Overlayer-induced anomalous interface magnetocrystalline anisotropy in ultrathin Co films

Lieping Zhong, Miyoung Kim, Xindong Wang, and A. J. Freeman
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208-3112
(Received 15 September 1995)

The full-potential linearized augmented-plane-wave method with the atomic force approach has been used to determine the interface structure and magnetocrystalline anisotropy (MCA) of a Co monolayer on Cu(111), with and without Cu overlayers. It is found in good agreement with experiment, that the interface MCA for a fully relaxed structure is in-plane with a value of −0.30 meV for Co monolayer (ML) on Cu(111). When capped with nonmagnetic Cu, the interface MCA changes dramatically: for one ML Cu coverage, it is perpendicular to the film plane with a MCA value of + 0.23 meV; for two ML Cu coverage, it rapidly drops to −0.02 meV. Our results confirm that the hybridization at the Co/Cu interface plays an important role in the interface MCA of Co/Cu systems. By comparing the results of the fully relaxed structures with those of unrelaxed structures, we also found that relaxation is important for accurate determinations of the interface MCA.

I. INTRODUCTION

Recently, there has been considerable effort aimed at developing high-density magneto-optic storage devices. Potential candidates are systems made up of magnetic layers spaced or sandwiched by nonmagnetic metals. These systems show promise of having enhanced magnetic moments, perpendicular magnetocrystalline anisotropy (MCA) and large Kerr rotation due to their reduced dimensionality. The majority of the studies, however, have focused on determinations of the magnetic moment and the interface anisotropy resulting from coverage by relatively thick overlayers.[1] It is only recently that investigations of the evolving magnetic behavior of an ultrathin film during interface formation have been performed due to the stringent requirements of *in situ* and monolayer-sensitive measurements to be carried out in ultrahigh vacuum. Advanced experiments have revealed some interesting behavior of these systems. For example, by using an *in situ* polar Kerr measurement, Engel *et. al.*[2] studied the perpendicular MCA of MBE-grown Co films with and without overlayers of various nonmagnetic metals. They found that the deposition of nonmagnetic metal overlayers could cause a dramatic change in the magnitude of the perpendicular anisotropy. The most pronounced is that of a Cu overlayer on a Co thin film, in which the perpendicular MCA is strongly peaked near one atomic layer coverage, and rapidly decreases from the peak value after only about two ML Cu coverage. This unusual anisotropy behavior was confirmed by Huang, *et al.*[3] in an *in situ* measurement of MCA in ultrathin Co films as a function of nonmagnetic Cu overlayer coverage.

The unusual behavior of the perpendicular MCA with overlayer coverage in these systems calls for a better understanding the origin of interface-induced MCA and the determination of the relative importance of structural and electronic contributions. It is clear from experiment that the interface MCA depends sensitively on the local environment of the magnetic ions, and thus the structural relaxation during interface formation can be important. Previous theoretical calculations on Co/Cu overlayer and sandwich systems,[4] however, used ideal unrelaxed structural models and consequently the comparison between the results so obtained and experiment may not be considered either quantitative or conclusive. Clearly, a more realistic structural model is called for.

In this paper, we present first principles results of the magnetic and MCA properties for three systems—clean, one ML, and bilayer Cu capped Co ML on Cu(111). As a first step toward the realistic modelling of the interface structure, the structural relaxation is achieved by the local density functional atomic force approach in the full potential linearized-augmented plane-wave (FLAPW) method.[5,6] For both the relaxed and unrelaxed systems, the interface MCA has been determined by the newly developed state-tracking[7] and torque methods.[8] In the following, we first describe the methodology and computational details in Sec. II. The results, including the relaxed interface structure, magnetic moments, and the MCA versus band filling from a rigid band point of view, are presented in Sec. III. Throughout Sec. III, we emphasize the effect of interlayer hybridization on both the magnetic moments and the interface MCA. And finally in Sec. IV, we present some conclusions.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

