Magnetocrystalline anisotropy of YCo$_5$ and related RECo$_5$ compounds

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I. INTRODUCTION

From a physical as well as from a technological point of view RECo$_5$ intermetallic compounds are of considerable interest. This is mainly due to the large magnetocrystalline anisotropy energy (MAE) of SmCo$_5$ which is about $3 \times 10^6$ ergs/cm$^3$ at low temperatures.$^{1-3}$ The anisotropy energy of YCo$_5$, which forms in the same hexagonal CaCu$_5$ structure with nearly identical lattice parameters,$^4$ is only a factor of 4 smaller,$^5-7$ and an order of magnitude larger than the anisotropy energy of bulk (hcp) cobalt$^8$ of $10^7$ ergs/cm$^3$. The origin of the large magnetic anisotropy of YCo$_5$ compounds is not very well understood. The difference between the MAE of RECo$_5$ compounds and YCo$_5$ is found to be quite well described in terms of the interaction of the localized 4$f$ electrons of a RE$^{3+}$ ion with phenomenological crystal and exchange fields at the RE site.$^{1-3}$ The values of these fields as determined by fitting to experiment are reasonably well known but the origin of crystal fields in metallic systems and the nature of the exchange fields are not well understood quantitatively; the importance of taking into account the dependence of the exchange field on the direction of the valence electron magnetization has been pointed out by Ermolenko.$^9$

The large anisotropy energy of YCo$_5$ has been associated with large orbital moments on the Co sites, the orbital moment on the 2$c$ sites being apparently particularly large. The existence of these orbital moments was first suggested on the basis of an analysis of the magnetic form factors measured in a polarized neutron study on a YCo$_5$ single crystal.$^{10}$ Almost all subsequent investigations of the MAE of YCo$_5$ have been interpreted in the light of this neutron work. By replacing some of the Co atoms with Ni, which occupies the 2$c$ site preferentially, and Fe, which preferentially occupies the 3$g$ site, a correlation was established between the 2$c$ site and the anisotropy energy.$^5$ In a study of the magnetization in high magnetic fields a (large) anisotropy in the magnetization of 4% was found.$^7$ From the analysis of a polarized neutron study of a NdCo$_5$ single crystal, the greater part of this magnetization anisotropy was attributed to the Co (2$c$) site.$^7$ In a later analysis, this anisotropy was attributed to the orbital moments on the Co sites, in particular to the Co (2$c$) site.$^{11}$

Studies of the hyperfine field have been used to probe the site dependence of the orbital moments by relating the anisotropic component of the hyperfine field to the anisotropy in the orbital moments. Heidemann et al.$^{12}$ have concluded from a neutron inelastic spin-flip scattering investigation of the hyperfine fields in YCo$_5$ that there is (i) no significant difference in the orbital moments on the 2$c$ and 3$g$ sites and (ii) that there is no simple proportionality between the hyperfine fields and the Co moments. Nuclear magnetic resonance (NMR) measurements of the hyperfine field have also been carried out.$^{13-15}$ Under the assumption that the orbital moment is proportional to the orbital hyperfine field, it was concluded from these studies that the large magnetic anisotropy of YCo$_5$ is related to a large orbital moment on the 2$c$ site.

Most of the information about the crystal fields and exchange fields in the RECo$_5$ compounds has been obtained indirectly by treating these interactions as free parameters in crystal-field calculations of the MAE and varying them so as to obtain reasonable agreement with the temperature dependence of the single-ion contribution to the MAE as determined experimentally. Values for the crystal-field parameter
A_{2}^{0}(r^{2})/k_{B}$ of $-180.1, -420.2$, and $-185$ K, and for the exchange-field parameter $\mu_{g}B_{\text{EX}}/k_{B}$ of 200.1, 240.2, and 100 K (Ref. 3) have been reported for SmCo$_{5}$. Studies of the hard-axis magnetization curves have been used to determine the exchange field acting on the RE ions. For Y$_{1-x}$Gd$_{x}$Co$_{5}$ alloys a value of the exchange field of 150 K was found.\textsuperscript{9} \textsuperscript{9155}Gd Mössbauer spectroscopy studies have allowed a determination of the electric-field gradients on the Gd site in GdCo$_{5}$\textsuperscript{16, 17} in a simple crystal-field picture based on ionic charges, the electric-field gradient at the nucleus is simply related to the crystal field seen by the 4$f$ electrons.

Independent information and insight can be obtained from \textit{ab initio} calculations based on the Hohenberg-Kohn-Sham density-functional formalism.\textsuperscript{18, 19} Within the framework of the local-spin-density approximation (LSDA) to the density-functional formalism, ground-state properties may be calculated without use of any free parameters; the only inputs are the crystal structure and lattice parameters. In this paper we will concentrate on the magnetic properties of YCo$_{5}$; in particular we will be interested to see whether the relatively large magnetocrystalline anisotropy energy of this compound can be calculated within the LSDA. In an earlier study of the MAE of Fe, Co, and Ni,\textsuperscript{22} we found that although the correct order of magnitude of the anisotropy energy could be calculated, the incorrect sign was obtained for Co and Ni. For Co the calculation was in error by 0.08 meV. Since the MAE per Co atom in YCo$_{5}$ is $\approx 0.76$ meV or almost an order of magnitude larger, an absolute error of 0.08 meV per Co atom would be a very acceptable result. We shall see that this is not the case. The straightforward LSDA calculation results in a MAE of 0.54 meV per unit cell which is about a factor of 7 too small and represents an error of 0.65 meV per Co atom. In addition, we find that the magnetization is also significantly underestimated. The orbital moment contribution to the magnetization is apparently too small, just as we found for Co. If a recently proposed orbital polarization term,\textsuperscript{23–25} whose main effect is to enhance the orbital moment, is included, then a magnetization of 8.0$\mu_{B}$ per unit cell is obtained compared to the experimental value\textsuperscript{2} of 8.3$\mu_{B}$. The corresponding anisotropy energy of 3.0 meV per unit cell is in acceptable agreement with the experimental value of 3.8 meV per unit cell. We find a strong correlation between the anisotropy energy and the average anisotropy in the orbital moment per Co atom.\textsuperscript{26} At the actual Fermi energy the orbital anisotropy on the 3$g$ site is larger than that on the 2$c$ site. No significant difference between the orbital moments on the 2$c$ and 3$g$ sites is found. In order to try and understand the discrepancy between this result and the picture derived from neutron scattering\textsuperscript{10} and confirmed by NMR,\textsuperscript{13–15} we calculated the hyperfine fields. It appears, however, that the hyperfine fields cannot be calculated with sufficient accuracy\textsuperscript{27} to allow the NMR experiments to be interpreted with confidence.

If we assume that the crystal-field and exchange interaction between the RE 4$f$ electrons and the other valence electrons is sufficiently weak that it may be treated as a small perturbation, then these parameters can be evaluated from first principles. The calculated second-order crystal-field parameter\textsuperscript{28} and the electric-field gradient are about a factor of 2–3 larger than the values extracted from experiment. The calculated exchange field agrees with the experimental values. Brief summaries of the results of the YCo$_{5}$ anisotropy-energy and crystal-field calculations GdCo$_{5}$ have been given in Refs. 26 and 28, respectively.

The paper is organized as follows. The theoretical methods used are described in Sec. II. In Sec. III the results of our calculations are described and compared with experimental results and other calculations. A brief summary with some conclusions is given in Sec. IV.

II. METHOD

Within the density-functional formalism,\textsuperscript{18} Kohn and Sham showed\textsuperscript{19} that the many-electron problem for the ground state of an inhomogeneous interacting electron gas in an external potential may be reduced to an effective independent particle problem, the Kohn-Sham equations\textsuperscript{19} which must be solved self-consistently, usually by iteration. In practical calculations explicit expressions for the exchange-correlation energy and potential are required and the usual approach is to make the local-spin-density-approximation.\textsuperscript{20, 21} In this work we have used two different methods to solve the Kohn-Sham equations. A full potential (FLAPW) version\textsuperscript{25} of the linear-augmented plane-wave (LAPW) method\textsuperscript{30} is used for calculations of the electric-field gradient, crystal-field parameters and contact contributions to the hyperfine field. In a so-called full potential method, there is no restriction imposed on the form of the potential or spin density; these are not assumed to be spherically symmetrical inside atom-centered spheres as in the muffin tin (MT) or atomic sphere (AS) approximations. By performing convergence tests on the number of plane waves in the basis, on the upper angular momentum used in the expansion of the potential around the atom sites and the spherical harmonic expansion of the plane waves inside a MT sphere, on the number of $k$ points\textsuperscript{31} used to sample the Brillouin zone (BZ) and on the number of fixed energies around which the energy linearization is performed, essentially exact solutions of the Kohn-Sham equations within the LSDA can be obtained. To obtain reliable results for the magnetization and the energy bands of YCo$_{5}$, we found that about 70 plane waves/atom were required so that matrices of rank 400 had to be diagonalized.

For calculations of the MAE a fine sampling of the Brillouin zone must be made and calculations with the FLAPW method would be very time consuming. In order to calculate the MAE, orbital moments, orbital contributions to the hyperfine field and local exchange interactions between RE 4$f$ magnetic moments and the valence electron magnetization we use the efficient linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA).\textsuperscript{30} In LMTO calculations a basis of typically 16 ($s$, $p$, $d$, and $f$) orbitals per atom is used making the LMTO method about two orders of magnitude faster than the FLAPW if the matrix diagonalization is the most computationally demanding step. If the ASA, in which the potential is assumed to have spherical symmetry inside atomic spheres which replace the atomic Wigner-Seitz cell, is used then this is the case.

