decreased as well.

In the derivation of the multiband version of the SP (Refs. 18 and 19)

$$IN = N \sum_{qll'} \left[\frac{N_{ql}}{N} I_{qll'} \frac{N_{ql'}}{N} \right] , \qquad (4)$$

(where N and N_{ql} are the total DOS and site, q, and angular momentum, l, projected DOS at E_F, and $I_{qll'}$ are the intra-atomic exchange integrals) it is assumed that the magnetization density is parallel in all space. For intermetallic compounds, where the magnetization can change sign between different atoms, this is not always true. Therefore a SP less than one does not necessarily imply a local stability of the paramagnetic state. The formalism for the multiband SP allows in a similar way a definition of a local SP for a specific atomic site $(\mathrm{SP})_{\mathrm{loc}}$;

$$(IN)_{\mathrm{loc}} = N_q \sum_{ll'} \left[\frac{N_{ql}}{N_q} I_{qll'} \frac{N_{ql'}}{N_q} \right] , \qquad (5)$$

where N_q is the site projected DOS at the Fermi level. The calculated $(\mathrm{SP})_{\mathrm{loc}}$ in Table II suggests that it is the intra-atomic exchange on the cobalt site I that is the main driving force towards the magnetic state in the case of $\mathrm{YCo_5}$ and $\mathrm{LaCo_5}$. Even for $\mathrm{CeCo_5}$ the Stoner criterion is fulfilled locally on the $\mathrm{Co_I}$ site and in fact, as will be seen later, a spin-polarized solution exists with a lower total energy than for the paramagnetic state also for this compound.

B. Spin-polarized calculations

The results from spin-polarized calculations for the three different compounds are summarized in Table IV and Fig. 5. For all compounds the spin-polarized state has a lower energy than the paramagnetic state. This is in nice accordance with the experimental fact that they are all ferromagnetic. Once more it is worth pointing out that $\mathrm{YCo_5}$ and $\mathrm{LaCo_5}$ have very similar properties. As expected from the calculated local Stoner products, $(\mathrm{SP})_{\mathrm{loc}}$, most of the moment is situated on the cobalt sites and is accordingly of $3d$ nature. In conflict with the simple rigid-band Stoner theory, magnetic moments antiparallel to the Co moments appear on the Y and La sites. These moments can be understood as induced by the hybridization between the Co $3d$ states and the Y $4d$ or La $5d$ states, in the way described below.

The Co $3d$ states are spin split by the intra-atomic ex-

TABLE IV. The calculated spin moments for the $R\mathrm{Co_5}$ compounds when spin-orbit coupling is omitted in the calculations. The computed total magnetic moment per unit cell, m_{spin}, the total local magnetic moment per atom for the different sites, $m_{\mathrm{Co_I}}$, $m_{\mathrm{Co_{II}}}$, and m_R, and the site and angular momentum projected spin moments per atom for the d and f states on the different sites, $m_{A\text{-}l}$, are given for the $\mathrm{LaCo_5}$, $\mathrm{CeCo_5}$, and $\mathrm{YCo_5}$ compounds.

Compound:	$\mathrm{LaCo_5}$	$\mathrm{CeCo_5}$	$\mathrm{YCo_5}$
m_{spin} (units of μ_B)	6.588	5.729	6.720
$m_{\mathrm{Co_I}}$ (units of μ_B)	1.434	1.278	1.439
$m_{\mathrm{Co_{II}}}$ (units of μ_B)	1.329	1.281	1.369
m_R (units of μ_B)	-0.267	-0.670	-0.265
$m_{\mathrm{Co_I}\text{-}3d}$ (units of μ_B)	1.456	1.306	1.466
$m_{\mathrm{Co_{II}}\text{-}3d}$ (units of μ_B)	1.366	1.312	1.401
$m_{R\text{-}4f}$ (units of μ_B)	-0.018	-0.415	-0.001
$m_{R\text{-}d}$ (units of μ_B)	-0.192	-0.201	-0.197