The Cu(111) substrate is simulated by an ideally constructed five layer slab with the two-dimension (2D) lattice constant taken from experiment (a_{Cu}=4.83 a.u.). Adatoms are put pseudomorphically over the fcc sites on the substrate and the vertical positions of all the atoms are optimized by calculating the atomic force acting on each atom. In the self-consistent FLAPW calculations, the core states are treated fully relativistically and the valence states are treated semirelativistically (i.e., without spin-orbit coupling). Using the von Barth–Hedin exchange-correlation potential and a variational basis set consisting of about 60 plane waves/atom, the Kohn–Sham equations were solved self-consistently. Within the muffin-tin (MT) spheres ($r_{\mathrm{Cu}}=r_{\mathrm{Co}}$ = 2.1 a.u.), lattice harmonics with angular-momentum l up to 8 are used to expand the charge density, potential and wave functions. Integrations over k space are substituted by summations over 18 special k points in the irreducible 2D Brillouin zone.[9]

TABLE I. Calculated equilibrium vertical position z (in a.u., measured from the center plane) and spin magnetic moment (M, in μ_B) of each atom. The differences in z position between fully relaxed and unrelaxed structures and the Co spin magnetic moment for unrelaxed structure are listed in parentheses for comparison.

	Cu(C)	Cu(I-1)	Cu(I)	Co	Cu(O1)	Cu (O2)
Co/Cu_5						
z	0.00	3.94 (0.00)	7.82 (−0.06)	11.52 (−0.30)		
M	0.00	0.00	0.01	1.57 (1.60)		
$Cu/Co/Cu_5$						
z	0.00	3.94 (0.00)	7.87 (−0.01)	11.66 (−0.16)	15.32 (−0.44)	
M	−0.01	−0.01	0.00	1.26 (1.40)	0.01	
$Cu_2/Co/Cu_5$						
z	0.00	3.94 (0.00)	7.88 (0.00)	11.77 (−0.05)	15.58 (−0.18)	19.24 (−0.46)
M	0.00	0.00	0.00	1.37 (1.41)	0.01	0.00

Self-consistent convergence is assumed when the average root mean square distance between the input and output charge densities is less than 2×10^{-4} e/(a.u.)^3 and spin densities is less than 0.5×10^{-4} e/(a.u.)^3.

In calculating MCA, we adopt a second variational approach to include the spin-orbit coupling (SOC) using the self-consistent scalar relativistic self-consistent potential. The SOC Hamiltonian matrix elements are calculated by integrating the derivative of the spherical potential over the MT region of the Co and Cu atoms, and the contributions from the interstitial regions and the vacuum regions are neglected. The SOC induced interface MCA is accurately determined by calculating the torque $T(\theta)$ at $\theta=45°$ as

$$T(\theta)=K_2\sin(2\theta)+2K_4\sin(2\theta)\sin^2(\theta). \tag{1}$$

and

$$T(\theta=45°)=K_2+K_4=E(\theta=90°)-E(\theta=0°)\equiv E_{\mathrm{MCA}}, \tag{2}$$

where θ is the angle between the magnetization direction and the film plane.[8] Thus, if the value of E_{MCA} is positive, the perpendicular magnetization prevails and vice versa. After the second variational diagonalization, the occupied states are determined by tracking the wave functions as in Ref. 7. The combination of state tracking and torque methods has been demonstrated to be very effective in accurately determining interface (surface) MCA.[10] We used 115 k-points in the 2D non-SOC irreducible BZ and the accuracy of the k-space integration was checked to be ±0.05 meV. The reduction of symmetry due to SOC is taken care of by summing over appropriate operations of the magnetic moment direction. In all the results presented below, the MCA energy is given without taking into account the depolarization effect which is the same for all the systems considered in this paper.

