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Calculated magnetocrystalline anisotropy of existing and hypothetical MCo_5 compounds

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Abstract

The magnetic properties, lattice parameters and formation enthalpies of existing and hypothetical MCo_5 compounds ($M = Y$, La, Th, Mg, Ca and Sr) are calculated within the framework of density functional theory. In these compounds the magnetocrystalline anisotropy energy is dominated by itinerant Co 3d contributions. Band energy calculations suggest that—within in a rigid band picture—anisotropy energies of comparable size to those of hard magnetic materials containing rare earths could be obtained by hole doping of YCo_5, e.g. by the substitution of Ca or Mg for Y. This idea is confirmed by the presented total energy calculations. However, the calculated enthalpies of formation suggest that $CaCo_5$ and $MgCo_5$ could only be prepared by non-equilibrium methods.

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Large magnetocrystalline anisotropy energy (MAE) is one of the primary reasons for the success of the RCo_5 compounds, principally $SmCo_5$, as base materials for permanent magnets. In general, there are two distinct contributions to the MAE in these systems: the one due to the localized 4f electrons of the rare earth (R) and that of the itinerant 3d electrons of cobalt.

In this study we focus on the magnetic properties of MCo_5 compounds ($M \neq R$), where the MAE is dominated by the Co 3d contributions. Band energy calculations [1,2] suggest that—within in a rigid band picture—much higher anisotropy energies could be obtained by hole doping, e.g. by substitution of Ca for Y.

We have investigated this possibility by means of total energy calculations in the framework of density functional theory. The calculations were performed with the relativistic version [3] of the full potential local orbital method [4] (RFPLO). In this scheme the 4-component Kohn–Sham–Dirac equation, which implicitly contains spin–orbit coupling up to all orders, is solved self-consistently. The Perdew–Wang [5] parameterization of the exchange-correlation (XC) potential in the local spin-density approximation (LSDA) was used. Orbital polarization corrections (OPC [6]) for Co 3d states were included in the calculations by adding a term $E^{\mathrm{opc}} = -1/2\sum_{\sigma} B_{\sigma} L_{\sigma}^{2}$ to the LSDA expression for the XC energy, where B_{σ} are Racah parameters and L_{σ} are the orbital moments of the Co 3d spin sub shells. Geometry

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optimizations and the calculation of formation enthalpies were done with the scalar relativistic version of FPLO [4] (except for $ThCo_5$, where spin–orbit coupling was included). The convergence with respect to the basis set was checked by employing a minimum basis (Y 4spd5spd; Co 3pd4sp) and an enhanced basis set (Y 4spdf5spd; Co 3spd4spdf) (and corresponding basis sets for the other compounds). With the exception of La, where the inclusion of 4f states is important, the effect of the enhanced basis was small. The convergence of the MAE with respect to Brillouin zone integration was checked with a series of calculations from 1728 up to 46656 **k**-points in the full Brillouin zone.

YCo_5 and $LaCo_5$. YCo_5 is a prototype for the investigation of itinerant magnetism within the RCo_5 series and has been studied in some detail both experimentally and theoretically (see Ref. [1] for an overview). Our calculated total moment of $8.07\,\mu_B$/f.u. including OPC is in good agreement with the measured value of $8.3\,\mu_B$, and also the anisotropy between the easy *c*-axis and the in plane direction of about $-0.3\,\mu_B$ is well reproduced by the calculations ($-0.22\,\mu_B$). The individual magnetic moments for the three crystallographically inequivalent sites are given in Table 1. The orbital moments for the two Co sites agree well with those derived from hyperfine field measurements (0.26 and $0.24\,\mu_B$), but are considerably smaller than those derived from spin-polarized neutron diffraction measurements (0.46 and $0.28\,\mu_B$; see Ref. [1] and references therein).

LSDA without OPC yielded $7.60\,\mu_B$ for the total magnetic moment, which is considerably less than the experimental value, due to an underestimation of the Co orbital moments. The LSDA values for the orbital moments of Co are $0.13\,\mu_B$ and $0.12\,\mu_B$ for the 2c and 3g site, respectively. These results are in a qualitative agreement with previous calculations, where total moments in the range of 7.4–$7.9\,\mu_B$ (LSDA) and 7.8–$8.7\,\mu_B$ (LSDA with OPC) were found. We note however, that most of the previous relativistic calculations did not use full potential schemes and thus give less reliable values than the present calculations.

The total moment of $LaCo_5$ calculated with OPC, $8.12\,\mu_B$, is close to the measured moment of about $8.5\,\mu_B$ [7]. LSDA yields $7.58\,\mu_B$. In contrast to YCo_5, the orbital moments on the two Co sites are nearly identical (Table 1) and the orbital contribution to the total moment is slightly enhanced.

Experimental values for the MAE of both YCo_5 and $LaCo_5$ are of the order 0.8 meV per Co atom and thus more than a factor 10 larger than the MAE of hcp-Co, which makes these compounds interesting both for fundamental research as well as for practical applications. Table 2 shows the calculated MAE together with the experimental values. LSDA predicts the correct sign of the MAE for YCo_5 and $LaCo_5$, but strongly underestimates its strength, which was also found in previous calculations, where values between −0.4 and 0.6 meV/f.u. were obtained. Upon inclusion of OPC, a semiquantitative agreement between the calculations and experiment is achieved, but the calculated MAE is still about a factor of two smaller than in experiment. The in-plane anisotropy is found to be negligible, as in previous calculations.

Hypothetical MCo_5 *compounds*. In the remainder of this article we want to investigate the possibilities for new high MAE materials based on the $CaCu_5$ structure. The effect of doping on the MAE can be roughly estimated by a simple shift of the Fermi level. In Fig. 1 we show the MAE of YCo_5 as a function of the number of valence electrons (band filling). Starting from a scalar relativistic density, the MAE is calculated in a one-step calculation as the band energy difference between two magnetization directions. Note that the approximate values of MAE obtained by this so-called force-theorem method deviate from the more accurate total energy differences given in Table 2. Both the LSDA and the OPC curve show a strong dependence on the band filling, with a sharp maximum at a doping level of

Table 2
MAE of YCo_5 and $LaCo_5$ in meV/f.u., calculated at the experimental lattice parameters

Compound	LSDA	OPC	Exp.
YCo_5	0.11	1.60	3.8
$LaCo_5$	0.38	2.84	4.4–5.6

The experimental values are quoted from Ref. [1].

Table 1
Calculated spin (M_s) and orbital (M_l) moments in μ_B for the three inequivalent sites of YCo_5 and $LaCo_5$

	M (1a)		Co (2c)		Co (3g)		M_{total}	
	M_s	M_l	M_s	M_l	M_s	M_l	calc.	exp.
YCo_5	−0.42	0.03	1.47	0.24	1.49	0.20	8.07	8.3
$LaCo_5$	−0.26	0.03	1.50	0.25	1.37	0.25	8.12	8.5

The calculations included OPC, the magnetization direction was along the *c*-axis. Experimental lattice parameters (as given in Ref. [1]) were used.