Magnetic properties of $SmCo_5$ and YCo_5

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We have studied the magnetic moments and magnetic anisotropy energy (MAE) of YCo_5 and $SmCo_5$ using full-potential linear augmented plane wave (LAPW) electronic structure calculations. Most previous calculations of the MAE for YCo_5, using local density approximation (LDA) for the exchange-correlation potential, have found values significantly smaller (~0.6 meV/f.u.) than experiment (~3.8 meV/f.u.). The rest of the MAE is attributed to many body corrections. Our LAPW calculations using the generalized gradient approximation (GGA) instead of LDA and including nonspherical corrections give values ~1.5 meV/f.u. The Co magnetic moment of $YCo_{5-x}Cu_x$, unlike the prediction of the virtual crystal approximation, decreases slowly with impurity concentration until dropping suddenly to zero at a critical dopant concentration. Correlation effects were found to be crucial for the MAE in $SmCo_5$. While GGA calculations give MAE for $SmCo_5$ of the wrong sign, including the LDA+U, correction brings it to ~21 meV/f.u., in good agreement with the experimental value of 13–16 meV/f.u. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1556154]

$RECo_5$ (RE=rare earth) compounds belong to a class of hard magnetic intermetallic 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. $SmCo_5$ and YCo_5[1] form in the same crystal structure, but the MAE of YCo_5 (3.8 meV/f.u.)[2] is only about a factor of 3–4 smaller than that of $SmCo_5$ (13–16 meV/f.u.)[3–5] while the MAE of hcp Co (0.065 meV/f.u.) is much smaller.[6] The large MAE found in these materials is due to (a) the spin-orbit (SO) interaction of the partially filled, localized 4f moment on the RE atom and (b) the spin-orbit interaction of the Co d orbitals within the anisotropic crystalline environment.

Electronic structure calculations were performed using the self-consistent full potential linearized augmented plane wave (FLAPW)[7] method within density functional theory (DFT).[8] The local density approximation (LDA) of Perdew and Wang[9] and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof[10] were used for the correlation and exchange potentials. Calculations were performed using the WIEN97 package[11] and the WIEN2k package.[12] Local orbital extensions[13] 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 Y, Co, and Sm sphere radii set to 2.31 a.u.. Spin-orbit (SO) interaction was incorporated using a second variational procedure.[14]

The crystal structure of YCo_5 and $SmCo_5$ 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 for

YCo_5 and 9.452 a.u. and 0.792 for $SmCo_5$. The Co sites are separated into two sets of inequivalent atoms, Co(2c) having twofold multiplicity and Co(3g) having threefold multiplicity (Fig. 1). Including spin-orbit coupling into the calculation lowers the symmetry when the field lies along the plane (to Pmmm, No. 47), separating the three atoms corresponding to Co(3g) into two inequivalent sites which have multiplicities of 2 and 1.[15]

LDA (or GGA) calculations incorrectly pin all of the f-orbitals at the Fermi energy (E_F) in $SmCo_5$ and other systems containing unfilled f orbitals. In order to eliminate this problem, the previous electronic structure calculations for $SmCo_5$ did not treat the f orbitals as valence electrons.[16,17] With the contribution of the f orbitals left out, the calculated magnetic moments calculated using these methods are simi-
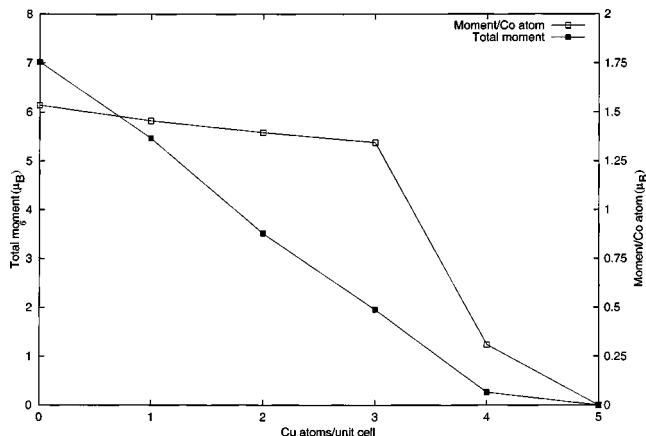

FIG. 1. Total and averaged Co moment of $YCo_{5-x}Cu_x$ as a function of doping.