III. RESULTS AND DISCUSSION

For clean, monolayer and bilayer Cu coated Co/Cu(111), the theoretical interface MCA is found to be highly sensitive to the presence of the Cu adsorbate and to structural relaxation. In the fully relaxed structure, the clean Co/Cu(111) shows an in-plane MCA with a value of −0.30 meV/per Co atom; when capped with 1 ML Cu, the MCA switches to be perpendicular with a value of 0.23 meV/per Co atom. The second Cu overlayer deposition leads to a decrease in the interface MCA, with a value of −0.02 meV/per Co atom (i.e., slightly in-plane). To study the effect of structural relaxation on the interface MCA, we also calculated the MCA of these same systems without any relaxation. The calculations show that the MCA is −0.31 meV/per Co atom for clean Co ML on Cu, 0.08 meV/per Co atom for 1 ML Cu overlayer coverage, and −0.05 meV/ per Co atom for 2 ML Cu overlayer coverage. Although the results of both calculations (i.e., with and without structural relaxation) show the same trend in the change of MCA versus Cu coverage, it is clear that structural relaxation is crucial in understanding the dramatic change observed experimentally.

That the interface MCA varies with Cu coverage and is sensitive to structural relaxation raises the question: *how do these factors affect the electronic and magnetic properties of these interface systems?* (It is these factors which correlate in a fundamental way with the MCA.) We try to answer this question in the following.

A. Interface structures and magnetic states

We first present the atomic structure, determined with multilayer relaxation. For all three cases considered, the equilibrium structures are determined by atomic force calculations in which all the final z-direction forces on all the atoms are almost zero (<3 mRy/a.u.) and thus the total energy reaches its minimum. In general, the adopted experimental lattice constant is slightly larger than that obtained through LDA calculations, and will lead to an overestimation of the relaxation. However, this discrepancy is within 3% and so will have no significant effect on the results given below. The calculated atomic positions are listed in Table I, which also gives the notation that defines the Cu layers.

For the clean Co/Cu system, relative to unrelaxed structure the fully relaxed surface Co layer is found to undergo a downward relaxation by 0.30 a.u., whereas the interface Cu has only a slight inward contraction by 0.06 a.u. Relative to the isolated Co monolayer and the Cu(111) substrate, the deposition of the Co monolayer on Cu(111) causes a de-

crease of the surface potential and (combined with the metallic screening effects) also squeezes the s,p electrons, which originally spread out in the vacuum of both the isolated Co monolayer and Cu(111) substrate. This results in a reduction of the Co magnetic moment as compared to that for the isolated Co monolayer.

After the deposition of 1 ML Cu, the Cu(O1) layer at the surface has a very large contraction (0.44 a.u.) relative to the unrelxed structure. Due to the screening of the surface Cu(O1) layer, the inward contraction of the Co layer in the clean case is reduced (to 0.16 a.u.). The deposition of Cu on Co/Cu(111) decreases the surface potential and leads to the Co atom obtaining 0.08 more electrons inside its muffin-tin sphere as a result of a loss of 0.11 majority spin electrons and a gain of 0.19 minority spin electrons. Subsequently, the Co magnetic moment is reduced to 1.26 μ_B—about 20% smaller than that in the clean Co/Cu(111) overlayer case.

At 2 ML Cu coverage, the relaxation of the Co layer is almost completely removed. As shown in Table I, the capped Cu bilayers [surface Cu(O2) and subsurface Cu(O1)] are relaxed downward by 0.46 and 0.18 a.u., respectively. Due to the further deposition of the Cu(O2) layer and structural relaxation, compared with 1 ML Cu on Co/Cu(111), the Co atom gains 0.04 majority spin electrons and loses 0.07 minority spin electrons as a result, the magnetic moment of the Co atom is increased to $1.37\mu_B$ from $1.26\mu_B$.

For the nonrelaxed case, where the magnetic moment of Co in the clean Co/Cu overlayer is $1.60\mu_B$, when a monolayer and bilayer Cu are added, the moment changes to $1.40\mu_B$ and $1.41\mu_B$, respectively. In all the systems considered, the induced Cu magnetic moment is less than 0.015 μ_B. This feature is consistent with the argument that the magnetic interaction between the magnetic Co and nonmagnetic Cu is weak because the Cu d states lie well below the Fermi energy.

The influence of the interface on magnetism for various systems is through hybridization, as discussed previously.[11] Here the presence of interface Cu was shown to have a significant influence on the magnetic moment of the Co layer through the hybridization between Co and Cu, as shown in Table I. The structural relaxation is shown to change the interatomic distance at the interface, and thus affects the strength of the hybridization, the strength of the SOC perturbation and thus the MCA energy, as shown below.

