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# Calculation of magnetic anisotropy energy in $YCo_5$

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**Abstract**

Previous calculations of the magnetic anisotropy of $YCo_5$ found values of about 0.6 meV/f.u. compared to the experimental value of 3.8 meV/f.u. These were all performed using LDA with and without including nonspherical corrections. We have applied GGA including non-spherical and relativistic $p_{1/2}$ corrections which results in the magnetic anisotropy energy to be 1.4 meV/f.u. This means a smaller than previously assumed portion of the magnetic anisotropy comes from orbital polarization and similar effects beyond density functional theory.


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*Keywords:* Magnetic anisotropy; Electronic structure; Magnetic moments

The intermetallic compounds $RECo_5$ (RE = rare earth) have been studied both experimentally [1,2] and theoretically [3–10] in the past due to their qualifications as permanent magnet materials. These materials are found to have a large magnetic anisotropy energy (MAE), which is defined as the difference between the ground-state energies due to rotation of the magnetic field. The large MAE found in these materials is due to two effects. The first effect is the spin–orbit interaction of the partially-filled, localized 4f moment on the RE atom. The second effect is the spin–orbit interaction of the Co 3d orbitals within the anisotropic crystalline environment. These effects both play important roles in understanding the MAE of $RECo_5$ compounds [11]. $SmCo_5$ and $YCo_5$ [11] form in the same crystal structure, but the MAE of $YCo_5$ (3.8 meV/f.u.) [12] is only about a factor of 4 smaller than that of $SmCo_5$ (16 meV/f.u.) [12]. While the partially-filled localized 4f shell on the RE atom strongly enhances the MAE in $SmCo_5$, the anisotropic environment of the 3d Co states gives a substantially larger value for the MAE in $YCo_5$ than in hcp Co (0.065 meV/f.u.) [13]. A theoretical understanding of the MAE of $RECo_5$ compounds should attempt to separate the effects of 3d Co spin–orbit effects from that of the 4f RE localization effects.

The "large" values of MAE for $RECo_5$ compounds, on the order of 1–20 meV/f.u., are still fairly small energy differences within density functional theory (DFT) calculations. Calculations of MAE require a dense k-point mesh and energy convergence of $10^{-3}$ eV or better out of a total energy on the order of $10^6$ eV. The all-electron, full-potential scheme which we employ means that using a dense mesh is even more time consuming.

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Table 1
Previous calculations of the magnetic anisotropy energy of $YCo_5$

| | |
|---|---|
| LMTO-ASA[a] | −0.40 meV/f.u. |
| LMTO-ASA[b] | 0.60 meV/f.u. |
| LMTO-ASA[c] | 0.50 meV/f.u. |
| LCAO[d] | 0.58 meV/f.u. |
| LMTO-ASA[e] | −0.39 meV/f.u. |
| LMTO-ASA[f] | −0.94 meV/f.u. |
| LMTO-ASA[g] | −0.82 meV/f.u. |

[a] Ref. [4]
[b] Ref. [7]
[c] Ref. [8]
[d] Ref. [10]
[e] V.P. Antropov, unpublished.
[f] S.V. Halilov, unpublished.
[g] R. Sabirianov, unpublished.

However, previous calculations of $YCo_5$ showed that the MAE converges quickly to its equilibrium value [7,10] with the number of k-points, which allows for reliable full-potential calculations.

Previous calculations of the MAE of $YCo_5$ have found values between −0.5 and 0.6 meV/f.u., much smaller than the experimental value of 3.8 meV/f.u. (Table 1) Many authors [4–10] have used the so-called orbital polarization correction (OPC) [14], an ad hoc addition to density functional calculations which artificially increases the spin–orbit interaction which is underestimated in conventional DFT calculations in order to get good agreement with the experimental value of the MAE. The OPC, by construction, increases the orbital moment and the MAE, but the microscopic justification for this procedure is questionable. While it is likely that lack of correlation effects in DFT lead to an underestimation of the MAE in $YCo_5$, it has been argued that the physics of the underestimation of the orbital moment in DFT is quite different from that assumed in the OPC [15,16]. The previous calculations have a large variation in the DFT value of the MAE (Table 1) which has been overlooked when OPC has been included. This makes it impossible to judge the role of the correlation effects beyond DFT in the MAE of $YCo_5$. In this paper we attempt a more systematic study of the MAE of $YCo_5$.

