Ab initio calculation of the magnetocrystalline anisotropy and spin and orbital moments of a bcc Co(001) surface

A. B. Klautau[1] and O. Eriksson[2]

[1]*Departamento de Física, Universidade Federal do Pará, Belém, PA, Brazil*
[2]*Department of Physics, Uppsala University, Box 530, SE-75121, Uppsala, Sweden*

The magnetocrystalline anisotropy (MAE) and spin and orbital moments of the (001) surface of bcc Co have been calculated by a first principles theory. The easy axis is found to be [100], in agreement with observations, and the size of the MAE is found to be substantially larger than the corresponding value of bulk bcc Co. The possibility of detecting this large surface MAE is discussed.

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I. INTRODUCTION

It has now been established that Co, which naturally occurs in a hcp structure, can be stabilized in a bcc crystal structure, by growth on a suitable substrate such as GaAs,[1] TiAl,[2] FeAl,[3] Ge,[4] or Au.[5] It is probable that there is a small distortion of the bcc lattice in these systems, due to lattice mismatch with the substrate. It is of course of interest to investigate the physical properties of this phase of Co both experimentally and theoretically. Consequently, the magnetic properties of bcc Co have been measured. Experimentally the magnetic moments of bcc Co films have been determined to be 1.3–1.5 μ_B/atom (Refs. 1 and 6–8) whereas theoretical calculations for bulk bcc Co give a larger magnetic moment, ~1.7 μ_B/atom.[9,10] A surface calculation[11] of the spin moments of bcc Co (001) gave a surface moment of 1.94 μ_B/atom and a gradual decrease of the layered projected moments, down to a value of 1.73 μ_B/atom, again resulting in magnetic moments that are larger than the experimental ones. The orbital moments were also measured[4] and it was found that, e.g., a 36-Å-thick bcc Co film has an orbital moment of ~0.14 μ_B/atom. This number should reflect a bulk value of bcc Co and is very close to the measured orbital moment of bulk hcp Co. On the theoretical side the orbital moment of bulk bcc Co was calculated to be ~0.15 (0.08) μ_B/atom when orbital polarization was included (omitted)[10] and in this theoretical work it was predicted that the orbital moments of bcc and hcp Co should be very similar, which as mentioned above was verified recently.[4]

Attention has also been focused on the magnetocrystalline anisotropy (MAE). Experimental studies show that the [100] axis is the easy axis[5] for bcc Co on top of a Au substrate, but unfortunately it was not possible to extract the size of the MAE. The [100] axis was also determined as the easy axis for bcc Co grown on a GaAs substrate.[12,13] In Refs. 7 and 14 a uniaxial component to the anisotropy was observed for rather thick bcc Co films and the MAE was shown to be of the order of μeV/atom, which is the same order of magnitude as bulk values for the 3d elements. Unfortunately no experimental studies of the MAE for thin bcc Co films have been reported, and the surface contribution to the MAE of bcc Co films is unknown. In this paper we attempt to address this issue and we present a theoretical prediction of the size of the MAE from the surface of bcc Co, in the hope that this will motivate an experimental study of the surface MAE of bcc Co. By varying the thickness of bcc Co layers on a substrate and measuring the MAE as a function of thickness it should be possible to extract experimental information about the surface MAE, much in the same way as the surface orbital moment has been extracted experimentally.[15]

II. THEORY

In our theory we made use of a slab geometry, consisting of seven layers of bcc Co for most of the calculations. For comparison, calculations with nine layers of bcc Co have also been done. The lattice parameter used in the calculations was 2.82 Å since this is what the experimental data dictates for bcc Co,[1,6,7] and no relaxation of the surface layers was done. The Kohn–Sham equations were solved by means of a full-potential linear muffin-tin orbital (FP-LMTO) method[16] in the local density approximation.[17] The muffin-tin orbitals were expanded in a series of spherical harmonics (with a cut off l_{max}=6), within the muffin-tin spheres. A Fourier series was used in expanding the density and potential in the interstitial region. A so called double basis set was used, involving two tails for each lm basis function. In order to speed up the convergence, a Gaussian broadening of 20 mRy was applied to each eigenvalue.[18] In the calculations of spin and orbital moments, 576 **k** points were used in the two-dimensional Brillouin zone (BZ). For the calculation of the MAE we used the force theorem,[19] in which the MAE between the [001] and [100] directions is evaluated from the expression