B. Magnetocrystalline anisotropy and banding filling

It is well known that MCA results from SOC, and the most important contribution is from the states close to the Fermi-energy. Owing to the strong exchange splitting in Co/Cu systems, the spin-up d bands contain almost no empty states in the range of the spin-down Co d band filling. The dominant part of the SOC induced energy, $E^{sl}(\boldsymbol{\sigma})$ is between the spin-down states, and thus the interface MCA is mainly from the spin-down states, i.e., ΔE^{dd}. Following a simple rigid band approach, we plot the variation of ΔE^{dd} against the number of valence electrons (Z) in Fig. 1, by changing the band filling through varying the highest occupied energy.

The band filling curve for clean Co/Cu exhibits qualitatively the same behavior as that of an isolated Co monolayer;[4] positive anisotropy dominates the beginning

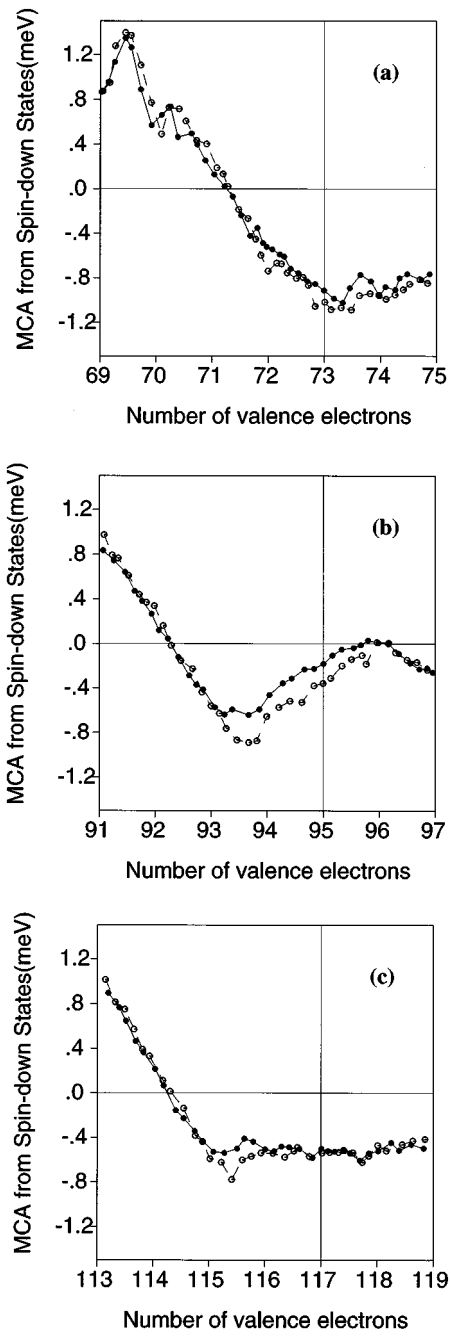

FIG. 1. Band filling dependence of the dominant MCA contribution from spin-down states ΔE^{dd} (in meV). The solid (open) cicles and solid (dash) lines denote relaxation (unrelaxation) case. Vertical lines mark the physical Fermi filling. (a) clean Co/Cu; (b) 1 ML Cu coated Co/Cu; and (c) 2 ML Cu coated Co/Cu.

part of filling the spin-down Co d bands ($Z\sim$ around 71). At near half-occupation of the spin-down Co d bands ($Z\sim$ 72 to 74), a negative bump develops in the band filling curve. This behavior is typical for all isolated monolayers, overlayers and sandwiches studied previously.[4] When capped with 1 ML Cu, a remarkable change happens at the half-filling region as shown in Fig. 1(b) ($Z\sim$ 94 to 96): the presence of the first Cu layer makes a strong positive contribution in this region. Surprisingly, when the second Cu layer is deposited, the band filling behavior is almost the same as in the clean