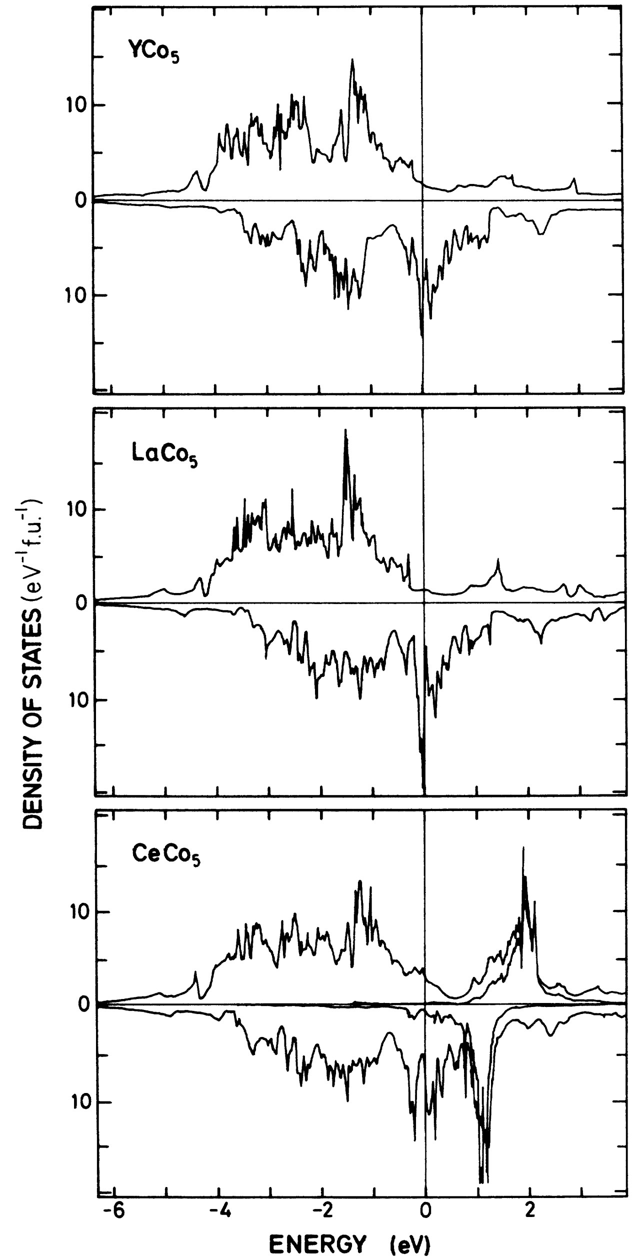

FIG. 5. The majority (above the zero line) and minority (below the zero line) spin density of states (DOS) for the three compounds $\mathrm{YCo_5}$, $\mathrm{LaCo_5}$ and $\mathrm{CeCo_5}$. For $\mathrm{CeCo_5}$ the Ce-$4f$ partial DOS is also shown. The Fermi energies are at zero.

change, therefore the hybridization between the Co 3*d* and the *R d* states will be different for the two different spins. Since the Co 3*d* and *R d* spin-down states (i.e., minority spin for the Co 3*d* states) are closer in energy than the spin-up states, the hybridization is stronger for the spin-down *d* states than for the spin-up *d* states. Hence more *R d* spin-down states will hybridize down into the spin-down bonding part of the *d* complex. To illustrate this a similar simplified approach as for the non-spin-polarized case will be used, again following closely the treatment in Ref. 16. The transfer of *R d* character into the bonding part of the DOS, $N^{\downarrow}_{3d-R\,d}$ and $N^{\uparrow}_{3d-R\,d}$, respectively, is calculated for the two different spins using Eq. (3) with the spin-dependent potential parameters given in Table V. For YCo_5 the values 1.01 and 0.50 are calculated for $N^{\downarrow}_{3d\text{-}4d}$ and $N^{\uparrow}_{3d\text{-}4d}$, respectively, which with fractional occupation numbers of about $(40+7)/50=0.94$ for spin up and $(40-7)/50=0.66$ for spin down gives a *Y* 4*d* moment of

$$\mu_{4d}=(0.94)(0.50)-(0.66)(1.01)\mu_B=-0.20\mu_B\ .$$

This value happens to exactly agree with the self-consistently calculated value. The same treatment for $LaCo_5$ gives 0.92 for $N^{\downarrow}_{3d\text{-}5d}$ and 0.49 for $N^{\uparrow}_{3d\text{-}5d}$ which corresponds to a La *d* moment of $-0.15\mu_B$ to be compared with $-0.19\mu_B$ from the full calculation. This discrepancy reflects the accuracy of the simplified perturbative model.