The previous calculations have been performed using the linearized muffin-tin orbital (LMTO) method within the atomic sphere approximation (ASA) or the linear combination of atomic orbitals (LCAO) method. Also, all of these calculations have used the local density approximation (LDA). In many circumstances, especially for the 3d metals, the generalized gradient approximation (GGA) yields better agreement with experiment for ground state energies than LDA. For example, GGA correctly finds that bcc Fe has a lower energy than fcc Fe which had not been found using LDA [17]. We will show that the inclusion of gradient corrections to the exchange-correlation potential in GGA and inclusion of the nonspherical components to the Hamiltonian and potential improves the calculated value of the MAE. The importance of these factors needs to be studied in order to understand how significant a role strong-correlation effects play in the MAE of $YCo_5$.

Electronic structure calculations were performed using the self consistent full potential linearized augmented plane wave (FLAPW) [18] method within DFT [19]. The LDA of Perdew and Wang [20] and the GGA of Perdew et al. [21] were used for the correlation and exchange potentials. Calculations were performed using the WIEN97 package [22] and the WIEN2k package [23]. Local orbital extensions [24] were included in order to accurately treat the upper core states and to relax any residual linearization errors. A well converged basis consisting of approximately 300 LAPW basis functions in addition to the local orbitals was used with both Y and Sm sphere radii set to 2.31 a.u. The results varied only within a few percent for reasonable choices of atomic radii (2.0–3.0 a.u.). The plane-wave cut-off parameters RKMAX and GMAX were chosen as 9 and 14, respectively. Further increase of the cut-off parameters did not change the results in an appreciable way. Spin–orbit (SO) interaction was incorporated using a second variational procedure [25], where all states below 1.5 Ry were included. Increasing this energy to 3.5 Ry did not change the final results. Finally, convergence with respect to the number of $k$-point in the Brillouin zone is illustrated in Table 2.

The crystal structure of $YCo_5$ is that of $CaCu_5$ (P6/mmm, No. 191). The experimental values of $a$

and $c/a$ used in the calculation are 9.313 a.u. and 0.806. The Co sites are separated into two sets of inequivalent atoms, CoI(2c) having 2-fold multiplicity and CoII(3g) having 3-fold multiplicity (Fig. 1). Including spin–orbit coupling into the calculation lowers the symmetry when the field lies along the plane, separating the 3 atoms corresponding to CoII(3g) into two inequivalent sites which have multiplicities of 2 and 1, respectively, [26].

This lowering of crystal symmetry due to inclusion of spin–orbit interaction is crucial to a correct understanding of the MAE of $YCo_5$. Before spin–orbit is included, the crystal symmetry is P6/mmm (No. 191) which is not changed when the magnetic field is applied along the $z$-axis. However, application of the field along the $x$-axis reduces the crystal symmetry to Pmmm (No. 47). While it is tempting to perform each calculation using the highest possible crystal symmetry, this may lead to a systematic error. Even when spin–orbit is not included, the program generates small amplitude components of the charge density with the wrong symmetry leading to errors in the energy on the order of 1–5 meV, the same order of magnitude as the MAE. These components slowly disappear with the number of $k$-points which makes $k$-point convergence very difficult. More stable results could be obtained by using the lowest common symmetry (Pmmm) for all field directions.