In Sec. II A we describe the approximations used to calculate the magnetocrystalline anisotropy energy of the itinerant valence electrons. In Sec. II B expressions for contact and orbital contributions to the hyperfine field are given. The
calculation of crystal-field parameters as well as the electric-field gradient is described in Sec. II C. In Sec. II E the approximations used to calculate local exchange interactions between the RE spin and the valence electron exchange magnetization are discussed. Some specific technical details of the LMTO and FLAPW calculations are given in Sec. II F.

### A. Itinerant electron anisotropy energy

Magnetocrystalline anisotropy refers to the dependence of the ground-state energy on the orientation of the magnetization and, microscopically, it occurs when both exchange-splitting and spin-orbit coupling are included in the Hamiltonian. In 3$d$ transition-metal systems the spin-orbit coupling parameter of the valence electrons is much smaller than the exchange-splitting and the bandwidth. One can therefore make the approximation of first solving the Kohn-Sham equations for the scalar-relativistic spin-polarized Hamiltonian self-consistently and of including the spin-orbit coupling in a subsequent non-self-consistent step. The Kohn-Sham eigenvalues then obtained by diagonalization of the Hamiltonian depend on the direction $\mathbf{n}$ of the magnetization. The change in total energy upon inclusion of the spin-orbit coupling, as given by the change in the single-particle eigenvalue sum, is correct to first order in the changes in the electron and spin densities occurring upon a rotation of the magnetization direction. The MAE due to the valence electrons is then approximately:

$$\Delta E = \Delta E^0(\mathbf{n}_1, \mathbf{n}_2) = \Delta E(n, \mathbf{n}_1) - \Delta E(n, \mathbf{n}_2)$$

$$= \sum_{i, k} \varepsilon_i(k, \mathbf{n}_1) - \sum_{i, k} \varepsilon_i(k, \mathbf{n}_2) = \int_{\text{BZ}} d\mathbf{k} \Delta \mathcal{E}_n(k).$$

where $n$ is the number of valence electrons. The band index $i$ must be summed over all occupied states up to the Fermi energy $\varepsilon^0_n(\mathbf{n}_a)$ and the wave vector $\mathbf{k}$ is the summation over the first Brillouin zone. $\Delta \mathcal{E}_n(k)$ is the anisotropy energy density in $\mathbf{k}$ space. At this point it will be convenient to choose the directions $\mathbf{n}_1$ and $\mathbf{n}_2$ to be the $x$ (the anisotropy in the basal plane is known to be small and can be neglected) and $z$ directions, respectively, and the explicit dependence of the anisotropy energy on the two magnetization directions will be suppressed from now on. As in our earlier work, the eigenvalue sums were evaluated directly with the improved tetrahedron method without having to use the density-of-states or number-of-states functions.

To investigate how the anisotropy energy depends on the location of the Fermi energy, we calculate the difference of two single-particle eigenvalue sums as a function of the non-integer band filling $q$ using the band structure calculated self-consistently for $n$ electrons. We call this quantity $\Delta \mathcal{E}_n(q)$. By plotting the corresponding generalized anisotropy energy density $\Delta \mathcal{E}_n(k,q)$ in the BZ as a function of the band filling $q$ we can identify the contribution of particular states $|i(k)|$ to the anisotropy energy. The dependence of the Fermi energy on the number of valence electrons $n$ and the magnetization direction $\mathbf{n}$ will not be shown explicitly in the following.

Atom projected orbital angular momenta oriented along $\mathbf{n}$ are calculated using

$$L(\tau) = \sum_{i,k} \langle \psi^i_{f,k}| \mathbf{n} \cdot \mathbf{L} | \psi^i_{f,k} \rangle \text{AS},$$

where $\psi^i_{f,k}$ is the eigenstate of energy band $i$ with wave vector $\mathbf{k}$ calculated for the magnetization direction $\mathbf{n}$ and the subscript AS indicates that the integral is performed over the atomic sphere of the atom $\tau$ in question.

The orbital moments obtained from LSDA calculations for Fe and Co (but not for Ni) are about a factor of 2 smaller than the experimental values. Recently it was shown that inclusion of a term proportional to $2L\mathbf{n} \cdot \mathbf{i}$ in the Kohn-Sham equations improved the calculated properties of certain $4f$ and $5f$ systems considerably and led to enhanced orbital moments in Fe, Co, and Ni. This so-called orbital polarization term (OP) is based upon an approximate $L^2$ dependence of the energy of the lowest term of a given configuration with respect to the average energy of all terms of the same configuration with maximum spin for an atom. This dependence is assumed to be transferred to the solid state.

For an atom obeying Russell-Saunders coupling, a $d^n$ or $f^n$ electronic configuration with maximum spin $S$ will split into terms with different values of the total orbital angular momentum $L$. The term with the largest $L = L_{\text{max}}$ is lowest in energy (Hund’s rules). The energy difference between this term with $L = L_{\text{max}}$ and the weighted average of the terms with maximum spin is

$$\delta E(n, L_{\text{max}}, S) = E(n, L_{\text{max}}, S) - \bar{E}$$

$$= E(n, L_{\text{max}}, S) - \frac{\sum_L (2L+1) E(n, L, S)}{\sum_L (2L+1)}.$$
The simple interpolation formula tends to overbind terms with nearly empty or nearly filled shells. $B$ and $E^3$ are Racah parameters.\textsuperscript{34} $B$ is given by
\begin{equation}
B = \frac{9 F^2 - 5 F^4}{441},
\end{equation}
where the Slater $F^k$ integrals are given by
\begin{equation}
F^k = \int \int \phi_d^*(r_1) \phi_d^*(r_2) \frac{2r^k}{r_{12}} r_1^2 r_2^2 dr_1 dr_2.
\end{equation}

in terms of integrals involving the radial $d$ wave function $\phi_d$. For a crystal we replace $\phi_d$ with the $d$ partial wave evaluated at the center of gravity of the occupied part of the $d$ band, $\phi_d(\vec{r}, r)$.

We have investigated the influence of orbital polarization on the calculated orbital moments and the MAE by including a term $-B L n \cdot I$ in the Hamiltonian and iterating to self-consistency with the magnetization direction parallel to the $c$ axis. This yields new self-consistent orbital angular momenta, orbital splittings $B L$ and a new self-consistent potential. It can be shown that upon a rotation of the magnetization direction, the change in total energy is given by the change in the one-particle sum correct to first order in the changes in the electron and spin densities and in the orbital angular momentum.\textsuperscript{35} Using the self-consistently determined orbital splittings the anisotropy energy may be calculated as previously [Eq. (1)], using the new self-consistent potential calculated including OP.

Classical magnetic dipolar interactions between magnetic moments are another source of anisotropy energy, not included in the theory described above. The interatomic magnetostatic energy, $E^{\text{dip}}$, is given by
\begin{equation}
E^{\text{dip}} = \frac{1}{c} \sum_{\tau, \tau'} \frac{1}{|R + \tau - \tau'|} \left( \mathbf{m}_\tau \cdot \mathbf{m}_{\tau'} \right) - \frac{3}{2} \left( \frac{(R + \tau - \tau') \cdot m_\tau}{|R + \tau - \tau'|^2} \left( (R + \tau - \tau') \cdot m_{\tau'} \right) \right),
\end{equation}
where $\mathbf{m}_\tau$ is the total magnetic moment in an atomic sphere centered on site $\tau$. After the shape anisotropy has been excluded,\textsuperscript{22} $E^{\text{dip}}$ can be determined for different orientations of the magnetic moments.

**B. Hyperfine fields**

The hyperfine field $B_{\text{hf}}$ at a nucleus comprises a Fermi contact interaction term,\textsuperscript{36} an orbital hyperfine field and dipolar contributions. The latter are of order $1$ T and are generally neglected. The Fermi contact interaction is determined by the magnetization density at the nucleus, while the orbital hyperfine field is related to the orbital moment of the valence electrons only; contributions from core electrons have been shown to be negligible ($\sim 0.1$ T).\textsuperscript{37} If it is assumed that the contact and orbital hyperfine interactions are proportional to the spin and orbital moments, respectively, then measurements of the hyperfine fields can be used to obtain information about the site dependence of the magnetization.

In our calculation of the hyperfine field $B_{\text{hf}}$, we follow the treatment of Blügel et al. who derived expressions for the orbital, dipolar, and contact contributions to the hyperfine fields, which should be used in conjunction with scalar relativistic wave functions.\textsuperscript{38} Because of the divergence of the (scalar) relativistic $s$ wave functions at the nucleus, the relativistic generalization of the Fermi contact hyperfine field (in SI units),
\begin{equation}
B_c = \frac{8 \pi \mu_0}{3} m(0),
\end{equation}
where $m(0)$ is the magnetization density at the nucleus, is
\begin{equation}
B_c = \frac{8 \pi \mu_0}{3} m_{av},
\end{equation}
where $m_{av}$ is an averaged magnetization density given by $m_{av} = \int dr \, \delta(r) m(r)$ and $m(r)$ is the magnetization density due to $s$ electrons. $\delta(r)$ is essentially a smeared out $\delta$ function, $\delta(r) = (1/4\pi r^2) \partial (S/\partial \rho)$, where $S(r)$ is the reciprocal of the relativistic mass enhancement $S^{-1}(r) = 1 + [\varepsilon + V(r)]/2mc^2$. The most important contribution to $B_c$ is obtained for $r$ values smaller than or of order of the Thompson radius $r_T = \varepsilon e^2/2mc^2$. Adapting Eq. (7) to the relativistic case by simply averaging the relativistic wave functions over the nuclear volume leads to overestimates of the contact hyperfine field.