In Fig. 5 the self-consistently calculated DOS is shown. From this it can be seen that both YCo_5 and $LaCo_5$ almost fulfill the criterion of being strong ferromagnets, in the sense that the majority spin states are close to being completely occupied for the Co 3*d* states.

The picture becomes modified once again when one proceeds to $CeCo_5$, because of the presence of occupied 4*f* states. As for the paramagnetic case the Co 3*d* states are now hybridizing both with the Ce 5*d* and the Ce 4*f* states. The spin dependence of the hybridization strength induces antiparallel magnetic moments on the cerium atoms, in the same fashion as for YCo_5 and $LaCo_5$, but now there is in addition a large contribution of Ce 4*f* character to the moment (Table IV). The same perturbative model as above has been applied to estimate the role of the hybridization with the Co 3*d* states both for Ce 5*d* and Ce 4*f* states.

TABLE V. The spin-up and spin-down potential parameters, Δ and *C*, from the spin-polarized calculations for the 3*d* states of cobalt, the 4*d* states of yttrium, the 5*d* states of lanthanum, and the 5*d* and the 4*f* states of cerium for the ferromagnetic RCo_5 compounds.

Compound:	$LaCo_5$	$CeCo_5$	YCo_5
Spin up			
$\Delta_{\text{Co-}3d}$ (Ry)	0.0081	0.0086	0.0086
$\Delta_{R\text{-}d}$ (Ry)	0.1168	0.1125	0.0900
$\Delta_{R\text{-}4f}$ (Ry)		0.0211	
$C_{\text{Co-}3d}$ (Ry)	−0.2460	−0.2423	−0.2680
$C_{R\text{-}d}$ (Ry)	0.2039	0.1670	0.1491
$C_{R\text{-}4f}$ (Ry)		0.0268	
Spin down			
$\Delta_{\text{Co-}3d}$ (Ry)	0.0090	0.0095	0.0095
$\Delta_{R\text{-}d}$ (Ry)	0.1162	0.1115	0.0890
$\Delta_{R\text{-}4f}$ (Ry)		0.0115	
$C_{\text{Co-}3d}$ (Ry)	−0.1519	−0.1539	−0.1715
$C_{R\text{-}d}$ (Ry)	0.1924	0.1499	0.1361
$C_{R\text{-}4f}$ (Ry)		−0.0159	

First for the Ce 5*d* states, $N^{\downarrow}_{3d\text{-}5d}$ and $N^{\uparrow}_{3d\text{-}5d}$ are calculated to be 1.41 and 0.71, respectively. With an extra electron relative to $LaCo_5$ and a smaller spin splitting, the fractional occupation numbers become $(41+6.5)/50=0.95$ and $(41-6.5)/50=0.65$ for spin up and spin down, respectively. This gives a Ce 5*d* moment of $-0.30\mu_B$. This estimated value is somewhat higher than the value $-0.20\mu_B$ obtained from the full calculation (Table IV).

For the Ce 4*f* states 1.29 and 0.31 are calculated for the transfer of character into the bonding spin-down states and spin-up states, respectively, which together with the same fractional occupation numbers as above corresponds to a 4*f* spin moment of $-0.60\mu_B$. This is a bit too high in comparison with the self-consistently calculated 4*f* moment $-0.41\mu_B$ as was earlier found also for the 5*d* moment. The fact that we find the difference between the simple estimation and the full calculation to be larger for $CeCo_5$ than for YCo_5 and $LaCo_5$ is not totally unexpected. The point is that $CeCo_5$ has got both 3*d*-5*d* and 3*d*-4*f* hybridization, and the Co 3*d* states are significantly influenced by both types of hybridization. Since the hybridization is strong, a first order perturbative approach is not quite valid, especially when there are two competing types of hybridization with the Co *d* states. To get the correct magnitude of the cerium moments a full self-consistent calculation is necessary, but for the qualitative analysis the perturbative model still produces a valid picture of what is going on in terms of induced moments due to hybridization.

The spin-polarized DOS of the self-consistent calculation for $CeCo_5$ is shown in Fig. 5. There it is clear that the Co 3*d* states are modified, compared to YCo_5 and $LaCo_5$, due to the hybridization with the Ce 4*f* states. Especially the 3*d* states highest in energy (i.e., around E_F) show little resemblance with the corresponding states in the reference compounds. This is in fact the main reason for the reduced Co moment in the $CeCo_5$ compound relative to YCo_5 and $LaCo_5$. Also shown in Fig. 5 is the 4*f* projected DOS for $CeCo_5$ with the hybridization tails reaching down into the bonding part of the DOS.