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lar to those of YCo_5 and the MAE is severely underestimated (~ 7 meV/f.u.[17] compared to the experimental value of 13–16 meV/f.u.[3–5]). Since the increase in the magnetic moments and MAE of $SmCo_5$ compared to YCo_5 is due to the presence of the unfilled f orbitals, such treatment of the f orbitals does not seem justifiable. Our calculations have included the f orbitals within the calculation using the LDA+U formalism which adds a Hubbard repulsion U to more properly split apart the localized f orbitals above and below E_F.[18,19]

Doping the Co sites with nonmagnetic atoms in $SmCo_5$ and YCo_5 changes the local Co crystalline environment and reduces the magnetic moments. It was observed that the total magnetization and the anisotropy field of annealed $Sm(Co_{5-x}Cu_x)$ decrease linearly as a function of Cu concentration, becoming zero around $x=3$.[20] The magnetic moment in $Y(Co_{5-x}Ni_x)$ shows a more sudden drop near the same critical concentration $x=3$.[21] In a recent linear muffin-tin orbital-atomic sphere approximation (LMTO-ASA) calculation, Yamada et al.[22] used the virtual crystal approximation (VCA)[23] for $Y(Co_{5-x}Ni_x)$, finding a modest drop in the magnetic moments around $x=2.5$ in an otherwise fairly linear regime.[22] However, no sudden drop in the magnetic moments was seen as found experimentally. Our supercell calculations of $Y(Co_{5-x}Cu_x)$ show that the total magnetic moment/unit cell decreases fairly linearly with Cu doping (Fig. 1), similar to the previous results found with Ni doping.[22] This suggests that the effect of Cu doping on magnetism is mostly due to the electronic doping, not simply to the nonmagnetic nature of Cu. However, if that were the case, one would not only expect total magnetic moment reduction but also somewhat delocalized Co moments, as expected in the VCA.[23] However, a closer inspection of our results reveals that the magnetic moment on Co is fairly local and little affected by the Cu doping until $x \sim 2.5$ where the moment rapidly falls to a small value before gradually decaying to zero (Fig. 1). We conclude that Co in doped YCo_5 can occur either in a high-spin or in a low-spin state, depending on the local environment. Presumably, in disordered alloys both spin states are present, the low-spin state in the locally Cu-rich regions, and the high-spin state elsewhere. The crossover concentration of $x \sim 2.5 - 3$ is characterized by a change from mostly high-spin Co to mostly low-spin Co. This crossover concentration is the same as has been observed experimentally for the decrease of the total magnetization.[24,25]

The previous calculations of the magnetic moments in $SmCo_5$ treated Sm f orbitals either as core rather than valence electrons[16] or not in the calculation at all.[17] The calculated moments in these calculations did not include the Sm f contribution. However, the moments for the $Co(2c)$ ($1.53 \mu_B$) and the $Co(3g)$ sites ($1.56 \mu_B$) agree well with the previous calculations.[16] The total spin moment of $12.2 \mu_B$ and the Sm orbital moment of $-2.8 \mu_B$ give a total magnetic moment of $9.4 \mu_B$ which agrees well with the experimental value of $8.9 \mu_B$.[26,27] The orbital moment of the Co d orbitals was found to be $\sim 0.1 \mu_B$, much smaller than that of the Sm f orbitals.

TABLE I. 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]Reference 28.
[b]Reference 29.
[c]Reference 30.
[d]Reference 31.
[e]V.P. Antropov (unpublished).
[f]S. V. Halilov (unpublished).
[g]R. Sabirianov (unpublished).