$$E_a = \sum_i \epsilon_i^{[100]} - \sum_i \epsilon_i^{[001]},$$

where, e.g., $\epsilon_i^{[100]}$ is an eigenvalue evaluated when the magnetization is quantized along the [100] direction and the sum is made up to the Fermi level (E_F). In a similar way the MAE between the [001] and [110] direction can be calculated. For these calculations a careful investigation of the MAE with respect to the number of k points has to be made, something which we present below.
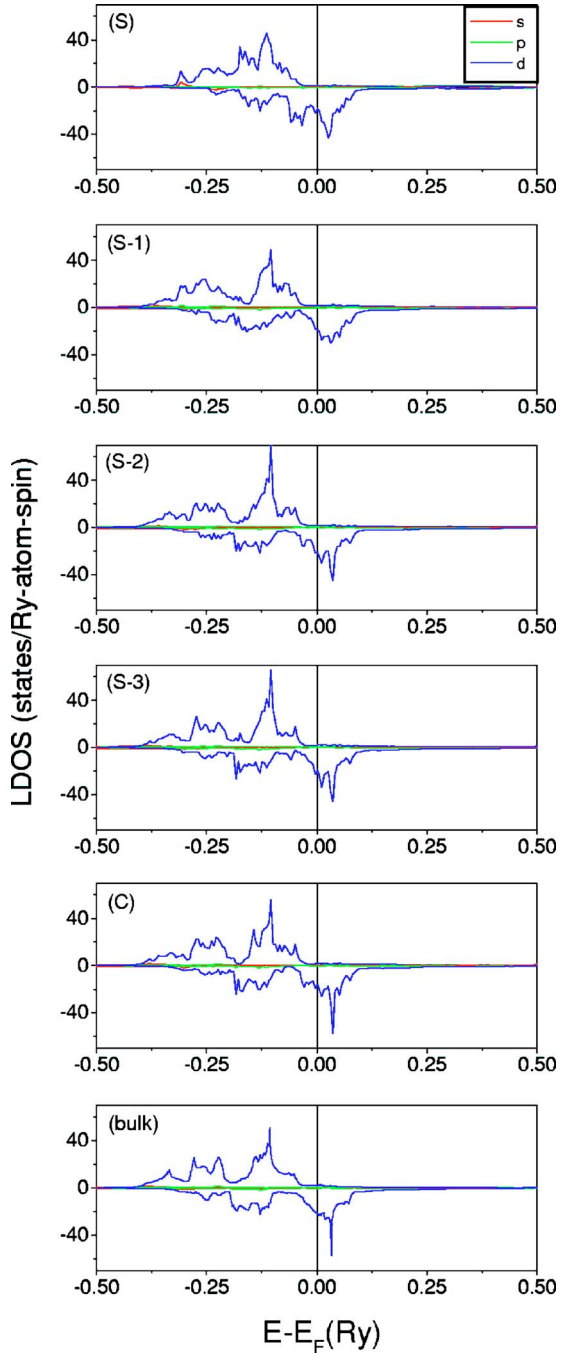
FIG. 1. (Color online) Density of states for a bcc Co surface. The Fermi level is at zero energy and is marked by a vertical line. The local DOS (LDOS) for Co bulk bcc is included for comparison.

TABLE I. Calculated layer resolved spin and orbital moments for a bcc Co surface using LSDA and GGA (values presented in parenthesis). Orbital polarization was not included.

| | Slab with seven layers | | | |
| | Present work | | Theory—Ref. 11 | |
layer	m_s	m_l	m_s	m_l
S	1.91 (1.90)	0.11 (0.11)	1.94	
$S-1$	1.70 (1.70)	0.07 (0.07)	1.71	
$S-2$	1.71 (1.71)	0.08 (0.08)	1.74	
C	1.69 (1.69)	0.07 (0.07)	1.73	
	Slab with nine layers			
layer	m_s	m_l		
S	1.90	0.11		
$S-1$	1.70	0.07		
$S-2$	1.71	0.08		
$S-3$	1.69	0.07		
C	1.71	0.08		

moment of ~ 0.08 μ_B/atom (without orbital polarization)[22] or ~ 0.15 μ_B/atom (with orbital polarization) was predicted.