Table 2
$k$-point convergence and the exchange-correlation functional dependence of magnetic anisotropy energy of $YCo_5$

| | |
|---|---|
| LDA $8 \times 8 \times 8$ | 0.54 meV/f.u. |
| LDA $8 \times 8 \times 8$ - $p_{1/2}$ | 1.31 meV/f.u. |
| LDA $10 \times 10 \times 10$ | 0.50 meV/f.u. |
| LDA $12 \times 12 \times 13$ | 0.56 meV/f.u. |
| GGA $8 \times 8 \times 8$ | 1.51 meV/f.u. |
| GGA $8 \times 8 \times 8$ - $p_{1/2}$ | 1.39 meV/f.u. |
| GGA $10 \times 10 \times 10$ | 1.61 meV/f.u. |
| GGA $12 \times 12 \times 13$ | 1.63 meV/f.u. |

Before discussing the MAE for $YCo_5$, let us discuss the spin and orbital magnetic moments calculated using FLAPW. In order to compare with previous calculations, a selection of past results are given here. The values given in Table 3 are the FLAPW results by Daalderop (which did not include orbital moments) [7], the LMTO-ASA results of Yamaguchi [8], and the LCAO results of Steinbeck [10]. The orbital moment is fairly substantial in the last two cases, on the order of about 10% of the spin moment, which increases the total moment of the system. Our results for the spin and orbital moments obtained using the FLAPW method are given in Table 4 along with the experimental values, where available. (While the reduced symmetry separates the CoII(3g) site

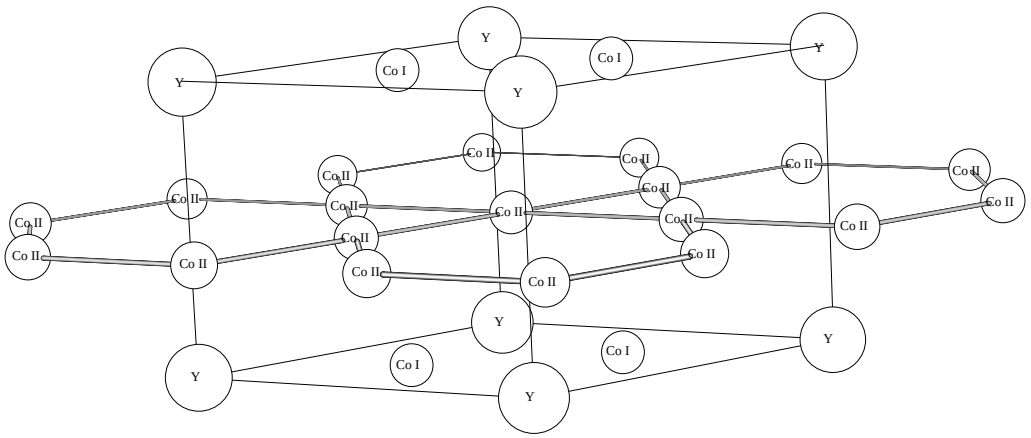


Fig. 1. Crystal structure of $YCo_5$. While Y forms a triangular lattice and CoI forms a hexagonal lattice in the $xy$ plane, the CoII lattice is neither triangular nor hexagonal in the $xy$ plane.

Table 3
Examples of spin and orbital moments for $YCo_5$ calculated by different methods [7,8,10]

| Calculated moment | FLAPW [7] | LMTO-ASA [8] | | | LCAO [10] | | |
|---|---|---|---|---|---|---|---|
| | Spin | Spin | Orbital | Total | Spin | Orbital | Total |
| Y | −0.27 | −0.37 | 0.03 | −0.34 | −0.18 | −0.03 | −0.21 |
| CoI(2c) | 1.46 | 1.47 | 0.11 | 1.58 | 1.46 | 0.13 | 1.59 |
| CoII(3g) | 1.51 | 1.66 | 0.13 | 1.79 | 1.52 | 0.11 | 1.63 |
| Interstitial | −0.28 | n/a | n/a | n/a | n/a | n/a | n/a |
| Total | 6.90 | 7.55 | 0.64 | 8.19 | 7.30 | 0.57 | 7.87 |