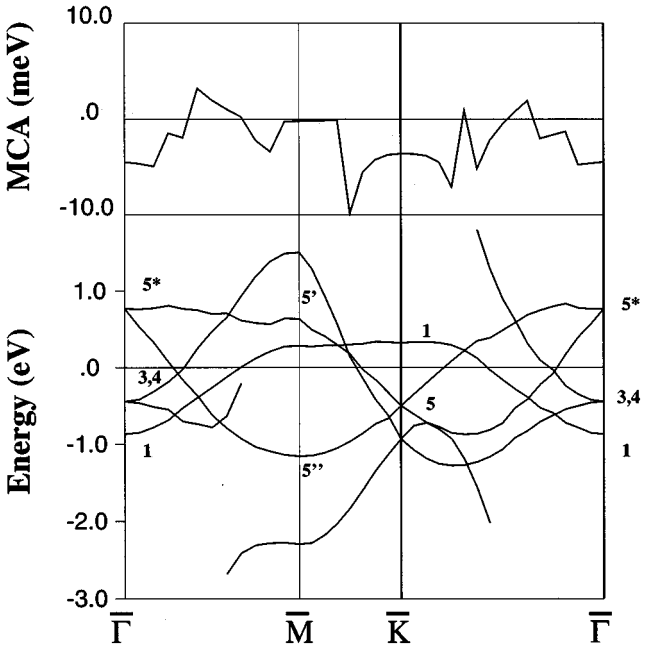

FIG. 2. MCA contribution ΔE^{dd} of the SOC between the spin-down states, correlated with the unperturbed spin-down band of the isolated Co monolayer. Band numbers 1, 3, 4, 5′ and 5″ stand for z^2, x^2-y^2, xy, yz, and xz states, respectively. Bands 5 and 5* denote hybridized xz and yz orbitals. Only states with more than a 50% d component are shown.

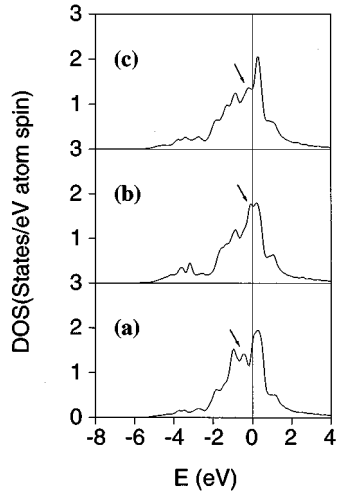

FIG. 3. Projected density of states for Co spin-down d states for : (a) clean Co/Cu; (b) 1 ML Cu coated Co/Cu; and (c) 2 ML Cu coated Co/Cu.

Co/Cu case, namely, the negative bump in ΔE^{dd} remains constant around half-occupation of the spin-down d bands ($Z \sim 116$ to 118).

The effect of structural relaxation is verified by comparing ΔE^{dd} versus band filling for the ideal interface structure shown in Fig. 1. Obviously, as in the clean and bilayer Cu coated case, the band filling curves almost overlap over the whole energy region for ideal and relaxed systems. For 1 ML Cu coverage, however, the structural relaxation causes a rigid upward shift in ΔE^{dd} at half-occupation of the spin down d bands ($Z \sim$ 93.5 to 96). The effect amounts to about 0.2 meV on ΔE^{dd}, and thus influences the value of the total interface MCA.

C. Electronic states and interface hybridization

In order to further understand the physical origin of the anomalous change of MCA versus interface structure, we have further analyzed the electronic states for these systems. For the free standing Co monolayer with (111) Cu lattice parameter, the spin-down bands along the high symmetry lines $\bar{\Gamma} - \bar{M} - \bar{K}$ in the 2D BZ are shown in the bottom panel of Fig. 2, and the MCA contribution from spin down states ΔE^{dd} is shown in the top panel. The band structure shows behavior similar to the Co(001) case,[4] namely, the out-of plane d_{z^2} and d_{xz}, d_{yz} states are located around E_F and show a small dispersion because of the small overlap between the neighboring Co atoms. The in-plane d_{xy} and $d_{x^2-y^2}$ states show large dispersion because of a strong interaction between the Co atoms in the film plane. Owing to the small dispersion around E_F, the coupling (through $L_{x,y}$ angular momentum component) between the $d_{xz,yz}$ bonding and the d_{z^2} anti-bonding states dominates around $\bar{\Gamma}$ and $\bar{K}$, and in most of the BZ, and results in a strong negative MCA energy ($-$ 0.85 meV/atom).