III. SPIN AND ORBITAL MOMENTS

The calculated spin and orbital moments for slabs with seven and nine layers of bcc Co are listed in Table I. For the exchange-correlation potential the local density approximation (LDA) was employed. For comparison, the moments were calculated with the generalized gradient approximation (GGA) as well, and it was found (see Table I) that the spin and orbital moments are not modified significantly when the GGA is used instead of the LDA. The orbital-polarization (OP) correction was not applied, as it is unclear if it improves on the calculated MAE.[23] It may be noted that our calculated spin moments agree rather well with the values reported in Ref. 11. The spin moment of the central layer in the slab is 1.69 μ_B/atom which is somewhat too large compared to the experimental value of $1.3-1.5$ μ_B/atom. It is also clear that both the spin and orbital moments reach a bulklike value already for the subsurface layer and that only the surface layer has spin and orbital moments that are substantially enhanced. Such enhancements have been demonstrated in the past, both for spin[24] and orbital[25] moments. We also note that the orbital moment of the central layer is quite close to the calculated orbital moment of bulk bcc Co.[10] The value of the orbital moment of the central layer of the bcc Co slab is also found to be close to the calculated orbital moment of bulk hcp Co (~ 0.08 μ_B/atom when no orbital polarization is taken into account.)[26] Hence, we come to the conclusion that bulk bcc Co and hcp Co should have similar orbital moments, which is in agreement with the experimental finding[4] and with previous theory.

IV. MAGNETOCRYSTALLINE ANISOTROPY

In Table II we show the calculated MAE for three choices of k-point meshes and it may be observed that the values of

Before we describe the main results of our manuscript, the evaluation of the MAE and the spin and orbital moments of the bcc Co surface, we show for completion the calculated electronic structure. Hence, Fig. 1 contains the layer resolved density of states (DOS) of our slab, and one may note that the shape of the DOS is typical for a bcc material and that the band filling is such that E_F cuts through a rather large peak in the spin down DOS, which should result in a large orbital moment.[20,21] This was indeed also found in the calculations of bulk bcc Co where, in Ref. 10, an orbital

TABLE II. FP-LMTO calculation of the magnetic anisotropy energy of the bcc Co(001) surface calculated for different number of k-point in the Brillouin zone and for the experimental lattice parameter of bcc Co. The results correspond to the difference between the energy for the spin pointing along the [001] direction and the [100], [110], and [111] spin directions. The values of the anisotropy coefficients K_1, K_2, K_3 are deduced from the MAE values using Eq. (1).

Co(001) bcc surface			
Magnetic anisotropy energy (meV)			
Number of k points	256	512	576
$E_a([100])$	−0.578	−0.599	−0.578
$E_a([110])$	−0.537	−0.544	−0.537
$E_a([111])$	−0.361	−0.367	−0.361
Anisotropy coefficients (meV)			
K_1	−0.548	−0.565	−0.544
K_2	−0.030	−0.034	−0.030
K_3	+0.103	+0.150	+0.103

the MAE are converged to within a few percent. Note that the most negative value of E_a represents the lowest energy direction and, hence, the easy axis. In our calculations we find that the [100] axis is the easy axis, which is in agreement with observations. It may also be noted that the magnitude of the MAE at the surface of bcc Co is much larger than the measured values for thick films (which are dominated by the bulk contribution). Hence, a large surface MAE of bcc Co should be possible to detect experimentally, by means of a careful study of the MAE of bcc Co as a function of Co thickness, much in the same was as has been done for orbital moments.[15] In Table II one may also note that the [001] axis (the reference level) is the hard axis and that rotating the magnetization direction to the [111], [110], and [100] directions successively lowers the total energy.

From the expression[27]

$$E_a = K_1 \sin^2\theta + \frac{(6K_2 + K_3)\sin^4\theta}{8} + \frac{(2K_2 - K_3)\sin^4\theta\cos 4\phi}{8}, \tag{1}$$

one may evaluate the anisotropy coefficients and they are also listed in Table II. It may be seen that the largest anisotropy coefficient is K_1 and, hence, one may approximate the expression as

$$E_a = K_1 \sin^2\theta. \tag{2}$$

A plot of the MAE as a function of polar angle θ is show in Fig. 2.

To investigate the influence of the thickness on the MAE we also performed calculations with nine layers in the slab geometry. In the calculation 576 k points were used in the two-dimensional BZ and the energy difference between the [001] and the [100] directions was −0.552 meV, which is
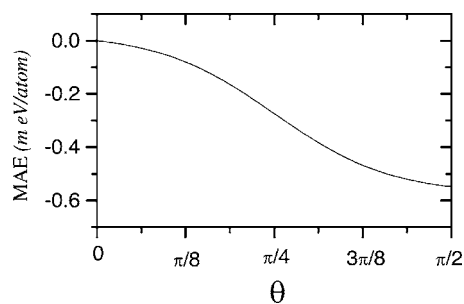

FIG. 2. Calculated MAE of the bcc Co(001) surface as a function of the polar angle θ, using Eq. (2).