The fact that there are two different cobalt sites in the unit cell has hitherto been neglected in our discussion of the electronic structure. The different symmetries of the sites, however, do not affect the magnetic moments much in the spin-polarized calculation. For YCo_5 and $LaCo_5$ the Co 3*d* moments on site I are about 5% and 7% larger than that on site II, respectively, but for $CeCo_5$ the moments are almost identical.

There are previously published calculations for YCo_5 which by and large agree with the present results. An augmented plane wave (APW) calculation by Malik *et al.*[20] gave for YCo_5 a total spin moment of $7.31\mu_B$ per formula unit which is 9% larger than that of the present work ($6.72\mu_B$, Table IV). Szpunar has performed a calculation using the continued fraction method (CFM),[21] which is not fully *ab initio*. This gave a Co 3*d* projected moment of 1.31 and $1.46\mu_B$/atom for sites I and II, respectively, and $-0.17\mu_B$ for the 4*d* moment of Y, which are of the same magnitude as those of the present work. However, in Fig. 6 where the presently calculated spin moments are compared with the experimental magnetic moments we notice that all the calculated magnetic moments are too low. A likely cause to this difference could be the neglect so far of orbital moments in the calculations, while there are clear experimental evidence for such contributions. In order to investigate this possibility the spin-orbit interaction has been included into our *ab initio* calculations.

C. Spin-orbit coupling

The spin-orbit coupling is introduced in the way proposed by Andersen.[12] To the semirelativistic LMTO Hamiltonian a spin-orbit term of the form

$$H_{SO}=\xi l\cdot s \tag{6}$$

is added. Here l and s are the angular and spin momenta and ξ the spin-orbit coupling constant. Due to the spin splitting of the bands and hence the existence of spin moments there will, through the spin-orbit coupling, be induced orbital moments. The extra term in the Hamiltonian is treated in a self-consistent way in the sense that the spin densities are reiterated to convergence. Since the spin-orbit coupling also affects the spin splitting, the spin moments are slightly changed compared to the spin-polarized calculations described above.

In Table VI the resulting magnetic properties are listed for RCo_5. Common to all three compounds are the fairly large local orbital moments on the cobalt atoms. It can also be noticed that the cobalt atoms of type I have a somewhat larger moment than those of type II. The orbital moments on the cobalt sites, which are mainly of 3*d* character, are parallel to the spin moments. This is in accordance with Hund's third rule which states that this should be the case for more than half-filled shells.

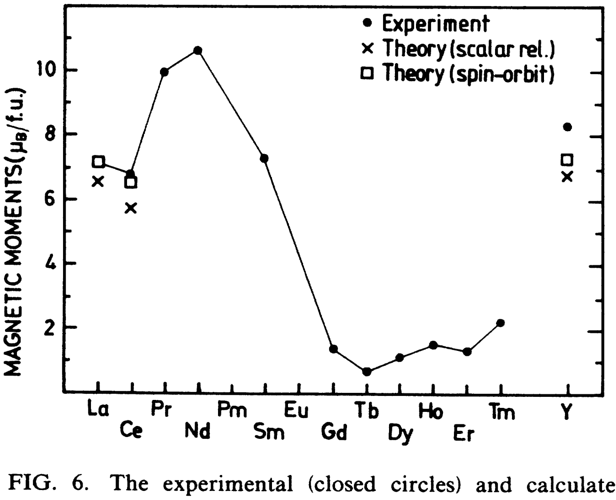

FIG. 6. The experimental (closed circles) and calculated magnetic moments (crosses and squares) per unit cell for the RCo_5 series and YCo_5 (R = La–Tm).

For YCo_5 a spin-polarized neutron diffraction experiment has been made by Schweizer and Tasset[22] where the contributions from the spin and the orbital motion to the total moments have been separated. Their results give very large local orbital moments on the cobalt sites, namely $0.46\mu_B$/atom for site I and $0.28\mu_B$/atom for site II. The existence of large orbital moments are also indicated by the investigation of the cobalt hyperfine fields with inelastic spin-flipped neutron scattering by Heidemann *et al.*[23] They estimate the local orbital moments to be $0.26\mu_B$/atom and $0.24\mu_B$/atom for sites I and II, respectively. The present calculation with spin-orbit coupling included give smaller local orbital moments, $0.14\mu_B$/atom and $0.10\mu_B$/atom, respectively, for sites I and II. A CFM calculation by Szpunar[24] with the spin-orbit constant ξ as a fitting parameter gave local orbital moments of $0.17\mu_B$/atom and $0.04\mu_B$/atom, respectively.