Similarly, the orbital contribution to the hyperfine field is given by\textsuperscript{38}
\begin{equation}
B_{\text{orb}} = \frac{2 \mu_0 \mu_B}{4\pi} L_{av},
\end{equation}
with
\begin{equation}
L_{av} = \sum_{\tau, \kappa} \langle \psi_{\tau, \kappa} | S(r) | \frac{\mathbf{n} \cdot \mathbf{l} }{r} | \psi_{\tau, \kappa} \rangle_{AS}.
\end{equation}

**C. Crystal-field parameters**

Most RE atoms in a solid may be regarded as being in an $f^{n-3}(sd)^3$ or trivalent electronic configuration, which is well separated from other configurations [such as $f^{n-2}(sd)^2$ or $f^{n-4}(sd)^4$] by $\sim 5$ eV. Within this trivalent configuration the term with the lowest energy is obtained by first maximizing the spin $S$ and then maximizing the orbital angular momentum $L$; the $4f$ electrons approximately obey Russell-Saunders ($LS$) coupling.\textsuperscript{39} Spin-orbit coupling splits each term into multiplets $2S+1L_J$, where the total angular momentum $J$ of the ground-state multiplet is given by $J = |L - S|$ or $J = |L + S|$ for less-than or more-than half filled $4f$ shells, respectively. When the RE atom is embedded in a crystal, the $(2J+1)$-fold degenerate ground state will split according to the irreducible representations of the point-group. Because of the localization, and the (relaxed) large intra-atomic electron-electron interactions of the $4f$ electrons of the RE atoms, the lowering of the point-group symmetry from spherical symmetry due to the crystalline environment usually represents a weak perturbation to the ground state of a RE atom in a solid.
The potential describing these crystal-field effects (felt by each \( f \) electron) can be expanded around the RE site (we omit the explicit site index) into radial and angular parts

\[
v(r) = \sum_{l\alpha} u_{l\alpha}(r) K_{l\alpha}(\hat{r}),
\]

where \( l\alpha \) labels the real lattice-harmonics \( K_{l\alpha} \) which have been symmetrized according to the local point-group symmetry. In order to make contact with previously published work we write the lattice harmonics in terms of the functions \( f_{lm}(r) \) used by Hutchings

\[
K_{l\alpha}(\hat{r}) = \sum_{l,m} c_{lm} f_{lm}(r) / r^l.
\]

For example, \( f_{20}(r) = 3z^2 - r^2 \). If all \( 4f \) one-electron states have the same radial dependence \( \phi_{l\alpha}(r) \), the matrix elements of the Hamiltonian between states of the ground-state multiplet \( |LSJM,M = M_J\rangle \) can be written

\[
\mathcal{H}_{MM'}^{\text{CF}} = \langle LSJM|(-e) \sum_{l} v(r)|LSJM'\rangle
= \sum_{l,m} A_{l}^{m}(r') \theta_{l}^{LSJ}(JM)|O_{l}^{m}(JM'),
\]

as a consequence of the Wigner-Eckart theorem, with

\[
A_{l}^{m}(r') = (-e) \sum_{\alpha} \int \phi_{l\alpha}(r)c_{lm}^{*}u_{l\alpha}(r)r^{l}dr.
\]

The crystal-field parameters are thus determined by the radial dependence of the potential \( u_{l\alpha}(r) \) and the \( 4f \) radial wavefunction \( \phi_{l\alpha}(r) \). \( \theta_{l}^{LSJ} \) is the ratio between two reduced matrix elements in the Wigner-Eckart theorem. If the \( O_{l}^{m} \) are chosen as Stevens operator equivalents to \( f_{lm} \) for the ground state \( |LSJ\rangle \) then \( \theta_{l}^{LSJ} = \alpha_{l}, \beta_{l}, \gamma_{l} \) for \( l = 2, 4, \) and \( 6, \) respectively. These have been tabulated in Refs. 42 and 40. As the crystal-field splitting is in general much smaller than the splitting between multiplets, one usually neglects the mixing-in of excited multiplets with different values of \( J \) in the Hamiltonian, as in Eq. (13). For \( f \) states, the number of crystal-field parameters \( A_{l}^{m} \) is limited to \( l \leq 6 \) and \( l \) even. The local point-group symmetry determines the coefficients \( c_{lm}^{\alpha} \), and this further restricts the number of independent parameters \( A_{l}^{m} \) for each value of \( l \). For the RE atom in RECo\(_{5}\), the local point-group symmetry is \( D_{3h} \), leading to independent parameters \( A_{l}^{0} \) with \( (l,m) = (2,0); (4,0); (6,0) \) and \( 6,6 \).

The simplest approximation to the one-electron potential \( v(r) \) is the electrostatic (Coulomb) part of the potential generated by the self-consistent charge density in the crystal. Within a muffin-tin sphere around the RE site it can be expressed as

\[
v(r) = \sum_{l\alpha} u_{l\alpha}(r) K_{l\alpha}(\hat{r}) = \sum_{l\alpha} \frac{4\pi}{2l+1} [U_{l\alpha}(r) + r' q_{l\alpha}] K_{l\alpha}(\hat{r}),
\]

where \( u_{l\alpha}(r) \) is divided into on-site and lattice contributions. The on-site contribution is

\[
4\pi \frac{2l+1}{2l+1} U_{l\alpha}(r) = 4\pi \int_{r}^{r'} \rho_{l\alpha}(r') r'^{2} dr',
\]

where \( \rho_{l\alpha}(r) \) follows from an expansion of the charge density around the RE atom and \( R \) is the radius of the muffin-tin sphere centered on the RE site

\[
\rho(r) = \sum_{l\alpha} \rho_{l\alpha}(r) K_{l\alpha}(\hat{r}).
\]

The lattice contribution which depends on the charge density outside the muffin-tin sphere, and on the requirement of continuity of the potential \( 43 \) is more complicated and will not be given explicitly here. We note that while splitting the potential into an on-site and a lattice contribution does not involve any approximation, for a continuous charge distribution it does require a somewhat arbitrary partitioning of the charge density as determined by the choice of the muffin-tin radius \( R \).

The on-site nonspherical potential generated by the \( 4f \) charge density, \( v_{l\alpha}^{0} \), should be excluded from \( v_{l\alpha} \) in Eq. (14). It corresponds to a self-energy of the \( 4f \) charge density that by itself does not give rise to a crystal-field splitting. We have spherically averaged the \( 4f \) charge density, treating the \( 4f \) states as core states but allowing the radial distribution to adjust to changes in the valence charge density. The nonspherical \( 4f \) charge density would influence the valence electron charge density but we have not investigated this further. \( v(r) \) is calculated self-consistently using the FLAPW method.

The anisotropy energy is the difference between the ground-state energies corresponding to the two directions of magnetization \( \hat{x} \) and \( \hat{z} \). On rotating the magnetization direction, the valence electron charge density and potential are assumed not to change and thus the crystal-field parameters, defined with respect to the crystal axes are unchanged. In the large exchange limit, the ground state has a maximal azimuthal quantum number \( M = M_{J} \) directed along the magnetization direction. The single ion anisotropy is then given by

\[
A_{2}^{0}(r^{2}) \alpha_{J, M = M_{J}} = |J| [3J_{z}^{2} - 3J_{z}^{2}] |J, M = M_{J}|
= \frac{3}{2} \frac{A_{2}^{0}(r^{2})}{3J_{z}^{2}} (2J_{z}^{2} - J).
\]

D. Electric-field gradient

The electric-field gradient (EFG) at the RE nucleus is given by

\[
V_{zz} = \left( \frac{\partial^{2}}{\partial z^{2}} - \frac{1}{3} \right) v(r) \bigg|_{r=0}
= \frac{\partial^{2}}{\partial z^{2}}(r^{2} K_{20}(\hat{r})) \lim_{r \to 0} \frac{v_{20}(r)}{r^{2}}
= 4e_{20} \lim_{r \to 0} \frac{v_{20}(r)}{r^{2}} = \sqrt{\frac{5}{\pi}} \lim_{r \to 0} \frac{v_{20}(r)}{r^{2}},
\]

where again the site index has been omitted for simplicity. If the \( 4f \) charge-density were located at the nucleus \( r \to 0 \), or if
v_{20}(r)/r^2 were independent of \( r \), then \( A_{f}^{0} \) would be equal to \(-e/4V_{zz}\). This follows from Eqs. (14) and (19). A different proportionality than \(-e/4\) is therefore entirely due to the on-site contribution of the potential; any deviation being caused by the overlap between the 4\( f \) corelike charge density and the nonspherical on-site valence charge density.

E. Exchange interaction

So far the valence electron MAE and single ion anisotropy have been treated separately. However, the directions of the localized RE moments and the valence electron magnetic moments are correlated. This exchange coupling, together with the crystal-field parameters and the MAE of the valence band electrons, determines to what extent the RE 4\( f \) spins interact with the on-site valence electron magnetization through local exchange interactions \( I_{i,jf'} \). The on-site valence electron magnetization is caused by the hybridization of the RE 5\( d \) bands with the Co 3\( d \) bands.\textsuperscript{46} The high-lying 5\( d \) bands hybridize more strongly with minority Co 3\( d \) bands than with majority 3\( d \) bands, due to the large exchange splitting of the Co 3\( d \) bands. Thus the magnetic moment derived from RE 5\( d \) valence electrons is directed antiparallel to the overall valence electron magnetization. Together with the local ferromagnetic exchange interaction \( I_{i,df} \) the direction of the total localized RE magnetic moment now depends on whether the 4\( f \) shell is more than or less than half filled, and on the magnitude of \( L \) compared to \( S \).

It has been pointed out by Liebs, Hummler, and Fähnle\textsuperscript{47} that the perturbative approach sketched above can be improved upon by performing two separate self-consistent field calculations with the 4\( f \) moments rotated by 180° and evaluating the change in the total energy. In this way the conduction electron spins are allowed to adjust to the reversed exchange field; this turns out to be an important quantitative effect.

