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First-principles calculation of the magnetic anisotropy energy of $(Co)_n/(X)_m$ multilayers

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The magnetocrystalline anisotropy energies of $(Co)_1/(X)_2$, $(Co)_1/(X)_5$, and $(Co)_n/(Pd)_m$ multilayers, where X=Cu and Ag and $n+m=3$ or 6, have been calculated from first principles by means of the linear muffin-tin orbitals (LMTO) method in the atomic-spheres approximation using the local-spin-density approximation. The easy axes of the multilayers considered are found to be perpendicular to the multilayer plane. The magnetocrystalline anisotropy energy is calculated to be largest for $(Co)_1/(Pd)_2$ and decreases with increasing Co thickness. These predictions are in agreement with experiment.

The magnetization of thin films of Co/Pd, Co/Pt, and Co/Au multilayers where the cobalt layer is only one or a few atomic layers thick is preferentially oriented perpendicular to the multilayer planes.[1,2] Based on this property, Co/Pt multilayers have already been shown to be a promising candidate as a high-density storage medium.[3] Measurements of the magnetic anisotropy energy density K, as a function of the Co thickness t, show that $Kt \approx 2K_S + K_V t$, where K_S and K_V are the interface and volume energy densities, respectively. When t is increased, the easy axis of the magnetization changes to an in-plane direction. For thin layers, the perpendicular orientation of the magnetization is apparently determined by the *interface* anisotropy.

It was first pointed out by Néel[4] that an enhanced anisotropy energy may occur at a surface due to the reduced symmetry. The itinerant-electron model used by Brooks to explain the ferromagnetic anisotropy in cubic crystals[5] was later applied to the problem of surface anisotropy.[6] More recently there have been attempts to calculate the very small magnetocrystalline anisotropy energies (MAE) of bulk crystals from first principles[7,8] within the framework of the local-spin-density approximation.[9] Much larger anisotropy energies have been predicted for free-standing monolayers of transition-metal elements.[10–12] However, in the calculations by Karas, Noffke, and Fritsche[11] and by Li, Freeman, and Fu[12] different easy axes are predicted for an Fe [001] monolayer than by Gay and Richter.[10] In order to compare with experiment, the interaction of the monolayer with the substrate must be taken into consideration.[13]

The origin of the measured anisotropy energy in multilayers is not well understood. The influence of structure,[14] interface mixing,[2] roughness, and (thickness-dependent) strain[15] have been considered. In this Rapid Communication the MAE of multilayers with *ideal* interfaces is examined. We present the results of first-principles calculations for $(Co)_n/(Pd)_m$ multilayers, where $n+m=3$ or 6, as well as for $(Co)_1/(X)_2$ and $(Co)_1/(X)_5$ multilayers, where X=Cu and Ag. We predict the occurrence of a perpendicular orientation of the magnetization for all multilayers considered. The MAE decreases with increasing Co thickness and of all the multilayers considered it is largest for $(Co)_1/(Pd)_2$. Where comparison is possible, the calculations are found to be in good agreement with experiment.

Within the framework of the local-spin-density approximation (LSDA), the MAE is calculated using the linear muffin-tin orbitals (LMTO) method in the atomic-spheres approximation (ASA).[16] The Kohn-Sham equations for the scalar-relativistic spin-polarized Hamiltonian are first solved self-consistently. The spin-orbit interaction is then included and the new Kohn-Sham eigenvalues are obtained by diagonalizing the full Hamiltonian. The so-called "force theorem"[17] is used to express the resulting change in the total energy for each orientation of the magnetization as a difference in sums of Kohn-Sham eigenvalues ΔE. Integrations over the Brillouin zone (BZ) are performed using the improved tetrahedron method.[18] The basis used consists of s, p, d, and f partial waves. A detailed description of the procedure, applied to bulk Fe, Co, and Ni, can be found elsewhere.[8] Before comparing the theoretical and experimental results, the demagnetization energy ΔE_D must be added to the MAE ΔE. ΔE_D is calculated by summing the interaction energies between magnetic dipoles on lattice sites in a film geometry.[19]