There is a better agreement between the experimental local Co spin moments,[22] $1.31\mu_B$/atom and $1.45\mu_B$/atom, and the presently calculated Co 3*d* moments, $1.47\mu_B$/atom and $1.40\mu_B$/atom for the two different cobalt sites, respectively. In the experiments no moment on the yttrium site could be detected while the calculations give a magnetic moment of $-0.24\mu_B$ per yttrium atom. However, spin-polarized neutron experiment have difficulties in resolving diffuse magnetic densities and it is not clear to what accuracy a zero moment could be inferred.

For the total magnetic moments we will compare with conventional bulk magnetization measurements. In Fig. 6 one can see that for YCo_5 there is a discrepancy between the experimental[25] [$8.33\mu_B$ per formula unit (f.u.)] and the theoretical value ($7.31\mu_B$/f.u.). This might be due to the too small orbital moments obtained in the calculations, especially since the difference between theory and experiment for the total moment is of the same magnitude as the difference in the orbital moment. Thus there are indications that the spin-orbit coupling alone is not able to explain the very large orbital moments on the cobalt sites.

As can be seen in Table VI, the calculations do show distinct differences between the two different cobalt sites. There seems to be a common feature in the theoretical results for the three compounds that the local orbital moments of site I are about 40–50% larger than those of site II. This relative difference in magnitude of the orbital moments is actually in agreement with experiment,[22] where the local orbital moment of site I is 64% larger than that of site II, although the absolute values of the orbital moments differ from theory by almost a factor of 3.

For $LaCo_5$ the results resemble those for YCo_5. The local 3*d* orbital moments are slightly larger in this case, $0.15\mu_B$/atom and $0.11\mu_B$/atom for sites I and II, respectively. This should be compared with $0.29\mu_B$/atom and $0.25\mu_B$/atom for the two sites which is estimated by Heidemann *et al.*[23] from their experiment. The agree-

TABLE VI. The magnetic moments from the spin-polarized calculations with spin-orbit coupling included. First, the spin, orbital, and total magnetic moments per unit cell (m_{spin}, m_{orb}, and m_{tot}) are given. Second, the spin, orbital, and total local magnetic moments in Bohr magnetons per atom (m_{Co_I}, m_{Co_II}, and m_R), and third, the site and angular momentum projected spin, orbital, and total magnetic moments in Bohr magnetons per atom for the d and f states of the different atoms ($m_{\text{Co}_\text{I}\text{-}3d}$, $m_{\text{Co}_\text{II}\text{-}3d}$, $m_{R\text{-}d}$, and $m_{R\text{-}4f}$) are presented.

Compound:		$LaCo_5$	$CeCo_5$	YCo_5
	m_{spin} (μ_B/f.u.)	6.575	5.644	6.722
	m_{orb} (μ_B/f.u.)	0.650	0.868	0.593
	m_{tot} (μ_B/f.u.)	7.225	6.512	7.315
m_{Co_I}	Spin	1.439	1.266	1.443
	Orbital	0.150	0.163	0.135
	Total	1.589	1.429	1.578
m_{Co_II}	Spin	1.321	1.267	1.368
	Orbital	0.109	0.103	0.097
	Total	1.430	1.370	1.465
m_R	Spin	−0.267	−0.689	−0.268
	Orbital	0.024	0.232	0.033
	Total	−0.243	−0.457	−0.235
$m_{\text{Co}_\text{I}\text{-}3d}$	Spin	1.462	1.296	1.472
	Orbital	0.150	0.164	0.135
	Total	1.612	1.459	1.607
$m_{\text{Co}_\text{II}\text{-}3d}$	Spin	1.358	1.300	1.402
	Orbital	0.110	0.105	0.098
	Total	1.468	1.405	1.500
$m_{R\text{-}d}$	Spin	−0.191	−0.202	−0.198
	Orbital	0.017	0.021	0.015
	Total	−0.174	−0.181	−0.183
$m_{R\text{-}4f}$	Spin	−0.019	−0.431	−0.001
	Orbital	0.003	0.207	−0.003
	Total	−0.016	−0.224	−0.004

ment with the experimental total magnetic moment[26] is good, 7.23μ_B (theor) compared to 7.1μ_B (expt) per formula unit. However, in the same series of experiments[26] lower magnetic moments for YCo_5 and $CeCo_5$ were found than in later experiments on single crystals.[25,27] So it might be expected that new experiments on single crystals of $LaCo_5$ would also give about 1μ_B larger moment per formula unit, i.e., a total magnetic moment of about 8μ_B per formula unit.