F. Details of the calculation

The CaCu\textsubscript{5} structure (space group No. 191) has hexagonal symmetry (point-group \( P6/mmm \)). Inequivalent Cu atoms occupy the 2\( c \) and 3\( g \) Wyckoff sites. For YCo\textsubscript{5} the lattice parameters used are \( a = 9.313 \) a.u. and \( c = 7.544 \) a.u.\textsuperscript{4} For GdCo\textsubscript{5} the lattice parameters are \( a = 9.398 \) a.u. and \( c = 7.500 \) a.u.\textsuperscript{5} The von Barth-Hedin parametrization of the exchange-correlation potential is used.\textsuperscript{20} The Brillouin-zone integration is performed using the improved tetrahedron method.\textsuperscript{31}

The LMTO basis states are the nearly orthogonal \( \Theta \) functions devised by Andersen and Jepsen.\textsuperscript{48} \( s, p, d, \) and \( f \) partial waves are included in the basis. Self-consistent charge densities are obtained using 2366 \( k \) points in the full Brillouin zone, corresponding to 133 inequivalent \( k \) points. The calculated atom-projected magnetic moments change by about 0.002\( \mu_{B} \) if 3600 \( k \) points (196 inequivalent \( k \) points) are used. Atomic sphere radii of Y and Co are 3.497 and 2.645 a.u., respectively, leading to a maximum overlap of about 14.2%, which is comparable to the overlap in a bcc lattice.

In the FLAPW calculations the nonoverlapping Y and Co muffin-tin radii were 3.10 and 2.31 a.u., respectively. A plane-wave cutoff of \( K_{\text{max}} = 3.5 \) a.u. was used, so that the basis contained about 415 plane waves or 70 plane waves per atom. In the second-variation step where the nonspherical terms in the potential are treated, an energy cutoff of \( e_{\text{max}} = 3.5 \) Ry was used, corresponding to about 85 basis

\[
I_{i,1f} = -\frac{2}{3} \int \phi_{i}^{2}(r)\phi_{j}^{2}(e_{F},r) \frac{A(r)}{4\pi r} r^2 dr. \tag{25}
\]

A comparison with the phenomenological exchange Hamiltonian, Eq. (20), shows that

\[
\mu_{B}B_{\text{EX}} = -\frac{1}{2} \sum_{i} \Delta n_{f} I_{i,df}. \tag{26}
\]

The 4\( f \) spins interact with the on-site valence electron magnetization through local exchange interactions \( I_{i,df} \). The on-site valence electron magnetization is caused by the hybridization of the RE 5\( d \) electrons with the Co 3\( d \) electrons.\textsuperscript{46} The high-lying 5\( d \) bands hybridize more strongly with minority Co 3\( d \) bands than with majority 3\( d \) bands, due to the large exchange splitting of the Co 3\( d \) bands. Thus the magnetic moment derived from RE 5\( d \) valence electrons is directed antiparallel to the overall valence electron magnetization. Together with the local ferromagnetic exchange interaction \( I_{i,df} \) the direction of the total localized RE magnetic moment now depends on whether the 4\( f \) shell is more than or less than half filled, and on the magnitude of \( L \) compared to \( S \).

It has been pointed out by Liebs, Hummler, and Fähnle\textsuperscript{47} that the perturbative approach sketched above can be improved upon by performing two separate self-consistent field calculations with the 4\( f \) moments rotated by 180° and evaluating the change in the total energy. In this way the conduction electron spins are allowed to adjust to the reversed exchange field; this turns out to be an important quantitative effect.
TABLE III. Calculated magnetic moments of YCo₅ within the muffin-tin and atomic spheres using the FLAPW (column 2) and LMTO methods (columns 3–7), respectively. The spin and orbital moments in columns 4 and 5 result from including spin-orbit coupling non-self-consistently. The spin and orbital moments in columns 6 and 7 were calculated self-consistently including spin-orbit coupling and orbital polarization. Experimental values for the total magnetic moment are 8.33 \mu_B (Ref. 7) and 8.13 \mu_B (Ref. 5) at 4.2 K, and 8.0 \mu_B (Ref. 7) and 7.99 \mu_B (Ref. 10) at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>FLAPW</th>
<th>LMTO</th>
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<tr>
<td></td>
<td>\sigma</td>
<td>\sigma</td>
</tr>
<tr>
<td>Y</td>
<td>-0.27</td>
<td>-0.31</td>
</tr>
<tr>
<td>Co(2c)</td>
<td>1.46</td>
<td>1.32</td>
</tr>
<tr>
<td>Co(3g)</td>
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<tr>
<td>Total</td>
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III. RESULTS AND DISCUSSION

Before describing the magnetocrystalline anisotropy energy of YCo₅ in Sec. III C, the calculations of the magnetization and hyperfine fields are presented in Sec. III A and Sec. III B, respectively. The results of the calculations of the crystal-field parameters, the electric-field gradient and the exchange field are discussed in Sec. III D.

A. Magnetization

The magnetic moment per unit cell as measured by several groups of workers on single crystals of YCo₅ is given in Table III together with the spin contribution to the magnetic moment calculated using the LMTO and FLAPW methods. The single-crystal measurements are in fair agreement with each other, values ranging between 8.0 and 8.4 \mu_B per unit cell. Measurements on powder samples tend to result in values for the magnetization which are about 1 \mu_B lower than the single-crystal data. A considerably lower spin magnetic moment of 6.8 and 6.9 \mu_B per unit cell is calculated using the LMTO and FLAPW methods, respectively. The discrepancy per Co atom with the experimental value is much larger than the difference found for the transition metal elements Fe, Co, and Ni. A possible reason for this discrepancy is the neglect of orbital contributions to the magnetization. Including spin-orbit coupling (non-self-consistently) in the Hamiltonian, a large orbital moment of 0.6 \mu_B per unit cell is found, whereby each Co atom contributes on average 0.12 \mu_B. This is about 50% more than the orbital moment of 0.08 \mu_B calculated in the same way for hcp Co. The spin magnetic moment is not changed significantly by including spin-orbit coupling so that a fairly large discrepancy with the experimental magnetic moment remains.

Inclusion of orbital polarization in local-spin-density calculations leads to increased orbital moments and considerably better agreement with experiment for several systems. For example, for hcp Co the calculated orbital moment is then 0.13 \mu_B, compared to the experimental value of 0.16 \mu_B, and the total magnetic moment is 1.70 \mu_B, compared with the experimental value of 1.75 \mu_B. Including both OP and SO interactions in the YCo₅ calculation, and iterating to self-consistency, a total orbital moment of 1.2 \mu_B is calculated, yielding a total magnetic moment of 8.0 \mu_B per unit cell. This value is in good agreement with the experimental values for single crystals. The discrepancy between the calculated and experimental magnetic moment per Co atom is approximately equal to the discrepancy found for hcp Co.

We thus find a very large orbital moment of 0.23 \mu_B on each Co atom. Magnetic form factor measurements by means of neutron-scattering experiments had already indicated the existence of large orbital moments. However, it was concluded from an analysis of these measurements that the orbital moment at the 2c site (0.46 \mu_B) is nearly twice that at the 3g site (0.28 \mu_B). In addition, it was found that the spin magnetization density around the 2c site extends in the basal plane, and deviates strongly from spherical symmetry. Our calculations do not support these two conclusions. We find equal orbital moments for each Co site and we find for GdCo₅ and YCo₅ using the FLAPW method that the deviation from a relative occupation of 0.2 for each c orbital within the muffin-tin sphere is \leq 0.01 at the 2c sites. However, at the 3g sites the deviation may amount to as much as 0.04 (i.e., 20%) for some of the d orbitals. The spin density within the muffin-tin spheres is not found to contain such large deviations from spherical symmetry as was deduced from the form factor measurements.

Comparison with previous work

In an early self-consistent spin-polarized augmented plane-wave calculation based on Slater’s Xα approximation with α = 1 (which is known to overestimate the tendency to ferromagnetic ordering), a total spin magnetic moment of 7.31 \mu_B per unit cell was found for YCo₅. In this calculation, the two inequivalent Co sites were considered to be equivalent.

A self-consistent LMTO calculation by Szpunar and Smith yielded a spin magnetic moment of \( m_{\text{sd}} = m_{Y} + m_{\text{Co}(2c)} \times 2 + m_{\text{Co}(3g)} \times 3 = -0.37 + 1.29 \times 2 + 1.44 \times 3 = 6.54 \mu_B \) per unit cell. The negative moment on the Y site is larger than the value which we found. This is probably attributable to Szpunar and Smith’s use of an atomic sphere which was 9% larger in volume than the atomic sphere which we used and to the interstitial spin density being negative in sign (as found, for example, in our FLAPW calculation; see Table III).

In another self-consistent LMTO calculation, Nordström et al. found a total spin magnetic moment per unit cell of \(-0.27 + 1.44 \times 2 + 1.37 \times 3 = 6.72 \mu_B \) which is in good agreement with the value which we found. Curiously, these authors find that the moment on the 2c site is larger than the...
TABLE IV. Measured and calculated hyperfine fields in Tesla for Fe, Co, and Ni and at the Co (2c) and (3g) sites in YCo₅ and GdCo₅. Core, valence, and orbital contributions to the hyperfine fields are listed separately. The orbital hyperfine fields, as well as the total hyperfine fields are calculated using spin-orbit coupling only (listed in the columns denoted by SO), as well as using spin-orbit coupling and orbital polarization (listed in the columns denoted by OP). Various experimental results are shown in the last column.