Co/Pd multilayers deposited on a polycrystalline Pd base with $[111]_{fcc}$ texture form films comprising close-packed planes of Pd and Co.[1] Their precise structure is not known experimentally. We will construct a model for the structure which is appropriate for multilayers where the Pd layer is sufficiently thick that it may be assumed to determine the in-plane lattice parameter. The parameters in this model are evaluated by performing first-principles calculations of the total energy using the full-potential linear augmented-plane-wave (FLAPW) method.[20]

In our structural model for $[111]_{fcc}$ $(Co)_n/(Pd)_m$ multilayers, we assume an *ABCABC* stacking sequence of close-packed planes. The resulting crystal structure has trigonal symmetry (point group D_{3d}), a basis consisting of three or six atoms, and primitive vectors that can be chosen as hexagonal lattice vectors with lengths a and c. The latter is expressed as $c = 2c_{Co\text{-}Pd} + (n-1)c_{Co\text{-}Co} + (m-1)c_{Pd\text{-}Pd}$, where $c_{A\text{-}B}$ denotes the perpendicular distance between neighboring A and B planes (Fig. 1). The in-plane nearest-neighbor (NN) distance a and the NN separation of Pd atoms in neighboring planes is assumed to be equal to that calculated for fcc Pd;

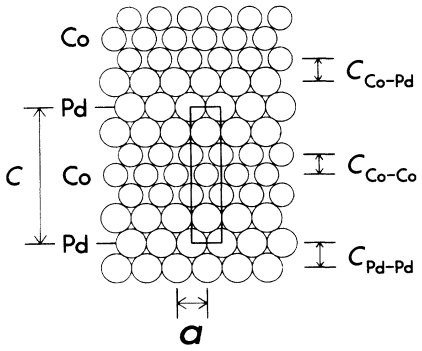

FIG. 1. Model for the structure of $(Co)_n/(Pd)_m$ multilayers containing three structure parameters: c_{Co-Pd}, c_{Co-Co}, and $a=(\frac{1}{2})^{1/2}c_{Pd-Pd}=a_{fcc}^{Pd}/\sqrt{2}$. The values of the parameters used are $c_{Co-Co}=1.84$ Å, $c_{Co-Pd}=1.99$ Å, and $c_{Pd-Pd}=2.22$ Å.

$a=(\frac{1}{2})^{1/2}c_{Pd-Pd}=a_{fcc}^{Pd}/\sqrt{2}$. The two remaining structural parameters c_{Co-Co} and c_{Co-Pd} were calculated by minimizing the total energy for trigonal Co_3 and Co_1Pd_2, respectively, keeping the in-plane NN distance a constant $(=a_{fcc}^{Pd}/\sqrt{2})$. The c/a ratio which we then find for strained trigonal Co_3 is 2.03, compared to $\frac{3}{2}(\frac{8}{3})^{1/2}\simeq 2.45$ for fcc Co. The resulting interplanar NN distances are only slightly smaller than those obtained from close packing of hard spheres. This model for the NN distances was also applied to the other $(Co)_n/(X)_m$ multilayers. The results to be discussed below are not sensitive to small changes in the structural parameters.

In previous studies of the MAE the convergence of the BZ integral of the Kohn-Sham eigenvalues has been an important source of uncertainty. In Fig. 2 the calculated MAE of $(Co)_1/(X)_2$ and $(Co)_1/(X)_5$ multilayers, with $X=$Pd, Cu, and Ag, is shown as a function of the volume element v used to evaluate the three-dimensional integral. An infinitely dense integration mesh corresponds to $v\rightarrow 0$. For the $(Co)_1/(X)_2$ multilayers satisfactory convergence is achieved and the estimated numerical accuracy of the MAE is ± 0.03 meV/unit-cell. The anisotropy energy of the $(Co)_1/(X)_5$ multilayers (open symbols) is less well converged because of computing-time limitations.[21]

The anisotropy energy of multilayers containing Cu and Ag is seen to be essentially equal and does not depend on the thickness of the Cu and Ag layers. The magnetic moments of Cu and Ag are $\lesssim 0.01\mu_B$ because their d bands are filled. The anisotropy energy of $(Co)_1/(Pd)_5$ is $\sim 10\%$ smaller than that of $(Co)_1/(Pd)_2$. In $(Co)_1/(Pd)_5$ the calculated spin moment on the Pd atoms decreases from $0.30\mu_B$ for the interface layer, to $0.13\mu_B$ for the next layer and is only $0.06\mu_B$ for the central Pd layer. For Pd layers thicker than 5 monolayers, we expect the MAE to change by less than its difference between $(Co)_1/(Pd)_2$ and $(Co)_1/(Pd)_5$ because the Pd atoms in the additional layers are neutral and have a magnetic moment of $\lesssim 0.04\mu_B$.