As concerns the rare-earth elements in the presently studied systems it is only cerium that has a large orbital moment. This is primarily of $4f$ origin and due to the less than half-filled $4f$ shell it is antiparallel to the $4f$ spin moment in accordance with Hund's third rule. When the orbital $4f$ magnetic moment, 0.21μ_B, is added to the $4f$ spin magnetic moment, $-0.43\mu_B$, the total $4f$ magnetic moment on the cerium atom becomes $-0.22\mu_B$ per atom. This $4f$ moment together with essentially the $5d$ spin moment give an appreciable total cerium moment of $-0.46\mu_B$.

For the cobalt sites in $CeCo_5$ the orbital moments are of the same size as for the reference compounds, 0.16μ_B/atom and 0.10μ_B/atom respectively, but the spin moments, 1.27μ_B/atom on both sites, are reduced relative to those of the reference compounds, due to the $3d$-$4f$ hybridization as discussed above. The calculated local cobalt moments of 1.43μ_B for site I and 1.37μ_B for site II are in agreement with the result of a spin-polarized neutron experiment of Lemaire and Schweizer[28] giving $1.3\pm0.3\mu_B$. From the experimental data they also claim that the cerium moment is less than 0.3μ_B which is in contrast to the result of this work. However, the moment of cerium searched for in that experiment was probably of a more localized form that that calculated in this work. Therefore, our calculated $4f$ moment on cerium, $-0.22\mu_B$, is not necessarily in disagreement with these data.

The reduced magnetic moments on the cobalt sites and the comparatively large antiparallel moment on the cerium atom work together to give a low total magnetic moment, 6.51μ_B per formula unit, for $CeCo_5$. This calculated total magnetic moment is close to the experimental value of 6.8μ_B measured at 77 K.[27]

The rather good agreement for the total magnetic moment is deeply connected to the way the cerium $4f$ states are treated in these calculations. If, instead of the itinerant $4f$ states in the calculation, a localized *LS*-coupled $4f$ shell is assumed on the cerium atom, a larger total magnetic moment would automatically follow. Then the valence electronic structure, without the $4f$ electron, would very much resemble that of $LaCo_5$. The spin part of the *LS*-coupled moment would be parallel with the Ce $5d$ moment due to the local $4f$-$5d$ exchange interaction. But, since the orbital part of the full localized moment is dominating and antiparallel to the spin part, the total $4f$ moment would be in parallel to the cobalt moments. Thus the total magnetic moment would be about $2.5\mu_B$ larger than for $LaCo_5$, which is in sharp contrast to the experimental data. In addition, without the hybridization between the cobalt $3d$ and the cerium $4f$, the cobalt moments would be of the same size as in those of the calculation for $LaCo_5$. Actually they would even be somewhat higher in $CeCo_5$ than in $LaCo_5$ due to the presence of the $4f$ spin moment. Therefore the experimental data for $CeCo_5$ suggest that the standard localized $4f$ picture is not appropriate for this system. The relative success of the present treatment implies that the Ce $4f$ states are itinerant. As such they will contribute to the bonding, which then explains the anomalously low lattice constants. Owing to the extensive calculations that are needed to determine the equilibrium volume this has not been attempted in the present work. However, the additional bonding pressure in $CeCo_5$ relative to $LaCo_5$ is about 45 kbar and derives from the $4f$ states. Assuming a bulk modulus of 1.5 Mbar for these systems, this extra bonding pressure would give a 2.6 Å^3 volume decrease relative to $LaCo_5$. To this value should also be added the decrease in volume due to the normal lanthanide contraction, which is about 0.9 Å^3. In total the volume difference between $LaCo_5$ and $CeCo_5$ is thus estimated to be 3.5 Å^3. This should be compared with the experimental value[15] of 3.8 Å^3. Thus the additional $4f$ bonding in $CeCo_5$ as compared to $LaCo_5$ explains its anomalous low volume.