<table>
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<tr>
<th></th>
<th>Core</th>
<th>Val</th>
<th>Orb</th>
<th>Total</th>
<th>Expt.</th>
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<tr>
<td></td>
<td>SO</td>
<td>OP</td>
<td>SO</td>
<td>OP</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
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<tr>
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<td>+5.5</td>
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<tr>
<td>YCo₅(3g)</td>
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<td>+8.9</td>
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<tr>
<td>GdCo₅(2c)</td>
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<td>+1.2</td>
<td>+9.3</td>
<td>-7.3</td>
<td></td>
</tr>
</tbody>
</table>

aReferences 14.
bReference 13.
cReference 12.
dReference 15.

moment on the 3g site. Both in our FLAPW and LMTO calculation we found the opposite ordering. When they included spin-orbit coupling, Nordström et al. found orbital moments on the 2c and 3g sites of 0.14 and 0.10μₜ, respectively, and of 0.26 and 0.17μₜ when orbital polarization was included. In both cases, the orbital moment on the 2c site is found to be larger than the moment on the 3g site whereas we find them to be equal.

B. Hyperfine fields

Hyperfine field measurements have played an important role in investigations of the magnetic properties of YCo₅. The hyperfine fields at the Co sites are strongly reduced with respect to those in hcp Co, and this has been interpreted as being partly due to large orbital moments. The anisotropy in the hyperfine fields has been related to an anisotropy in the orbital moments and local anisotropy energies were then derived from these anisotropies. Since our calculations are at variance with the assignment of orbital moments to the 2c and 3g sites, it is important to see whether the simple interpretation of the NMR measurements by Streever is well founded.

In Table IV we list calculated hyperfine fields in YCo₅, GdCo₅ and Fe, Co, and Ni. The calculations for the transition-metal elements agree with previously published results that do not take OP into account. The difference between the theoretical and experimental results is about 8 T for Fe, 0 T for Co, and 3 T for Ni. Including orbital polarization only increases the discrepancy due to the enlarged orbital hyperfine field. The calculated hyperfine field of hcp Co then differs from the experimental value by about 4 T.

The calculated orbital hyperfine fields in YCo₅ are twice as large as those in hcp Co. Just as the orbital moments on the 2c and 3g sites scarcely differ, there is no essential difference between the orbital hyperfine fields on these two sites. The large difference in the total hyperfine fields of −4.2 T at the 3g site and +4.6 at the 2c site is caused by a positive contact valence contribution to the hyperfine field at the 2c site rather than by different orbital moments, as has been assumed. This result does not depend on whether or not the orbital polarization term is used. The total hyperfine field results from a cancellation of contact and orbital contributions and its interpretation is complicated by the polarization of the core electrons by the valence electron magnetization. There is a large spread in the values measured experimentally but irrespective of which values are chosen for comparison, it can be seen that the orbital polarization term does not lead to an improvement in the calculated values.

The hyperfine field at the 3g sites is quite sensitive to the RE atom. When Y is replaced with Gd (see Table IV), the valence contact term at the 3g site changes significantly, much more than that at the 2c site, resulting in nearly identical hyperfine fields at both sites in GdCo₅. A large discrepancy between experimental and theoretical results exists whose origin is not clear. It has been shown that orbital effects from the core electrons are negligible.

C. Anisotropy energy of YCo₅

Many experiments have been carried out in an attempt to explain the origin of the large magnetocrystalline anisotropy of YCo₅. We have outlined above how large orbital moments were found on the Co atoms in YCo₅, with the largest orbital moment being found on the 2c site, how a correlation was established between the 2c site and the anisotropy energy, how a large anisotropy in the magnetization was attributed to the 2c site, and how hyperfine field measurements were used to associate a local anisotropy energy with the anisotropy in the orbital moments on the 2c site in particular. However, these conclusions about the origin of the anisotropy energy are based on some unproven assumptions such as the existence of a local anisotropy energy. In this section we describe calculations of the anisotropy energy and orbital moments within the itinerant electron model which allow us to establish a correlation between the anisotropy energy and the anisotropy in the orbital moment and study in some detail the origin of the anisotropy.

YCo₅ has n = 48 valence electrons per unit cell. In Fig. 1 the anisotropy energy ∆Eₘ(n) is plotted as a function of the volume element used to perform the Brillouin-zone integral; it is seen to be well converged irrespective of whether orbital polarization is or is not included (open and filled circles, respectively). In both cases it is positive, thus favoring an orientation of the magnetization along the c axis.

In Fig. 2, ∆Eₘ/q is shown for the range of band fillings 44 < q < 52 (corresponding to the energy range −2.5 < Eₚ(q) < −1.7 eV). The solid and dashed curves were
both calculated using a mesh of $30 \times 30 \times 32$ k points in the full Brillouin zone, the densest mesh shown in Fig. 1. This corresponds to using 4097 and 1547 irreducible k points when the magnetization is oriented in the x and z directions, respectively. The dashed curve was obtained by including spin-orbit coupling only in the Hamiltonian, whereas to obtain the solid curve spin-orbit coupling and orbital polarization were included. Both curves exhibit two distinct peaks which are labeled A and B in the figure. We will explain the origin of these two peaks beginning with the case where only spin-orbit coupling is included.

### 1. Spin-orbit coupling only

For band fillings $45 < q < 51$ an easy axis parallel to the c axis is favored. The amplitudes of the peaks A and B are about a factor of 2 smaller than the experimentally determined anisotropy energy shown as a dashed horizontal line in the figure. The magnetocrystalline anisotropy energy at a band filling corresponding to stoichiometric YCo$_5$, $\Delta E^0(n)$, is about a factor of 7 smaller than the experimental value. The anisotropy energy is zero when all the d bands are filled (for $q > 54$). When the Fermi energy is lowered into the d band complex, we find an anisotropy energy density $\Delta E^0(k,q)$ which varies in magnitude and sign throughout the BZ. The sign of $\Delta E^0(q)$ in general results from summing compensating contributions. In the sense that it depends on the outcome of a complicated cancellation, the sign of $\Delta E^0(n)$ is accidental. When there are degenerate bands present at a Fermi energy $E_F(q)$, the local contributions appear and vanish when the Fermi energy is displaced by an amount comparable to the spin-orbit coupling constant. If this band degeneracy occurs over a substantial volume of the Brillouin zone then an important contribution to the anisotropy energy can result. For example, if the spin-orbit interaction $\xi_{d}\cdot s$ were to split degenerate energy bands by $\pm \xi_{d}$, as happens for eigenstates with $m = \pm 2$ character, and if 0.03 electrons participated in the splitting, this would yield a peaked structure in $\Delta E^0(q)$ with a maximum value of the anisotropy energy of 2 meV for a typical value of $\xi_{d} = 72$ meV.

We begin with feature A in $\Delta E^0(q)$ at a band filling of $q = 46.6$ [corresponding to an energy about 0.1 eV below the actual Fermi energy $E_F(q = n)$], and then examine the changes that occur when the bands are filled with more electrons until 48 valence states are occupied. The peaked structure of this feature on the scale of $\xi_{d}$ indicates that degenerate energy bands may play a role in the anisotropy energy. In order to study the anisotropy energy density $\Delta \mathcal{E} n(k,q)$, the BZ was first divided into 10 slabs of thickness $0.2(\pi/c)$, parallel to the $\Gamma KM$ basal plane. By integrating the anisotropy energy density in each of these slabs it was found that only a part of the Brillouin zone was responsible for most of the total anisotropy energy of 2 meV. About half of this anisotropy energy originates in the two slabs adjacent to the basal ($\Gamma KM$) plane of the BZ. The two neighboring slabs [between $\pm 0.2(\pi/c)$ and $\pm 0.4(\pi/c)$] together account for a quarter of the anisotropy energy. Thus 75% of the anisotropy energy is generated in 40% of the BZ. In Fig. 3 the anisotropy energy density in the two slabs adjacent to the basal plane is shown in a fishnet-contour plot representation in the $(G_1, G_2)$ plane. For each value of $(k_x, k_y)$ the anisotropy energy density has been averaged by integrating $\Delta \mathcal{E}^n(k,q)$ from $k_z = -0.2(\pi/c)$ to $k_z = +0.2(\pi/c)$ and smoothing with a Gaussian to allow the result to be plotted. The positive sign of the anisotropy energy is seen to be determined by the band structure at and in the vicinity of the high-symmetry point $K$ and along and around the high-symmetry lines $\Gamma K$ and $\Gamma M$. 

---

**FIG. 1.** Convergence of the anisotropy energy of YCo$_5$ as a function of the volume element $v$ used to perform the BZ integral. The number of divisions of the reciprocal-lattice vectors corresponding to each volume are indicated at the top of the figure. The filled circles refer to calculations where only spin-orbit coupling was used (SO). The data points shown as open circles were calculated including spin-orbit coupling and orbital polarization (OP). The horizontal lines were obtained by a least-squares fit through the data points using a weight $1/v$ for each data point. Positive values of the anisotropy energy correspond to a preference for the magnetization to be oriented parallel to the c axis.

**FIG. 2.** Anisotropy energy $\Delta E^0(q)$ versus band filling q. Dashed curve: spin-orbit coupling only. Solid curve: spin-orbit coupling and orbital polarization (mesh $30 \times 30 \times 32$ k points). Dotted curve: spin-orbit coupling and orbital polarization (mesh $6 \times 6 \times 6$ k points). The experimental anisotropy energy is denoted by a horizontal dashed line. In the top of the figure an energy scale is denoted (in eV). The Fermi energy corresponding to $q = n = 48$ is at $-2.06$. 

Within 0.5 eV of the Fermi energy a set of Co minority-spin energy is denoted by the horizontal dashed line at energy interval atom in the unit cell and five rows, which are labeled according to the orbital character. For an arbitrary k point there is no relationship between the orbital character on crystallographically equivalent atoms. The symmetry of the \( \Gamma K M \) direction shown is such that the two Co\( (2c) \) atoms are equivalent and the first and second Co\( (3g) \) atoms are also equivalent. We anticipate our main conclusions by noting that the states which make the most important contribution to the MAE of YCo\( _5 \) are the states with mainly \( d_{\gamma \gamma} \) and \( d_{\chi \chi} \) character which are doubly degenerate at the \( K \) point at \(-2.2 \) eV and at the \( \Gamma \) point where they are almost degenerate with the Fermi energy. The states at \( K \) have mainly Co\( (3g) \) but also some Co\( (2c) \) character, those at \( \Gamma \) have mixed Co\( (3g) \) and Co\( (2c) \) character.