Upon contact with a nonmagnetic substrate at the interface, the energies and wave functions of the Co-d_{z^2} and $d_{xz,yz}$ states (both point out of the plane) are changed by the interfacial hybridization. These hybridizations are sensitive to the local interface structure and are expected to affect the strength of the SOC perturbation between the Co-$d_{xz,yz}$ and the Co-d_{z^2} states and thus the MCA energy. Figure 3 sketches the calculated density of states (DOS) for the Co spin down d states. The different hybridization between Co and Cu due to structural changes in the interface is clearly shown by the DOS peaks in the range -1.0 to 1.0 eV with respect to E_F. Especially for the peak just below E_F, there is an abrupt change versus Cu coverage; the location and the height of this peak is greatly enhanced and reaches a maximum with 1 ML coverage. This feature is consistent with the magnetic moment of Co in these systems. As shown in Table I, for the clean case the magnetic Co layer is at the surface and the hybridization between magnetic Co and nonmagnetic Cu atoms is expected to be weak. The presence of the interface Cu layers, instead of vacuum, reduces the magnetic moment of Co through the strong interaction and hybridization.

Thus, it is clear that the effects of the nonmagnetic substrate on the MCA in the Co layer arise mainly from the hybridization with the Co-d_{z^2} and $d_{xz,yz}$ states. Obviously, as revealed in an effective ligand interaction model (ELIM),[4] (i) the energy separation between the Co and substrate d bands and (ii) the strength of the interfacial hybridization play a key role in determining the MCA energy. The stronger the hybridization, the more the perpendicular MCA prevails. This makes a connection between the above DOS features and the interface MCA in clean, monolayer and bilayer coated Co/Cu systems. In fact, for the clean case, the hybridization only occurs between the Co surface layers and the Cu substrate. The interaction between magnetic Co atoms and nonmagnetic Cu atoms is expected to be stronger with Cu adsorption. As shown in the Table I, the presence of the

interface Cu atom is shown to reduce the Co magnetic moment through the strong interaction and hybridization with the bonding Co bands. This interaction results in an upward shift in energy of these bonding Co states, which are the out of plane Co-d_{z^2} and $d_{xz,yz}$ states, and a strongly positive MCA contribution exists through the angular momentum components L_z coupling between the occupied d_{xz} and empty d_{yz} bands.

The presence of the Cu adsorption layer instead of vacuum is somewhat similar to the Co/Pd case,[12] where, due to the hybridization between the out-of-plane Co bonding d_{xz} (d_{yz}) states with the interface Pd atom, the large *d*-*d* bonding strength and high energy of the Pd *d* band cause a substantial component of these Co states (bands) to be shifted upward, and thus lead to a strong positive (perpendicular) Co-Pd interface MCA. In fact, for the Cu overlayer system, due to the surface potential, the Cu *d* states are higher in energy than their bulk counterpart, and so have a strong interaction with Co and an upward shift of the Co *d* states as shown in Fig. 3. The result is a positive contribution to the interface MCA.

A similar argument can be applied to explain why the second Cu layer deposition leads to a decrease of the interface MCA. Note that for a bilayer Cu coverage, Cu(O1) is located in the subsurface, whereas for a monolayer Cu coverage, the interface Cu(O1) is at the surface. Obviously, the energies of the *d* orbitals for surface Cu atoms are higher than those of subsurface Cu atoms, because the subsurface Cu is more bulk-like. According to the effective ligand interaction model (ELIM),[4] the strength of the Co-Cu hybridization will be stronger if the interface Cu is located at the surface and thus the interface MCA of the Co layer is more positive.