IV. SUMMARY AND CONCLUSIONS

In this paper we have reported on calculations of magnetic properties for the intermetallic compounds $CeCo_5$, $LaCo_5$, and YCo_5. The details of the electronic structure have been described. The most important feature derives from the hybridization between the $3d$ states of cobalt and the valence d or valence d and f states of the rare-earth atom. First, for the reference compounds YCo_5 and $LaCo_5$ the hybridization between the Co $3d$ and the R d gives rise to bonding states mainly of Co $3d$ character but also with some R d character. A substantial part ($\sim 80\%$) of these bonding states are occupied. Since the cobalt $3d$ states are spin split, the strength of the hybridization is different for the d states of different spins. This spin dependence of the hybridization is shown to give rise to antiparallel spin moments on the cobalt and the rare-earth atoms. This mechanism is general and can, with some modification due to intra-atomic exchange interaction with the localized $4f$ states, be applied to the whole RCo_5 series.

Second, for $CeCo_5$ there is in addition to this $3d$-$5d$ hybridization also a hybridization between the cerium $4f$ states and the cobalt $3d$ states. This hybridization is strong enough to move down about one $4f$ state per cerium atom below the Fermi level and form a $4f$ hybridization tail. The spin dependence of the hybridization induces also in this case an antiparallel alignment of the Ce $4f$ spin moment and the Co $3d$ moment. While the induced spin moments on the yttrium or lanthanum atoms are relatively small the spin moment on the cerium atom is quite large since it has contributions both from $5d$ and $4f$ electrons.

The contribution to the bonding states from the itinerant Ce $4f$ states in the hybridization tail explains the anomaly in the lattice constants for cerium in the RCo_5 series. The extra bonding in the $CeCo_5$ compound causes the atomic volume to decrease in comparison to the other members of the series.

In the calculations where the spin-orbit coupling is included substantial orbital moments are induced on the cobalt sites and in the case of $CeCo_5$ also on the cerium site. On the cobalt sites the orbital moments point in the same direction as the spin moments but on the cerium site the $4f$ orbital moment points in the opposite direction to the local spin moment, all in accordance with Hund's third rule. The fact that large orbital moments appear on the cobalt sites is in agreement with experiment although the measured values are considerably larger than the theoretical ones.[22] This deviation might possibly be due to the neglect of some sources to anisotropy in the present calculations, as, for instance, nonspherical contributions to the charge density. This discrepancy deserves further studies in the future.

A plot of the calculated total magnetic moments against the experimentally measured values show that, with the exception of YCo_5, there is a very good agreement between theory and data for the absolute values of the moments. The disagreement for YCo_5 is perhaps surprisingly large but can partly be explained by the theoretical underestimation of the orbital part of the magnetic moment. However, a perfect agreement would perhaps have been unrealistic with the limits of accuracy of calculations within the local-spin-density approximation.[29] For $LaCo_5$ the agreement is very good, but, as mentioned earlier, there are doubts about the quality of the experimental data.[26] So a similar discrepancy as for YCo_5 is expected here too, and this would then again be attributed to the too low theoretical orbital moment. Therefore it is more significant to notice that the trend of the moments is correctly reproduced by theory. Thus the theory could account for the anomalous small magnetic moment of the $CeCo_5$ compound. This anomaly was shown to be caused by the strong hybridization between the cobalt $3d$ states and the cerium $4f$ states. Although the $4f$ spin moment is partially canceled by the orbital part, it forms together with the $5d$ spin moment a nonnegligible magnetic moment on the cerium site. Its direction is opposite to the moments on the cobalt sites. This fact, together with the fact that the cobalt $3d$ states, which are considerably distorted due to the additional $3d$-$4f$ hybridization not present in $LaCo_5$ and YCo_5, produce a smaller Co magnetic moment, explain the decreased total magnetic moment for the $CeCo_5$ compound relative to $LaCo_5$ and YCo_5.