The magnetocrystalline anisotropy (*without* contributions from dipolar interactions) is seen to favor an orientation of the magnetization perpendicular to the multilayer plane ($\Delta E>0$) for all multilayers considered. We want to check how sensitive this prediction is to various approximations which have been made. Since only the Kohn-Sham eigenvalues enter into the calculation of the MAE, we need to know (i) how a given approximation affects the energy bands and, in particular, the energy bands around the Fermi energy and (ii) how such shifts in the energy bands around the Fermi energy affect the anisotropy energy. We study $(Co)_1/(Pd)_2$ in particular detail.

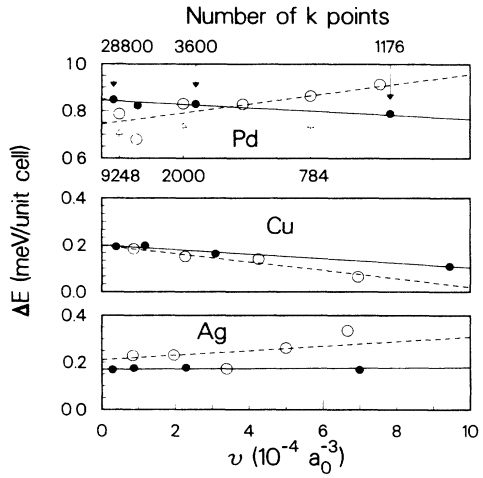

FIG. 2. The magnetocrystalline anisotropy energy per unit cell, ΔE, of $(Co)_1/(X)_2$ (●) and $Co_1/(X)_5$ (○) multilayers for $X=$Pd, Cu, and Ag, plotted as a function of the tetrahedron volume v used to perform the integration over the Brillouin zone. The number of **k** points used in the BZ integration for $(Co)_1/(Pd)_2$ [$(Co)_1/(Pd)_5$] is indicated at the top (bottom) of the upper panel. The sign of ΔE is such that $\Delta E>0$ favors a perpendicular orientation of the magnetization.

We first examine the sensitivity of the MAE to the position of the Fermi energy itself. By using the LMTO-ASA band structure calculated self-consistently for $(Co)_1/(Pd)_2$ (with $n=29$ valence electrons) and filling the energy bands to an energy $E_F(q)$ (where q is a noninteger number of electrons) the anisotropy energy is calculated as a function of q. For $|q-n|<0.25$, corresponding to $|E_F(q)-E_F(n)|<0.08$ eV, the change is less than 5%.

We next modify the band structure of $(Co)_1/(Pd)_2$ by changing the parameters in the structural model. For each set of parameters the MAE is calculated from first principles. When the volume is reduced uniformly by 8%, the MAE changes by only 10%. To achieve the same change in the MAE, the Co-Pd interlayer separation must be changed by $\pm 4\%$. A perpendicular orientation of the magnetization is thus predicted to occur for a wide range of values of the structural parameters. The bands in the neighborhood of the Fermi energy shift by up to 0.1 eV corresponding to these structural changes.

We also examine the effect on the MAE of treating the spin-orbit interaction self-consistently. Because the spin-orbit coupling parameter for Pd d states is so large ($\xi_d^{Pd}=0.23$ eV), it is not *a priori* clear that this is unnecessary. We first solve the Kohn-Sham equations, including the spin-orbit coupling and with the spin-quantization axis chosen perpendicular to the multilayer plane, self-consistently. The charge and magnetization densities thus obtained were used as input to a calculation of the MAE using the force theorem. The MAE was unchanged. We

have thus verified that our prediction of a perpendicular orientation of the magnetization is not sensitive to a number of approximations made in the calculations. The MAE does not depend strongly on shifts of order 0.1 eV in the bands close to the Fermi energy.