Table 4
Spin and orbital moments for $YCo_5$, calculated in the present work, along with experimental values, where available [27]

| | Calculated spin moment | Calculated orbital moment | Experimental spin moment [27] | Experimental orbital moment [27] |
|---|---|---|---|---|
| Y | −0.16 | 0.01 | | |
| CoI(2c) | 1.58 | 0.11 | 1.44 | 0.28 |
| CoII(3g) | 1.54 | 0.13 | 1.31 | 0.46 |
| Interstitial | −0.57 | n/a | n/a | n/a |
| Total | 7.06 | 0.62 | | |
| Spin + orbital | | 7.68 | | 8.30 |

into two inequivalent sites, for ease of comparison the average of the Co moments at these two sites is used for CoII(3g) site in the table.) The total spin moment agrees very well with the FLAPW value by Daalderop. The interstitial contribution to the spin moment is larger in our calculation, but this may be due to the particular choice of muffin-tin radius which may increase or decrease the size of the interstitial region. The magnitude of the orbital moment is very similar to Yamaguchi and Steinbeck. Comparing to the experimental value [27], the CoI(2c) spin moment is larger than that at the CoII(3g) site, though by a smaller amount than found experimentally. Similarly, the orbital moment is larger at the CoII(3g) site than at the CoI(2c) site, though by less than seen experimentally.

Previous DFT calculations of the MAE for $YCo_5$ are given in Table 1. As can be seen, these values are significantly smaller than the experimental value of 3.8 meV/f.u. The deviation from the experiment has been attributed to orbital polarization. In most of these calculations, the directions of the magnetization are $\mathbf{n}_1 = \mathbf{z}$ and $\mathbf{e}_2 = \mathbf{x}$ in the energy differences ($\mathrm{MAE} = E(\mathbf{n}_2) - E(\mathbf{n}_1)$). While the bond directions in the hexagonal unit cell are usually chosen as (0 0 1) and (−1 2 0), the energy difference has been computed, as in the previous calculations, between (0 0 1) and (1 0 0).

These previous calculations using LMTO-ASA (linearized muffin tin orbitals within the atomic sphere approximation) [4,7,8] and FP-LCAO (full-potential linear combination of atomic orbitals) [10] agree in terms of the band structure and the calculated spin and orbital moments, but not in the MAE. While full potential methods, including our calculation and the previous LCAO calculation [10] must arrive to the same result at self-consistency, differences can arise in the LMTO-ASA depending on its implementation. In LMTO-ASA the same expansion of the Bloch states is used and the same Hamiltonian equation [28] is solved in each of the codes. However, variations in the muffin-tin radii

and differences in the treatment of the Coulomb potential between muffin-tin spheres can lead to differences $\sim$1–5 meV, the order of the MAE in $YCo_5$, even when the results appear fully converged. Therefore, full-potential methods may be better than the ASA for calculating sensitive phenomena such as the MAE.

While LDA-LMTO-ASA results obtained with different versions of the LMTO code differ greatly, most of them even having the wrong sign for the MAE, the LDA-LCAO calculation and our LDA-LAPW results, both of which do not use any shape approximation for the crystal potential, agree very well. It is generally believed that relativistic effects are important only near the nuclei where the crystal potential is very symmetric, so ASA methods are good for evaluating relativistic effects. Indeed, the orbital moment, calculated using LMTO-ASA are close to those without any shape approximation (Tables 3 and 4). However, the MAE is a small difference in the relativistic effects, depending on the magnetization direction, and it is possible that this small difference can manifest itself further away from the nucleus, so it remains unclear whether the ASA is sufficiently accurate for the MAE. The large variation in the LMTO results, depending upon which code is used, indicates that nonspherical effects are important. To check this conclusion, we repeated our calculations, now removing all nonspherical components from both the charge density expansion inside the MT spheres and the Hamiltonian itself (this is a more severe approximation than the ASA, for the latter implicitly includes some nonspherical effects in the overlap regions). We found that the MAE for $YCo_5$ is $-9.34$ meV/f.u. without nonspherical components compared to 1.51 meV/f.u. when they are included using GGA and $-0.83$ meV/f.u. compared to 0.53 meV/f.u. using LDA. The nonspherical corrections are even more important in the GGA calculation.

