Electric-field control of surface magnetic anisotropy: a density functional approach

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Abstract. In a recent experiment, Weisheit \textit{et al} (2007 \textit{Science} 315 349) demonstrated that the coercivity of thin L\textsubscript{10} FePt and FePd films can be modified by the external electric field in an electrochemical environment. Here, this observation is confirmed by density functional calculations for the intrinsic magnetic anisotropy. The origin of the effect is clarified by means of a general and simple method to simulate charged metal surfaces. It is predicted that the coercivity of thin CoPt films is much more susceptible to electric field than that of FePt films.

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1. Introduction

Magnetoelectric (ME) phenomena have experienced a revival in recent years, both for their fundamental importance and for expected device applications [1]. New single-phase multiferroic systems have been synthesized [2], and large room-temperature ME effects have been observed in layered heterosystems [3]. In the latter case, the interface is responsible for coupling essentially bulk electric and magnetic behavior, respectively, of adjacent layers, e.g. via transmitting lateral strain. Very recently, particular attention has been paid to pure interface effects. Here, one symmetry requirement for ME coupling, the absence of space-inversion symmetry, is always fulfilled [4]. One specific example is the predicted change of the interface magnetic moment of BaTiO$_3$/Fe upon ferroelectric polarization reversal [5]. Later, an electric-field-induced change of coercivity has been found in this system [6].

This observation parallels another one, the electric-field-induced modification of coercivity by up to 4.5% in ferromagnetic L1$_0$ FePt- and FePd-(001) thin films, in an electrochemical environment [7]. FePt and related CoPt thin films or nanoparticles [8] are considered promising for high-density magnetic storage applications for their large bulk magneto-crystalline anisotropy energy (MAE) [9]. On the other hand, surface effects become increasingly important if film thickness or particle size is reduced.

The observed electric-field dependence of the coercivity was originally [7] compared with bulk calculations of the MAE with variable electron number [10]. In this course, two strong assumptions were employed: (i) a linear dependence of the MAE on the electron number and (ii) the equivalence of bulk and surface anisotropy. It will be shown that these assumptions do not hold in general. Related experimental data on the electric-field sensitivity of the MAE in highly anisotropic CoPt films have not been reported yet, since (i) and (ii) suggest a much smaller effect than in FePt films.

The present investigation explains the experimental results by dedicated calculations in the framework of density functional theory (DFT). To this end, a simple and general method to model the electronic structure of charged metal surfaces is applied. It will be demonstrated that (i) the experimentally observed change of coercivity by electrochemical charging of thin FePt films can be understood by assuming a single-charged atomic surface layer; (ii) the coercivity of CoPt films is expected to be much more sensitive to an applied electric field than that of FePt films; (iii) the lower limit of film thickness, where a separation into surface and bulk MAE makes sense, amounts to about ten atomic layers in FePt and CoPt, but quantum size oscillations rule the MAE of FePd and CoPd films up to at least twice this thickness. Such a separation into bulk and surface contributions, similar to bulk and surface total energies of non-magnetic systems, is a common practice in micromagnetic simulations but is not standard in density functional calculations.

2. Computational details

The films were modeled by symmetric tetragonal supercells (space group P4/mmm) with composition T(MT)$_x$ (M = Fe, Co; T = Pd, Pt; $x = 1, \ldots, 8$) (see figure 1). Surface termination by Pt or Pd was chosen in accordance with the experimental situation [7]. The substrate/film interface was omitted in the calculations since the experimental film thickness of 2–4 nm is larger than half of the largest considered slab thickness. Local spin-density approximation (LSDA)-optimized lattice parameters of the bulk phases (table 1) were used to define the
Table 1. Compilation of calculated LSDA data: equilibrium lattice constants $a_0$ and $c_0$ of the bulk L1$_0$ structures, bulk, $K_v$, and surface, $K_s(\Delta q)$, anisotropy energies for three values of the surface charge, $\Delta q$. $K_s(\Delta q)$ has been obtained by one-parameter fits according to equation (1) using data for slabs with $x = 4$–8, as given in figure 2.

|        | $a_0$  | $c_0$  | $K_v$  | $K_s$  | $\Delta q$ |
|--------|--------|--------|--------|--------|------------|
|        | [Å]    | [Å]    | (meV)  | (meV)  |            |
| FePt   | 2.704  | 3.668  | 3.27   | 0.0    | 2.34       |
|        |        |        |        | 0.1    | 2.06       |
|        |        |        |        | 0.2    | 0.89       |
|        |        |        |        | 0.0    | 0.07       |
| FePd   | 2.673  | 3.702  | 0.17   | 0.1    | 0.02       |
|        |        |        |        | 0.2    | 0.00       |
|        |        |        |        | 0.0    | 0.03       |
| CoPt   | 2.679  | 3.625  | 1.36   | 0.1    | −0.76      |
|        |        |        |        | 0.2    | −1.64      |
| CoPd   | 2.618  | 3.670  | 0.045  |        |            |

Figure 1. T(MT)$_x$ supercell (here, $x = 3$) in relation to the experimental situation [7]. The solid frame denotes the unit cell of the model, and the dotted frame indicates the relation between the film surface in the experiment and the model slab. The experimental film contains more atomic layers than the model, and the validity of the latter is checked by finite-size scaling. Electrochemical electron accumulation at the surface is modeled by a neutral surface layer with modified nuclear charge.

atomic distances. Surface layer relaxation modifies the calculated electric field dependence of the surface MAE in FePt by about 5% and has been neglected in the presented data.