If instead the standard model for the rare-earth $4f$ shell, i.e., with a conventional localized $4f$ moment, had been applied to the $CeCo_5$ compound, the moment would be predicted to be larger than in, for instance, $LaCo_5$. However, experimentally the $CeCo_5$ moment is lower than the $LaCo_5$ moment. This experimental fact is well explained by the present theory, where the $4f$ states are treated as itinerant. Previously, similar conclusions as regards the $4f$ states were reached for $CeFe_2$, $CeCo_2$, and $CeNi_2$. The $CeFe_2$ system is a ferromagnet and several crucial experiments were suggested for the verification of the theory. Since $CeCo_5$ is also a ferromagnet the same type of experiments, such as magnetic form factor measurements and spin-polarized photoelectron spectroscopy investigations, would be most useful for this system as well.

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[1] H. R. Kirchmayr and C. A. Poldy, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 2, p. 55.

[2] K. J. Strnat, in *Ferromagnetic Materials,* edited by E. P. Wohlfarth and K. H. J. Buschow (North-Holland, Amsterdam, 1988), Vol. 4, p. 131.

[3] K. H. J. Buschow, Rep. Prog. Phys. **40**, 1179 (1979); in *Ferromagnetic Materials,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. 1, p. 297.

[4] D. Gignoux, F. Givord, R. Lemaire, H. Launois, and F. Sayetat, J. Phys. (Paris) **43**, 173 (1982).

[5] D. Givord, J. Laforest, R. Lemaire, and Q. Lu, J. Magn. Magn. Mater. **31-34**, 191 (1983).

[6] For a review see, for instance, J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

[7] L. L. Hirst, J. Phys. Chem. Sol. **35**, 1285 (1974); B. Coqblin and A. Blandin, Adv. Phys. **17**, 281 (1968); R. Ramirez and L. M. Falicov, Phys. Rev. B **3**, 1225 (1972); B. Johansson, Philos. Mag. **30**, 469 (1974); J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106 (1982).

[8] A. Iandelli and A. Palenzona, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1979), Vol. 2, p. 1, and references therein.

[9] B. Johansson (Ref. 7); F. R. de Boer, W. H. Dijkman, W. C. M. Mattens, and A. R. Miedema, J. Less-Common Met. **64**, 241 (1979).

[10] A. Yanase, J. Phys. F **16**, 1501 (1986); O. Eriksson, B. Johansson, H. L. Skriver, J. Sjöström, and M. S. S. Brooks, Phys. Rev. B **40**, 5270 (1989); D. D. Koelling, Solid State Commun. **43**, 247 (1982).

[11] O. Eriksson, L. Nordström, M. S. S. Brooks, and B. Johansson, Phys. Rev. Lett. **60**, 2523 (1988); J. Phys. (Paris) **49**, C8-693 (1988).

[12] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[13] H. L. Skriver, *The LMTO Method* (Springer-Verlag, Berlin, 1984).

[14] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[15] P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (American Society for Metals, Ohio, 1986).

[16] M. S. S. Brooks, O. Eriksson, and B. Johansson, J. Phys. Condens. Mat. **1**, 5681 (1989).

[17] O. K. Andersen, W. Klose, and H. Nohl, Phys. Rev. B **17**, 1209 (1978).

[18] S. H. Vosko and J. P. Perdew, Can. J. Phys. **53**, 1385 (1975).

[19] M. S. S. Brooks, O. Eriksson, and B. Johansson, Phys. Scr. **35**, 52 (1987).

[20] S. K. Malik, F. J. Arlinghaus, and W. E. Wallace, Phys. Rev. B **16**, 1242 (1977).

[21] B. Szpunar, Physica B+C **130B**, 29 (1985).

[22] J. Schweizer and F. Tasset, J. Phys. F **10**, 2799 (1980).

[23] A. Heidemann, D. Richter, and K. H. J. Buschow, Z. Phys. B **22**, 367 (1975).

[24] B. Szpunar, J. Less-Common Met. **127**, 55 (1987).

[25] J. M. Alameda, D. Givord, and Q. Lu, J. Appl. Phys. **52**, 2079 (1981).

[26] W. A. J. J. Velge and K. H. J. Buschow, J. Appl. Phys. **39**, 1717 (1968).

[27] H. O. Gupta, S. K. Malik, and W. E. Wallace, J. Magn. Magn. Mater. **42**, 239 (1984).

[28] R. Lemaire and J. Schweizer, J. Phys. (Paris) **28**, 216 (1967).

[29] A discussion of the accuracy of the calculated magnetic moments in related intermetallic compounds is, for instance, given in R. Coehoorn, Phys. Rev. B **39**, 13 072 (1989).