The MAE is more sensitive to the unfilled Sm f orbitals and is far more difficult to compute. Previous LDA 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 I). Many authors[28–31] have used the so-called orbital polarization correction (OPC), an ad hoc addition to density functional calculations which artificially increases the spin-orbit interaction which is underestimated in conventional DFT calculations. 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.[18,19] 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 in the charge density expansion inside the muffin-tin spheres and in 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[11] without including the $p_{1/2}$ corrections. The most recent version of the WIEN code, WIEN2k,[12] includes the so-called $p_{1/2}$ extension,[7] a relativistic correction for the $\ell=1$ and $j=1/2$ (i.e., the $p_{1/2}$ state) states where the radial dependence of the wave function is not treated correctly in the second variational application of the spin-orbit

TABLE II. The k-point convergence and the exchange-correlation functional dependence of magnetic anisotropy energy of YCo_5.

LDA $8\times8\times8$	0.54 meV/f.u.
LDA $8\times8\times8-p_{1/2}$	1.31 meV/f.u.
LDA $10\times10\times10$	0.50 meV/f.u.
LDA $12\times12\times12$	0.56 meV/f.u.
GGA $8\times8\times8$	1.51 meV/f.u.
GGA $8\times8\times8-p_{1/2}$	1.39 meV/f.u.
GGA $10\times10\times10$	1.61 meV/f.u.
GGA $12\times12\times13$	1.63 meV/f.u.

TABLE III. MAE of $YCo_{5-x}Fe$ and $SmCo_{5-x}Fe_x$ calculated at lattice parameters of the pure compounds.

YCo_5	1.51 meV/f.u.	$SmCo_5$	21.6 meV/f.u.
YCo_3Fe_2	−0.90 meV/f.u.	$SmCo_3Fe_2$	16.6 meV/f.u.
YCo_2Fe_3	0.00 meV/f.u.	$SmCo_2Fe_3$	4.79 meV/f.u.
YFe_5	−1.59 meV/f.u.	$SmFe_5$	3.94 meV/f.u.

interaction. Calculations with and without the $p_{1/2}$ corrections are compared in Table II. 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 II). Note that our calculations *without* the $p_{1/2}$ corrections agree well with the previous full-potential linear combination of molecular orbitals calculation,[31] however, these corrections substantially change the results.

Within the LDA+U formalism, the values of U and J represent the on-site Coulomb repulsion and the onsite exchange, respectively. We estimated U and J for f electrons in a quasiatomic approximation through the relations $U = \partial \epsilon_{f\downarrow}/\partial n_{f\uparrow}$ and $J = \partial(\epsilon_{f\uparrow} - \epsilon_{f\downarrow})/\partial(n_{f\uparrow} - n_{f\downarrow})$, where ϵ_f is the energy of the quasiatomic f level and n_f the occupancy.[19] The values of $U = 5$ eV and $J = 0.8$ eV were found for Sm in $SmCo_5$ and the electronic structure and, more importantly, the MAE were found not to change much with U. When U and J are not included in the calculation, the GGA calculation gives the f orbitals fixed at the Fermi energy with a MAE of −11.0 meV/f.u. The inclusion of U and J in the LDA+U calculation gives 21.6 meV/f.u.,[32] agreeing well with the measured value of 13–16 meV/f.u.[3–5]

The MAE has been calculated for two series of doped systems, $Y(Co_{5-x}Fe_x)$ and $Sm(Co_{5-x}Fe_x)$. The minimum energy configuration for both of the pure systems was found to lie at the experimental lattice parameters. However, the effect of changes in the volume and c/a ratio of the lattice due to the dopant atoms has not been considered, but the lattice parameters of the pure compounds have been used (Table III). In both cases, the magnetic moments increase slightly with the replacement of Co with another magnetic atom, Fe. However, the MAE of $Y(Co_{5-x}Fe_x)$ and $Sm(Co_{5-x}Fe_x)$ decrease as Fe is added, so Fe is a poor dopant to increase the MAE in these compounds. Further study of the changes of the band structure and density of states will hopefully lead to a more systematic understanding of the effects of doping on the MAE in these systems.

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[32] It seems that the results may be sensitive to whether the LDA+U correction is applied before or after the spin-orbit correction; the results quoted in this paper correspond to the latter, but we find that the MAE in $SmCo_5$ is ~9 meV smaller in the former case.