When the spin-orbit coupling is included, the energy bands in this energy range display pronounced differences if the magnetization is directed along or perpendicular to the c axis. In Fig. 6 the minority-spin band structure (in the absence of spin-orbit coupling) and the band structures from which the anisotropy energy density was generated are shown along lines of high symmetry for two directions of the magnetization. Correlating plots of the anisotropy energy density as shown in Fig. 3 with these band structures shows that if the magnetization is directed along the c axis, there is a net energy gain from the splitting of the encircled energy bands because the bands which are shifted to higher energies by the spin-orbit interaction are unoccupied. Thus the encircled energy bands at the \( K \) point are the states mainly responsible for the preference for a c-axis-oriented magnetization for this band filling.

In the absence of spin-orbit coupling, these bands are doubly degenerate at an energy \( \varepsilon = -2.20 \) eV and have mainly Co\-d \( m = \pm 2 \) character (i.e., \( d_{\gamma \gamma} \) and \( d_{\chi \chi} \) symmetry). These states are split by the spin-orbit coupling to \( \varepsilon = -2.27 \) eV and \( \varepsilon = -2.13 \) eV if \( n \parallel c \), and are left nearly degenerate if \( n \perp c \). We expect the contribution to the anisotropy energy from these two states in the vicinity of \( K \) to be maximal at \( \varepsilon = -2.20 \) eV, and to vanish at \( \varepsilon = -2.33 \) eV and \(-2.11 \) eV. This positive contribution to the anisotropy energy density can be seen in Fig. 3. There is a similar contribution to the anisotropy energy from two bands which were nearly degenerate in the absence of spin-orbit coupling from \( \Gamma \) to nearly halfway along \( \Gamma K \) and \( \Gamma M \).

FIG. 3. Anisotropy energy density (from a calculation with spin-orbit coupling) in the basal plane of the Brillouin zone obtained by averaging over a slab of thickness \( 0.4(\pi/a_c) \), for a Fermi energy of \(-2.17 \) eV which corresponds to a band filling of \( q = 46.6 \) and the peak A in Fig. 2. Solid (dashed) contours represent positive (negative) contributions to the anisotropy energy, respectively. Mainly \( K, \Gamma K, \) and \( \Gamma M \) contribute to the preference for a magnetization direction along the c axis.

In Fig. 4 the band structure of the majority-spin (left panel) and the minority-spin (right panel) electrons is shown along the high-symmetry lines in the basal plane. The Fermi energy is denoted by the horizontal dashed line at \(-2.06 \) eV. Within 0.5 eV of the Fermi energy a set of Co minority-spin d bands is separated from the remaining Co d bands.

The d orbital character of the minority-spin bands in the energy interval \(-2.5<\varepsilon<-1.7 \) is shown in Fig. 5 in a representation where the thickness of an energy band is proportional to the orbital character. Because the free-electron-like \( spf \) character in this energy range is small and fairly uniform, it is not shown. There are six columns, one for each atom in the unit cell and five rows, which are labeled according to the orbital character: \( d_{\gamma \gamma}, d_{\chi \chi}, d_{\gamma \chi}, d_{\chi \gamma}, \) and \( d_{\chi \chi} \). For an arbitrary k point there is no relationship between the orbital character on crystallographically equivalent atoms. The symmetry of the \( \Gamma K M \) direction shown is such that the two Co\( (2c) \) atoms are equivalent and the first and second Co\( (3g) \) atoms are also equivalent. We anticipate our main conclusions by noting that the states which make the most important contribution to the MAE of YCo\( _5 \) are the states with mainly \( d_{\gamma \gamma} \) and \( d_{\chi \chi} \) character which are doubly degenerate at the \( K \) point at \(-2.2 \) eV and at the \( \Gamma \) point where they are almost degenerate with the Fermi energy. The states at \( K \) have mainly Co\( (3g) \) but also some Co\( (2c) \) character, those at \( \Gamma \) have mixed Co\( (3g) \) and Co\( (2c) \) character.

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In the absence of spin-orbit coupling, these bands are doubly degenerate at an energy \( \varepsilon = -2.20 \) eV and have mainly Co\-d \( m = \pm 2 \) character (i.e., \( d_{\gamma \gamma} \) and \( d_{\chi \chi} \) symmetry). These states are split by the spin-orbit coupling to \( \varepsilon = -2.27 \) eV and \( \varepsilon = -2.13 \) eV if \( n \parallel c \), and are left nearly degenerate if \( n \perp c \). We expect the contribution to the anisotropy energy from these two states in the vicinity of \( K \) to be maximal at \( \varepsilon = -2.20 \) eV, and to vanish at \( \varepsilon = -2.33 \) eV and \(-2.11 \) eV. This positive contribution to the anisotropy energy density can be seen in Fig. 3. There is a similar contribution to the anisotropy energy from two bands which were nearly degenerate in the absence of spin-orbit coupling from \( \Gamma \) to nearly halfway along \( \Gamma K \) and \( \Gamma M \).

FIG. 4. Energy bands without spin-orbit coupling along the high-symmetry lines in the basal plane of the BZ, for the majority-spin electrons (left panel) and the minority-spin electrons (right panel). The Fermi energy is indicated by the dashed horizontal line.
At \( \Gamma \), these two states are degenerate in the absence of spin-orbit coupling; they are also indicated by filled circles in Fig. 6. They lie very close to the Fermi energy \( \varepsilon_F(q = 48) \) and their splitting provides the only large contribution to the anisotropy energy from in or around the \( \Gamma KM \) plane which favors a \( c \)-axis orientation of the magnetization (see Fig. 7).

The contributions from \( K \), \( \Gamma K \), and \( \Gamma M \) are seen to favor an in-plane magnetization for this band filling. The positive anisotropy energy from around \( \Gamma \) is compensated by a negative anisotropy energy from the remainder of this slab with the anisotropy energy of the total slab being negative. The reason why the anisotropy energy is still positive at \( q = 48 \) (Fig.

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**FIG. 5.** The orbital character of the minority-spin energy bands along the lines \( \Gamma K \) and \( KM \) in the energy interval \( -2.5 < \varepsilon < -1.7 \) is indicated for the six atoms in the unit cell (columns). The thickness of the band is proportional to the orbital character (there is a minimum thickness, however). The Fermi energy is indicated by the dashed horizontal line.

**FIG. 6.** Influence of the magnetization direction on the energy band splittings when spin-orbit coupling is included. The minority-spin energy bands are shown in the left-hand panel for reference. Right-hand panel: magnetization direction along the \( c \) axis. Middle panel: magnetization in the \( \Gamma M \) direction. The splittings of the states which are encircled are discussed in the text. The Fermi energy is indicated by the dashed horizontal line.
FIG. 7. See the figure caption of Fig. 3. The anisotropy energy density is plotted for the actual Fermi energy of -2.06 eV, corresponding to a band filling of \( q = 48 \). Only \( \Gamma \) and a small region around it make a positive contribution to the MAE (favoring a \( c \)-axis orientation).

2) is that there is a positive contribution from the neighborhood of the \((AHL)\) planes of the BZ. Finally, raising the Fermi energy even further to 0.18 eV, corresponding to a band filling of \( q = 49.8 \) (peak \( B \) in Fig. 2), the positive anisotropy energy is generated in the 40% of the zone adjacent to the \( AHL \) plane. It is related to the lifting of a double degeneracy at the \( H \) point.

2. Spin-orbit coupling and orbital polarization

The influence of spin-orbit coupling and orbital polarization is maximal in the special situations when degenerate energy bands with \( m = \pm 2 \) character occur, as at \( \Gamma \) and \( K \), and when \( \mathbf{n} \) is parallel to \( c \). Because the dependence of the minority-spin minority-spin block of the Hamiltonian on the direction of the magnetization is \((BL + \frac{1}{2} \xi_d)\mathbf{n} \cdot \mathbf{n}\), the orbital polarization term in the Hamiltonian essentially represents an enhancement of the spin-orbit coupling parameter. With a Racah \( B \) parameter of about 0.14 eV, and \( L = 0.23 \), the orbital splitting factor \( BL \) is about equal to the spin-orbit splitting \( \frac{1}{2} \xi_d = 0.036 \) eV. When orbital polarization is included in the calculations, the overall shape of \( \Delta E^s(q) \) is unchanged (Fig. 2). However, the amplitude of the anisotropy energy curve increases by about a factor of 4, consistent with a \( \xi^2 \) estimate for the dependence of the anisotropy energy on \( \xi \), using perturbation theory for uniaxial systems. The calculated anisotropy energy of \( \text{YCo}_5 \) of about 3 meV/unit cell is in quite good agreement with the experimental value of 3.8 meV/unit cell.