The calculations were performed with the relativistic version [11] of the full-potential local-orbital method (FPLO 6.00-24) [12, 13]. The LSDA in the parameterization of [14] was applied. The valence basis comprised the $(n)$spd, $(n + 1)$spd and $(n + 2)$s states, where
$n = 3 \ (4, 5)$ for Fe and Co (Pd, Pt). Convergence of all parameters was checked, including the Brillouin zone (BZ) integration mesh for the linear tetrahedron method with the Blöchl corrections. A $30 \times 30 \times 1$ subdivision of the full BZ, used for the reported results, guarantees convergence of the MAE within 2%, compared with a $60 \times 60 \times 1$ mesh. To reduce the computational effort, the presented data were obtained using the so-called force theorem (FT) [15]. In this approach, the MAE is calculated as the difference between the band energy sums of two calculations with spin quantization axes parallel and perpendicular to the slab surface, respectively, $\text{MAE} = E_{\text{band}}^{||} - E_{\text{band}}^{\perp}$. Both calculations start from the same self-consistent charge density (here, a scalar relativistic solution of the Kohn–Sham equations is used) and carry out a single full relativistic iteration step to evaluate $E_{\text{band}}$. The energy differences between inequivalent directions parallel to the slab surface is negligible and thus not considered.

Two issues have to be considered if one intends to simulate charged metallic surfaces using DFT. First, constant voltage conditions are frequently used in experiments, e.g. in electrochemistry. In theory, this would correspond to grand canonical statistics with a constant chemical potential $\mu$ [16] and a screening charge depending, e.g., on the direction of magnetization. The FT method, on the other hand, does not consider any charge relaxation due to rotation of the magnetic moment. Thus, this method has to be applied together with fixed electron numbers and the more tedious grand canonical problem is circumvented.

The second issue concerns the choice of the position and shape of charges to model the external electric field. Different models have been used in the literature (see [17] and references therein). Here, the focus is on the influence of the surface charge on the magnetic properties of the films, rather than on particular properties of the electrochemical double layer. Therefore, the technically simplest procedure is employed by adding charges $\Delta q$ at the nuclear positions of the surface atoms. The same amount of electrons are added to preserve the charge neutrality. We checked the validity of this procedure by additional calculations using the slab version of FPLO [18]. In these scalar relativistic calculations, an external homogeneous electric field was applied to a free-standing Pt(FePt)$_4$ slab. As expected, the population analysis showed that the resulting induced charge is mainly located at the surface Pt layer. An opposite charge of about 10% of the surface charge was found on the subsurface Fe layer, and further, much smaller and oscillating charges on the other inner layers. The additional electrons of our model ($\Delta q$) have a similar distribution with 0.8 $\Delta q$ located at the surface layer. Thus, one should expect that adding a nuclear charge $\Delta q$ only at the surface layer should model the impact of an external electric field on the MAE with an accuracy of about 10%.

This approach is similar to the recently applied virtual crystal approximation [19] with the important difference that our method is site-selective to allow an appropriate description of the charged metal surface. This method is superior to the rigid band model frequently applied to predict the MAE of alloys [10, 20] as it takes the effect of additional charges on the electronic structure into account self-consistently. The use of this method is not restricted to MAE calculations. It can also be applied to predict other intrinsic properties of charged metallic surfaces. Moreover, the method can most easily be implemented into any electronic structure code.
Figure 2. MAE ($\Delta q, x$) of FePt, FePd, CoPt and CoPd slabs. Squares (black, full lines), circles (red, dashed) and diamonds (blue, dotted) denote data for surface charges $\Delta q = 0, 0.1$ and 0.2, respectively. The lines are one-parameter fits of the data at $x > 3$, MAE$^\text{fit}(\Delta q, x)$ of equation (1).

3. Results and discussions

Figure 2 shows MAE($\Delta q, x$) of FePt, FePd, CoPt and CoPd slabs. The surface charge in experiments ranges between 0.054 and 0.136 electrons per surface atom (external voltage between 400 and 1000 mV, assumed specific capacitance 30 $\mu$F cm$^{-2}$) [7]. A somewhat broader range is considered here. Variations of shape anisotropy are two orders of magnitude weaker than the spin–orbit related change of surface anisotropy and thus are not included. Consider first uncharged slabs (black squares and full lines). Here, perpendicular anisotropy (MAE > 0) with an easy magnetization axis normal to the surface is found for most cases, with exceptions for PtCoPt triple layers and for Pd(CoPd)$_x$ with $x = 1, 3, 4$. Calculations by Meyerheim et al on (PdCo)Pd$_x$ and (PdCo)$_2$Pd$_x$ slabs found in-plane and perpendicular anisotropies, respectively,
in agreement with the present results (note the somewhat different composition) [21]. Recent calculations for PtFePt triple layers give lower values compared to the present data [22], mainly due to the use of different lattice parameters.