close to the value obtained from the seven layer calculation. We also calculated the contribution from different atomic layers to the total MAE

$$\Delta E = \sum_L \Delta E_L, \tag{3}$$

($L = S, S-1, S-2, S-3, C$), where following Ref. 28 ΔE_L can, to a good approximation, be calculated as

$$\Delta E_L \approx F_L^{001}(\bar{E}_F) - F_L^{100}(\bar{E}_F). \tag{4}$$

Here $\bar{E}_F$ is the average Fermi energy from a calculation with magnetization in directions $\sigma = [001]$ and [100], and $F_L^\sigma(E)$ can be calculated from the type-projected number of states $N_L^\sigma(E)$

$$F_L^\sigma(E) = \int_{-\infty}^E N_L^\sigma(\epsilon)d\epsilon. \tag{5}$$

The total and layer-projected MAE of a nine layer Co(001) bcc surface are shown in Fig. 3. We found that
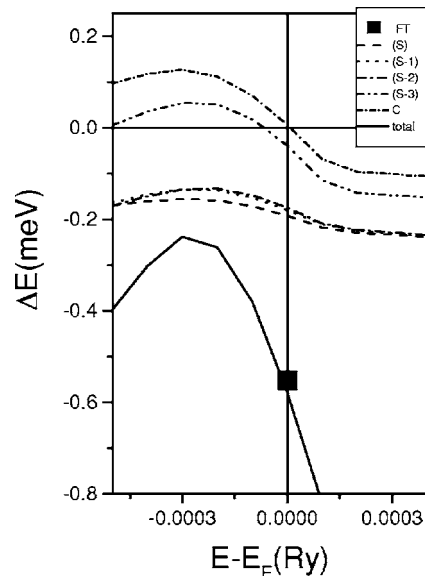

FIG. 3. Total and layer-projected MAE of a nine layer Co(001) bcc surface. The filled square is the MAE obtained from the force theorem (FT). The contribution from the interstitial region is much smaller and was omitted.

about 33% of the total MAE originates from the surface layer, 31% and 30% from the $S-1$ and $S-2$ layers, respectively, and the two central layers ($S-3$ and C) give bulklike values. It should also be noted that the calculation from Eqs. (3)–(5), summing all layers, agrees with the value from the force theorem (filled square in Fig. 3).

V. CONCLUSION

In conclusion we have shown that the MAE of the surface of bcc Co is rather large and hence should be possible to detect experimentally. The reason for the enhancement of the MAE at the surface is of course the breaking of the cubic symmetry at the surface. In perturbation theory this causes the spin-orbit coupling to enter as $\propto \xi^2$ instead of $\propto \xi^4$ for cubic systems, with the result of a MAE that becomes orders of magnitude larger.[29] This is the case both for bulk materials,[30] multilayers,[31] and surfaces,[32] For the surface of bcc Co we obtain the [100] axis as the easy axis, which is in agreement with experimental studies of thick Co surfaces. However, the easy axis of bulk bcc Co, if it could be stabilized, would be [111], since for bcc FeCo alloys the easy axis changes from [100] to [111] at a Co concentration of 50% and the easy axis for the Co rich alloys (also when extrapolating to 100% Co concentration) is the [111] direction.[33] It should be noted, however, that there exist experimental measurements of the anisotropy of thick films of bcc Co that indicate that the easy axis of bulk bcc Co is [100].[34] This work concerns Co grown on a 110 surface of GaAs, and the [100] easy axis is probably either the result of a large surface contribution to the MAE (which is actually consistent with the results presented here) or due to magnetoelastic couplings due to strains in these thick films.

In addition the easy axis of Fe/Co(001) multilayers showed a trend in the MAE that is quite similar to that of the bulk alloys, i.e., a transition away from the [100] direction at an effective Co concentration of $\sim 50\%$.[35] In this case the easy axis was [110] since the shape anisotropy of thicker magnetic films is known to align the magnetization in plane, which prevents a [111] orientation. This comparison serves to show that the electronic structure of the Co(001) surface is sufficiently distinct, to produce a different easy axis both from bulk bcc Co (111 direction) and from Co-rich FeCo alloys and Fe/Co multilayers. It is, according to Fig. 3, for the three topmost surface layers where the electronic structure is sufficiently different to produce a distinct and different MAE compared to bulk bcc Co.

We have also calculated the spin and orbital moments of the bcc Co surface. For the spin moments we find good agreement with previous bulk and surface calculations, whereas experimental values of the moment are somewhat too low compared to theory. Regarding the orbital moment we find an enhancement of the surface moment compared to the bulk value, with $\sim 60\%$ and that the orbital moment of bulk bcc Co should be similar to that of hcp Co. This is in agreement with previous theory[10] and is actually a finding that was predicted by Söderlind *et al.*[10] one decade ago and it is in agreement with subsequent observations.[4]

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