The spin-orbit coupling gives rise to an anisotropy in the magnetic moment which is also enhanced by the orbital polarization. In Fig. 8 the anisotropy in the magnetic moment and its decomposition into an orbital moment anisotropy and a spin moment anisotropy is shown as a function of the band filling. Typically, the anisotropy in the orbital moment is about a factor of 5 larger than the anisotropy in the spin moment. Projecting out the anisotropy in the orbital moment onto the Co atoms at the 2\( c \) and 3\( g \) sites as a function of the band filling, peaks \( A \) and \( B \) are seen to be mainly attributable to the Co atoms at the 2\( c \) sites. For example, at peak \( A \) the anisotropy in the orbital moment of a Co atom at the 2\( c \) and 3\( g \) site is 0.09 and 0.03\( \mu_B \), respectively. The difference in the anisotropy for the two types of Co atoms is even more pronounced at peak \( B \), where the anisotropy is almost entirely due to that of the Co atoms at the 2\( c \) sites. However, at the Fermi energy of \( \text{YCo}_5 \) (\( q = 48 \)), the situation is reversed and the anisotropy in the 2\( c \) site orbital moment is negligible. For \( q = 48 \) the anisotropy in the total magnetic moment is calculated to be 0.13\( \mu_B \) per unit cell. This anisotropy has been measured\(^7\) and found to have a value of 0.31\( \mu_B \) per unit cell.

The similarity between the \( \Delta E^s(q) \) and the \( \Delta L^s(q) \) curves is striking, and allows us to decompose the anisotropy energy into site-dependent contributions. Using perturbation theory for uniaxial systems, a roughly linear relation between the anisotropy energy and the anisotropy in the orbital moment is expected\(^{56,26} \) with a proportionality factor of \( \frac{1}{2} \xi_d \), or, in the case of orbital polarization, \( \frac{1}{2}(BL + \frac{1}{2} \xi_d) \sim 0.036 \) eV. In the case of degenerate energy bands, one expects a proportionality factor which is about a factor of 2 larger. Although the ratio \( \Delta E^s(q)/\Delta L^s(q) \) certainly is not constant, it is generally of this order of magnitude.

The large measured orbital moments have been thought to be associated with a strong asphericity in the spin density of the Co atoms at the 2\( c \) sites.\(^{10} \) Experimentally, about 60% of the spin density was found to have \( m = \pm 2 \) character. In Sec. III A we already discussed that this is not found in the calculations. However, there is a large density of \( |m| = 2 \) states just below the Fermi energy. In Fig. 9 the minority Co \( d \) density of states is shown as a function of the band filling. The Fermi energy corresponding to \( q = 48 \) states is located on the edge of a steep peak in the density of states (DOS), which extends from about 45.8 to 48.5 filled valence states. The peak consists of 54% Co (2\( c \)) character and 46% Co

![Diagram](Image)
The anisotropy energy as a function of \( q \) is calculated from the density of states calculated with a mesh of \( 6 \times 6 \times 6 \) \( \mathbf{k} \) points (corresponding to a total of 80 irreducible \( \mathbf{k} \) points) with the results for the \( 30 \times 30 \times 32 \) mesh calculation, then we see in Fig. 2 that all of the important features are reproduced very well using the smallest regularly spaced mesh which includes all of the points of high symmetry. We will now show that the most important
The contributions to the anisotropy energy from these \( k \) points are shown in the top six panels of Fig. 11. The arrows in Fig. 11 indicate the positions of the energy levels at each \( k \) point, and a thick arrow denotes degenerate energy levels (in the absence of spin-orbit interaction). Upward (downward) pointing arrows denote minority (majority) spin eigenstates. The anisotropy energy at each \( k \) point is broadened using a Gaussian with a width of 0.06 eV, and multiplied with a weight factor \( w_k \). The total anisotropy energy curve, shown in the bottom left panel, is obtained by summing the weighted contributions from each \( k \) point. The weight factor of a particular \( k \) point is determined by its number density in the BZ. If the magnetization direction is chosen parallel to the \( x \) axis (parallel to the reciprocal-lattice vector \( G_2 \)), then the two \( K \) points in the BZ, \( \frac{1}{2}(G_1 + G_2) \) and \( \frac{3}{2}(G_1 + G_2) \), are equivalent. One of the \( M \) points, \( M_2 = \frac{1}{4}G_2 \), is not equivalent to the other two \( M \) points, \( \frac{1}{2}G_1 \) and \( \frac{3}{2}(G_1 + G_2) \), denoted by \( M_1 \). The same is true of the \( H \) and \( L \) points, respectively. The contributions from the inequivalent \( M_1 \) and \( L_1 \) (\( M_2 \) and \( L_2 \)) points are indicated by the solid (dashed) curves. The weight factors for the special points \( \Gamma, K, M_1, \) and \( M_2 \), (and similarly for \( A, H, L_1 \), and \( L_2 \)) are then chosen as 1/12, 1/6, 1/6, and 1/12.

Broadening the curve in Fig. 11(a) with a Gaussian of width 0.1 eV yields the dashed curve in Fig. 11(b), which has a similar functional dependence on the band filling as the full calculation, represented by the solid curve, but differs by a roughly constant amount. The origin of the two peaks, \( A \) and \( B \), in the lifting of degeneracies at \( K \) and \( H \), respectively, is made particularly clear in this analysis. The origin of the discrepancy between the two curves in Fig. 11(b) can be found by examining Fig. 3. We see that there is a large positive contribution to the MAE from an annular region about \( \Gamma \) but that the contribution from the \( \Gamma \) point itself is negative. The dotted curve in Fig. 2 shows that an only slightly better sampling is required to correct for this error.

In this work and in earlier work\(^\text{33}\) we have found that the lifting of degeneracies at points of high-symmetry and along symmetry lines makes an important contribution to the magnetocrystalline anisotropy energy. In uniaxial systems two situations may arise which are illustrated in Fig. 12. There we sketch the energy band dispersion \( \epsilon_{k_y} \) as a function of the in-plane \( k \) vector \( k_y \) of two states in the vicinity of a point of high symmetry where the two states are degenerate in the absence of spin-orbit coupling. The states with \( m = \pm 2 \) contribute to the anisotropy energy from these \( k \) points.
Character 

The electric-field gradient (EFG) and the crystal-field parameter $A_2^0$ at the RE site are determined by the electrostatic potential at or close to the nucleus; the EFG is determined by the anisotropy in the electrostatic potential at the nucleus while the $4f$ crystal field splitting is determined by the sampling of the electrostatic potential around the maximum in the $4f$ radial wave functions which is about 0.5 a.u. from the nucleus. If the charges which give rise to the potential do not overlap the $4f$ charge density as, for example, in a point charge model, then the second-order crystal-field parameter is proportional to the electric-field gradient with a proportionality factor $-\frac{1}{6}$. For example, $V_{zz} = 10^{20} \text{ V/m}^2$ would correspond to $A_2^0 = -812 K a_0^{-5}$. In this section the EFG and crystal-field parameters calculated for GdCo$_5$ are compared with experimental results and the contributions to both quantities analyzed. We also report the value of the exchange-field coupling rare-earth and valence electron spins as calculated within the LSDA.

4. Comparison with previous work

Nordstrom et al.,$^{53}$ have calculated the MAE of YCo$_5$ making essentially the same approximations as we have made and reaching essentially the same qualitative conclusions. However, some of the technical details of their LMTO-ASA calculations were different, as we saw earlier when discussing the magnetization, and this results in some significant quantitative differences. For example, these authors did not obtain well converged values of the MAE integral. Including spin-orbit coupling only, they found values of the MAE which were positive (thus favoring a $c$-axis orientation) for three different finite integration meshes. The value obtained by extrapolating to infinitesimal volume was, however, negative. The best value of the MAE obtained with spin-orbit coupling and orbital polarization was a factor of 2 smaller than the experimental value and there was a very large uncertainty in this value. By using the improved tetrahedron method,$^{51}$ we have a very small (numerical) uncertainty in our values of the MAE as can be seen in Fig. 1.
The results of our calculations of the EFG of Gd in GdCo5 are given in Table VI. The calculated EFG is about a factor of 2 larger than the measured value and the discrepancy is even larger than that found by Coehoorn. In the table, the EFG is split up into a number of different contributions. The contribution of the semicore states was calculated by taking the self-consistent charge density obtained using 6p valence states and 5p core states and treating the 5p states as bands in one iteration. As these semicore bands are split off from the valence bands, the 5p charge density states can be obtained easily, yielding a contribution of −18% to the EFG. The contribution of the 5p states to the EFG hardly changes if, treated as bands, they are iterated to self-consistency. Thus the semicore contribution is not sensitive to the detailed shape of the potential.

The EFG may be further analyzed in terms of lattice and on-site contributions as defined in Eq. (15). The lattice contribution is only 10^{20} V/m^2, or less than 1% of the EFG, which reflects the small difference from charge neutrality of the atoms. The physical origin of the EFG lies in the deviation from spherical symmetry of the valence charge density on the Gd site. This nonspherical charge density can be resolved into \( l - l' \) contributions for each spin direction (an \( l - l' \) contribution to the charge density is constructed from partial waves within the muffin-tin sphere with angular momentum \( l \) and \( l' \), respectively). 98% of the EFG comes from \( p-p \) and \( d-d \) contributions to the charge density, where the latter is about a factor of 8 smaller than the former. This result is similar to that found by Coehoorn et al. for the Gd compounds with the ThCr2Si2 structure.

These “diagonal” contributions can be broken down further into terms which describe the asymmetry of the \( p_x \), \( p_y \), and \( p_z \) and of the \( d_{2z^2-r^2} \), \( d_{3x^2-r^2} \), \( d_{xy} \), \( d_{yz} \), and \( d_{zx} \) occupation numbers and terms which only involve radial integrals. However, the occupation numbers and the normalization of the radial wave functions depend on the somewhat arbitrary choice of muffin tin (or atomic-sphere) radius. The dominance of the \( p-p \) contribution to the EFG suggests that the origin of the discrepancy with experiment should be sought here.

### Table VI. Crystal-field parameters in GdCo5 separated into on-site and lattice contributions in units of K, together with the expectation values of the radial 4f wave function (in Bohr atomic units). The on-site contribution has been separated into a 5p-5p semicore contribution and valence electron contributions.