Initially, we computed the MAE using the FLAPW WIEN97 package [22] without including the $p_{1/2}$ corrections. We found MAE of about 0.5 meV/f.u. using LDA, which agrees with the previous full-potential calculation [10], increasing to 1.6 meV/f.u. when gradient corrections were included (Table 2). The integration was performed using the modified tetrahedron method [29]. Special attention has been paid to convergence with respect to the number of **k**-points in the total unit cell. Increasing the density of the mesh from $8\times8\times8$ to $10\times10\times10$ changed the MAE in $YCo_5$ by only about 10%. Increasing the mesh to $12\times12\times13$ had nearly no change in the GGA results while the LDA results changed again by about 10%, closer to the $8\times8\times8$ value. Calculations of the MAE with a smaller number of **k**-points, which are not given here, show a larger variation in values. The number of **k**-points is considerably smaller than what is found in calculations of the MAE of elemental Fe, Co, or Ni [30] which is not surprising since the MAE is much larger. This number of **k**-points is similar to those used in previous calculations of the MAE in $YCo_5$ [4,7,8,10], with somewhat faster convergence, perhaps due to the improved tetrahedron integration method [29].

The most recent version of the WIEN code, WIEN2k [23], includes the so-called $p_{1/2}$ extention [18]. It is known that a solution of the Dirac radial equation for $l=1$ and $s=\frac{1}{2}$ (i.e., the $p_{1/2}$ state), being finite at the nucleus, cannot be adequately represented as a linear combination of a number of solutions of the radial Schrödinger equation with $l=1$ which are all zero at the nucleus. This difficulty can be circumvented if the second variational basis, scalar-relativistic by construction, is augmented by a few fully relativistic local orbitals corresponding to $l=1$ and $s=\frac{1}{2}$. This extension is very important for atoms with shallow semicore p-states. The $p_{1/2}$ corrections can be considered as a way to better approximate the second variational basis set with spin–orbit to the basis set of the nonvariational Pauli equation. In principle, a large effect of the $p_{1/2}$ extensions may signal important relativistic effects beyond spin–orbit which has been included here. In our case, both Y and Co have semicore p-states at 3–5 Ry below the Fermi level, so we included the $p_{1/2}$ local orbitals for both atoms.

Calculations with and without the $p_{1/2}$ corrections are compared in Table 2. Inclusion of the $p_{1/2}$ corrections reduces the GGA results from 1.6 to 1.4 meV/f.u. However, the LDA results increased from 0.5 to 1.3 meV/f.u. (Table 2) Note

that our calculations *without* the $p_{1/2}$ corrections agree well with the previous full-potential LCAO calculation [10], however, this correction substantially change the results.

There is still significant difference between the calculated value of the MAE and experiment. This may be due to enhanced relativistic effects on Co beyond spin–orbit, but the light mass of Co makes this unlikely. This may also be due to relativistic effects on Y. We have repeated our calculation of the MAE of $YCo_5$ but removed the Y atom from the cell without changing the remaining Co substructure. The calculated MAE is 1.4 eV/f.u. compared to 1.6 meV/f.u. in $YCo_5$. It seems unlikely that Y plays a significant role in the MAE in $YCo_5$. The remaining possibility is the inclusion of correlation effects beyond LDA/GGA which have not been investigated here, which can be included using either OPC (which have been used successfully before [4,7,8,10]) or LDA + U (which we are presently investigating).

To conclude, we performed first principle calculations of the MAE of $YCo_5$ using a highly accurate LAPW code without any approximation to the shape of the crystal potential. We found that with a correct treatment of $p_{1/2}$ states both LDA and GGA produce MAE of 1.3–1.4 meV/f.u. without OPC or any other strong-correlation correction, substantially larger than what has been seen in previous calculations. However, these calculations still underestimate the MAE. We have also found that nonspherical corrections are numerically important so that full potential calculations are preferable over those done within the ASA.

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