Finally, we compare the energy bands calculated with the LMTO-ASA method with those obtained using the FLAPW method in which no shape approximation to the potential is made. Differences between the energy bands at **k** points that contribute significantly to the anisotropy energy are found to be $\lesssim 0.05$ eV relative to E_F. We conclude that use of a full-potential method will not lead to qualitatively different predictions. In a calculation of the MAE with such a method, it would be very difficult to demonstrate the convergence of the Brillouin-zone integral for a unit cell containing six atoms because of the computational time required.

Experimental[14] and calculated results for Kt of $(Co)_n/(Pd)_m$ multilayers are compared in Fig. 3. The error bars indicate the degree of convergence of the calculations; for six atoms per unit cell, it is ~ 0.1 meV. The demagnetization energy of ~ -0.09 meV/Co-atom which favors an in-plane magnetization is included in the calculated values shown. A perpendicular orientation of the magnetization and a decrease in the anisotropy energy with increasing Co thickness are predicted, in agreement with experiment. However, the decrease of Kt with increasing t is about a factor of 3 larger than that caused by the demagnetization energy only. For thick Co layers this slope will be determined by the sum of $\Delta E + \Delta E_D$ for strained trigonal Co. We have calculated the MAE, ΔE, for Co_3 for various c/a ratios in a range from 2.45 (fcc Co) to 2 keeping a constant. We find it to be less than 0.03 meV/Co-atom so that asymptotically the slope will be determined by ΔE_D. We conclude that the preference for a perpendicular orientation of the magnetization must be attributed to the presence of the Co/Pd interface and that the influence of the Co/Pd interface extends beyond the Co interface layer.

Of all the multilayers considered, the anisotropy energy is largest for $(Co)_1/(Pd)_2$. The large MAE may not be attributed to the strained Co layer because the mismatch between Co and Pd is intermediate between the Co-Ag and Co-Cu mismatches. The large spin-orbit coupling on the Pd site does play an important role by introducing large splittings in the strongly hybridized Co and Pd d bands within 1 eV of the Fermi energy. Setting ξ_d^{Pd} to zero leads to reduced splittings and the MAE is approximately halved.

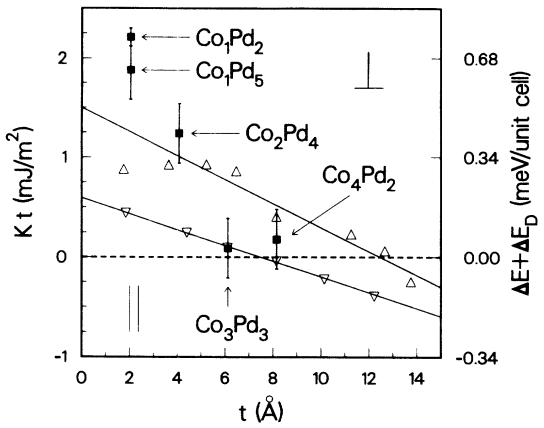

FIG. 3. Product of the anisotropy energy density K and Co thickness t as a function of t for polycrystalline $[111]_{fcc}$ multilayers deposited at $T_s = 50\,^\circ$C (▽) and $T_s = 200\,^\circ$C (△) (den Broeder *et al.*, Ref. 14), compared with the *ab initio* calculated values. $K > 0$ corresponds to a perpendicularly oriented magnetization. The magnetocrystalline anisotropy energy plus demagnetization energy per unit cell, $\Delta E + \Delta E_D$, is equal to KtA, where A is the Co cross-sectional area (Ref. 14). The straight lines are fits to the experimental data points. Error bars indicate the estimated numerical accuracy of the calculation.

In summary, we have shown that the preferential orientation of the magnetization of all the $[111]_{fcc}$ multilayers considered is perpendicular to the multilayer planes. The calculated anisotropy energies agree remarkably well with results from room-temperature magnetization measurements on Co/Pd multilayers[14] (Fig. 3), and on Co/Ag and Co/Cu multilayers[22] performed in our laboratory. It is important to determine the temperature dependence of the anisotropy energy. In view of the results presented here, an experimental study of the anisotropy energy of $(Co)_1/X$ multilayers, containing epitaxially grown monolayers of cobalt, would be extremely interesting.

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