Surface charges added to both sides of the symmetric slabs shift the total anisotropies (figure 2). An intriguing field-induced sign change of the MAE is found for particular ultrathin FePd and CoPd slabs.

The thickness dependence of the MAE is almost linear for FePt and CoPt. Deviations occur for very thin slabs due to the interaction between the two surfaces. For thicker slabs, $x > 3$, oscillations are seen that can be attributed to quantum well states confined in the slabs [23]. In the latter region, much stronger relative deviations from the fits are found for FePd and CoPd, where the MAE is considerably smaller than in the Pt systems. Any quantum size effect should be suppressed in order to compare with experiment, since the effect of quantum well states is extinguished by surface roughness and since the interaction between the surfaces/interfaces is negligible for the experimental film thickness. To this end, the data for $\text{MAE}(\Delta q, x)$ have been fitted to the phenomenological expression

$$\text{MAE}^{\text{fit}}(\Delta q, x) = x \times K_v + 2 \times K_s(\Delta q),$$

where $K_v$ is the volume contribution, obtained by independent FT bulk calculations. $K_s(\Delta q)$ is the surface contribution and is the only fit parameter. The factor of 2 originates from the use of symmetric slabs with two surfaces. Slabs with $x < 4$ are excluded from the fit in order to avoid a sizable influence of surface–surface interaction (note that $x < 4$ data points deviate from the lines in figure 2 for all systems).

Numerical data for $K_v$ and $K_s$ are compiled in table 1. For comparison, two-parameter fits to the same data points without using the independent bulk value were carried out. It is reassuring that for all systems except CoPd the fitted values of the bulk MAE ($K_v$) deviate by less than 6% from the calculated values, confirming proper convergence of the MAE for thicker slabs to the bulk value and independence of the volume anisotropy of the surface charge. For CoPd, both bulk and surface anisotropies are smaller than the quantum size effects and hence, no fit data are included in table 1. The important conclusion to be drawn for the Pt systems is that the surface anisotropy is considerably influenced by the charge added. In the case of CoPt, $\delta K_v/\delta \Delta q \approx -8 \text{meV e}^{-1}$ per surface atom. This value is about three times larger than the $\Delta q$-derivative of $K_v$ in hypothetical charged CoPt bulk [10]. Quite recently, Duan et al [24] evaluated the surface MAE of a 15 ML Fe slab in electric fields and found $\delta K_v/\delta \Delta q \approx -2.4 \text{meV e}^{-1}$ (estimated from figure 4 of [24]).

We now compare the present slab results with experimental data [7]. For this aim, figure 3 shows MAE versus $\Delta q$ for two specific slab geometries, $x = 4$ and 8, together with the fitted surface contribution, $2K_s$. The data are normalized to $\Delta q = 0$. All curves almost coincide over the whole range for the strongly anisotropic FePt and CoPt compounds. Thus, a film thickness of about 10 atomic layers is sufficient to allow a separation of the surface (interface) and volume magnetic anisotropy. In contrast, even the $x = 8$ data of the thickest considered slab oscillate around the fit curve for FePd and CoPd, due to quantum size effects. Thus, it is not possible to extract reliable numbers for the electric-field dependence of the surface MAE for the considered Pd systems. The $K_s$ data given in table 1 for FePd should only be taken as rough estimates.

In the experimental $\Delta q$ range, 0.054–0.136, the surface MAE of CoPt varies almost linearly, while a negative second derivative is found for FePt (figure 3). The latter behavior has indeed been observed for the coercivity of FePt films [7]. Assuming an experimental film
thickness of 2(4) nm and the mentioned variation of $\Delta q$, a reduction of the total MAE by 3% (1.5%) is found from the calculated $K_v$ and $K_s(\Delta q)$ for FePt, to be compared with an observed reduction of the coercivity by 4.5% (1.7%) [7]. CoPt, that has not been investigated in related experiments yet, is predicted by the present calculations to be an even more interesting system: films with a thickness of 2 nm should show a variation of the MAE by $-9\%$. Yet larger effects are expected for ultrathin films. The reason for this is that CoPt has only about half the bulk MAE of FePt, while its surface MAE is as susceptible to external voltage as that of FePt.

4. Conclusions

Summarizing, a simple DFT approach accessible to any relativistic electronic structure method has been introduced to determine the surface contribution to the magneto-crystalline anisotropy of metallic magnetic films in external electric fields. It was found that the surface magnetic anisotropy of both FePt and CoPt can be essentially modified by surface charges. The effect is much smaller in FePd and CoPd, where the dependence on the film thickness is complicated due to quantum size oscillations. In the considered L1$_0$ FePt and CoPt compounds, such
Oscillations are less important for films thicker than about 10 atomic layers due to the large values of bulk and surface anisotropies. Surface anisotropy data are difficult to access in a direct experiment. Thus, the calculated results may provide important input information for micromagnetic simulations. The method used to simulate charged metal surfaces should also be valid to estimate other related properties.

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