<table>
<thead>
<tr>
<th>(( l m ))</th>
<th>( \langle r' \rangle )</th>
<th>( A_l^m(\langle r' \rangle) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>On-site</td>
<td>Lattice</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(40)</td>
<td>2.11</td>
<td>−3</td>
</tr>
<tr>
<td>(60)</td>
<td>8.58</td>
<td>0.5</td>
</tr>
<tr>
<td>(66)</td>
<td>8.58</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 1.
\(^{b}\)Reference 2.
\(^{c}\)Reference 3.

14×10^{21} V/m^2 was calculated for \( V_{zz} \), compared to experimental values of 9.7×10^{21} V/m^2 reported by Steenwijk et al. and 8.2×10^{21} V/m^2 reported by Tomala et al. The larger discrepancies found for these compounds raise the question as to whether the neglected lattice contribution is more important in these materials. However, we should note that the discrepancies are substantially larger than the lattice contributions found in the ionic compound Li_{3}N.
The influence of the nonspherical $4f$ charge density on the valence electron charge density should be studied carefully.

Where the lattice contribution to the potential is already very important for $A^0_l$, it becomes even more so for the higher order crystal-field coefficients; over 80% of the value for $A^0_l$ and $A^0_0$ comes from the lattice contribution. This may be seen in Figs. 13 and 14, where the on-site contribution to the Coulomb potential energy, $V_{\text{on}} = (-e)[4 \pi l/(2l + 1)]U_{l0}(r)$, and the total Coulomb potential energy, $V^0_l(r) = (-e)U_{l0}(r)$, are shown as a function of the distance from the nucleus, $r$. The difference between these two terms is the lattice contribution which scales as $r^4$ for an $A^0_l$ crystal-field parameter. The $4f$ radial charge density, normalized so that $\int_0^r \rho_{4f}(r)dr = 1$, is shown together with the ratio $F(r) = I(r)/I(R)$, where $I(r) = \int_0^r \rho_{4f}(x)\rho_2(x)dx$. The curve $F(r)$ shows that 80% of the $A^0_0$ parameter is accounted for by the integral within 1.5 atomic units of the nucleus. On the other hand, only 30% of the fourth-order crystal-field parameter is generated within the same volume. The magnitude of the fourth-order crystal-field parameter is determined by the overlap of the tail of the $4f$ radial wave function with the $r^4$ lattice potential, while the on-site contribution to the potential is negligible.

The large influence of the lattice potential on the crystal-field parameters indicates that a self-consistent calculation of the nonspherical potential is important. By performing first a self-consistent warped muffin-tin calculation (yielding a potential which is spherically symmetric within the muffin-tin sphere and is represented by a plane-wave expansion in the interstitial region), and then taking the full nonspherical output charge density from a single iteration, we find that the EFG is given quite accurately (within 5% of the self-consistent value). However, the crystal-field parameters calculated in the same way differ from the values calculated with a fully self-consistently calculated charge density by a factor of 2. Whereas the on-site potential is described reasonably well, the lattice potential which should ensure continuity of the potential, has not yet reached its converged value.

In a recent paper, Richter et al.\(^6^0\) have carried out a calculation of $A^0_l(r^3)$ for SmCo$_5$ and, in order to compare with our results,\(^2^8\) also for GdCo$_5$. The basic approximations which they make are the same. They work within the local-spin-density approximation and adopt a perturbative approach to describe the interaction between the atomiclike $4f$ configuration with the self-consistently calculated valence electron density. Their calculation was based upon a linear combination of atomic orbitals band structure formalism which makes it difficult to carry out a detailed comparison of the results. For GdCo$_5$ they find a value of $A^0_0(r^3)$ of $-950$ K compared to our value of $-763$ K. The agreement for the higher $l$ values of $A^0_0(r^l)$, which are dominated by the lattice contribution, is even better. Richter et al. suggest that their non-self-consistent treatment of the non-spherical on-site charge density may be responsible for the 20% difference between their and our values of $A^0_0(r^3)$.

Yamaguchi and Asano have performed FLAPW calculations very similar to ours for a number of compounds including GdCo$_5$.\(^6^1\) Treating the $5p$ states as core (band) states, they obtain values for $A^0_0(r^3)$ in GdCo$_5$ of $-769 \text{ }(-707)$ K compared to our values of $-850 \text{ }(-763)$ K. Whereas we treat the $4f$ states as core states, Yamaguchi and Asano treat them as band states. This may certainly account for the slightly differing results.

3. $B_{\text{EX}}$

Finally, we come to the exchange field. The energy cost to flip the $4f$ spins is phenomenologically described by the ex-
exchange Hamiltonian, Eq. (20). The local exchange integrals calculated for GdCo$_3$ by means of Eq. (25) are $I_{x^2-y^2}$ and $I_{xy}$, and $I_{xy}$ are 77, 113, and 85 meV, respectively. Together with the partial magnetic moments $\Delta n_0 = 0.049$, $\Delta n_0 = 0.078$, and $\Delta n_0 = 0.349$ the exchange energy per spin [Eq. (24)] is 21 meV, corresponding to an exchange field of 360 T. The exchange field is seen to be mainly due to the interaction of the 4$f$ spins with the 5$d$ electrons. The experimental value for GdCo$_3$ as measured with the high-field freepowder method by Liu et al. is 240 T. The agreement is only moderate.

Liebs, Hummler, and Fähnle have improved upon the perturbative approach which we have followed by straightforwardly evaluating the change in the total energy when the 4$f$ moments are rotated. To do this they performed two self-consistent field calculations; one for the ground-state configuration and another for an excited configuration with the rare-earth 4$f$ spins reversed. In this way the conduction-electron spins are allowed to adjust to the reversed exchange field. For GdCo$_3$ they calculate a value for the exchange field of 239 T (Ref. 63) using the LMTO-ASA method with the 4$f$ states treated as open core states. A similar result has been obtained by Liu et al. using the augmented spherical wave method and treating the 4$f$ states as band states. They calculate the exchange field to be 237 T and confirm that there are substantial changes in the conduction-electron moments when the 4$f$ spins are reversed.  

IV. SUMMARY AND CONCLUSIONS

Using first-principles calculations it is shown that an important contribution to the magnetization of YCo$_3$ is due to orbital moments on the Co atoms. Introducing a dependence of the potential on the orbital moment which increases the calculated orbital magnetic moments and the magnetocrystalline anisotropy energy led to better agreement with experiment without changing the functional dependence of the MAE on the band filling $q$.

Contrary to the conventional interpretation, the orbital moments on the two types of Co sites are found to be nearly equal. The anisotropy in the total orbital moment as a function of the band filling is found to follow the same trend as the magnetocrystalline anisotropy energy, and is mainly determined by the anisotropy energy in the orbital moment of the Co atoms at the 2$c$ sites, as had been proposed as an interpretation of a number of experiments. However, the band-filling dependence is such that for YCo$_3$ the anisotropy in the orbital moment on the 3$g$ site is much larger than that on the 2$c$ site. The calculated second-order crystal-field parameter and electric-field gradient are too large in comparison with experiment. Lattice contributions to the potential are shown to be important for a determination of the crystal-field parameter, but not for the EFG. In an analysis of the origin of the magnetocrystalline anisotropy energy, we have found that degenerate energy bands in the neighborhood of the Fermi level play an important role. A large peak in the density of states is found just below the Fermi level, which has mainly Co (2$c$) $d_{x^2-y^2}$ and $d_{xy}$ character. Angle-resolved photoemission should be capable of detecting the large magnetization-direction-dependent energy band splittings which we consider to play an important role in determining the observed magnetocrystalline anisotropy. Our calculations of the anisotropy energy as a function of the band filling indicate that anisotropy energies at least twice as large as those found for YCo$_3$ are, in principle, possible without having to resort to including rare-earth ions. g-factor measurements are necessary to obtain more reliable evidence that a large orbital moment contributes to the magnetic moment.

A large scatter in the experimental data for the hyperfine fields prevents a conclusive comparison with our calculated results.

ACKNOWLEDGMENT

We have had numerous discussions with Reinder Coehoorn about various aspects of the work presented here. We are grateful for his drawing our attention to Refs. 62 and 63.

is not expected to result in any significant changes to the results reported here [M.S.S. Brooks (private communication)]


In calculations for Co, and multilayers which contain Co, we found that iterating the Hamiltonian with spin-orbit coupling included did not lead to different results.


This value differs slightly from the values reported by Eriksson et al. in Ref. 25. For bcc Fe, hcp Co and fcc Ni we calculate orbital moments of 0.077, 0.129, and 0.076 μ_B, respectively, compared to values of 0.06, 0.14, and 0.07μ_B reported by Eriksson et al. 0.09, 0.14, and 0.07μ_b reported by Söderlind et al. Our orbital polarization calculations were carried out with an s,p,d,f basis and with 165, 196, and 196 inequivalent k points, respectively. The corresponding spin moments were 2.144, 1.573, and 0.604μ_B.


When determining the magnetocrystalline anisotropy energy using the Sucksmith-Thompson method, account must be taken of the anisotropy of the magnetic moment. Energies of about 5 meV/unit cell result when this is neglected (Refs. 5 and 6), otherwise an energy of about 3.8 meV/unit cell is found (Ref. 7).

J. Friedel, in The Physics of Metals, edited by J.M. Ziman (Cambridge University Press, Cambridge, 1969). Earlier on we argued that the most important contribution to the c-axis orientation came from the splitting of a doubly degenerate state. The energy gain from such a splitting is ~ξ and is not consistent with the observed quadrupling of the anisotropy energy when the spin-orbit coupling parameter is effectively doubled. The reason for this apparent contradiction is that the number of electrons whose energy is lowered by the spin-orbit interaction increases when the spin-orbit coupling parameter increases. The actual dependence of the anisotropy energy on ξ depends on the band dispersion.