When relaxation is introduced, the positive MCA is enhanced for the 1 ML Cu coverage. This can be understood by the strength of the interfacial hybridization. However, owing to the relaxation, the interatomic distance between Co and Cu in the monolayer Cu coated case is the smallest, and hence has the strongest hybridization between them. This is confirmed by the Co magnetic moment listed in Table I, which is the smallest among the three cases. When 2 ML Cu is considered, the relaxation of Co and interface Cu atoms are released by the screening. This effect increases the interatomic distance between Co and interface Cu, and weakens the interaction between them. According to the ELIM idea,[4] the positive contribution to the interface MCA is expected to be smaller than for the system with 1 ML Cu coverage.

These results are to be compared with the Co/Cu(001) overlayer and sandwich systems,[4] where the downward shift of out of plane states responsible for the interface MCA changes from a more negative MCA (-0.38 meV) in the overlayer to near zero (-0.01 meV) in the sandwich. Here in the Co/Cu(111) overlayer with different Cu coverage, the MCA change is caused by two effects, the presence of the interface and relaxation. On the Co/Cu surface, due to the surface effect the energy of the coated Cu *d* band was brought closer to the bonding Co *d* bands and thus has a strong interaction with the out-of-plane Co states. This results in an upward shift of these Co bands, and a strong positive MCA contribution exists through L_z coupling between occupied d_{xz} and empty d_{yz} bands. More Cu deposition is expected to decrease the surface effect on the Co/Cu interface and then to weaken the interaction strength, and thus the interface MCA decreases drastically.

IV. CONCLUSION

The results of first principles calculation for the interface MCA of Co monolayer on Cu(111) substrate and monolayer and bilayers Cu capped Co/Cu determined by the FLAPW band method in the state tracking approach and torque method were presented and discussed. In good agreement with experiment, the easy axis of the systems considered here is found to be in the layer plane for clean Co/Cu (-0.30 meV), perpendicular to the layer plane (0.23 meV) for a Cu coverage of 1 ML, and back to in-plane (-0.02 meV) upon further Cu deposition. The Cu coverage induced MCA change in these systems is understood by the difference in energy separation between the *d* bands of Co and the coated Cu layer. It is also found that the strength of the interfacial hybridization changes by both the surface effect and atomic relaxation, which play an important role in the interface anisotropy. Since, this behavior is also expected in the Co/Ag and Co/Au systems, further investigations are in progress.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (Grant No. N00014-94-1-0030) and grants of computer time at the Pittsburgh Supercomputing Center supported by the NSF Division of Advanced Scientific Computing and the Arctic Region Supercomputing Center. We thank J. I. Lee of Inha University, Korea for a critical reading of the manuscript and helpful discussions.

[1] F. J. A. den Broeder, W. Hoving, and P. J. H. Bloemen, J. Magn. Magn. Mater. **93**, 562 (1991), and references therein.

[2] B. N. Engel, M. H. Wiedmann, R. A. Van Leeuwen, and C. M. Falco, J. Appl. Phys. **73**, 6192 (1993); B. N. Engel, M. H. Wiedmann, and C. M. Falco, *ibid.* **75**, 6401 (1994).

[3] F. Huang, G. J. Mankey, and R. J. Willis, J. Appl. Phys. **75**, 6406 (1994).

[4] D. S. Wang, R. Wu, and A. J. Freeman, J. Magn. Magn. Mater. **129**, 237 (1994)

[5] E. Wimmer, H. Krakauer, M. Weinert, and A.J. Freeman, Phys. Rev. B **24**, 864 (1981), and references therein.

[6] Defined as the first derivative of the total energy with respect to the atomic position, the force calculated in the FLAPW approach contains both the Hellmann–Feynman term and the Pulay correction terms. See, for example, J. M. Soler and A. R. Williams, Phys. Rev. B **40**, 1560 (1989) and R. Yu, D. Singh, and H. Krakauer, *ibid.* **43**, 6411 (1992).

[7] D. S. Wang, R. Wu, and A. J. Freeman, Phys. Rev. Lett. **70**, 869 (1993).

[8] X. D. Wang, D. S. Wang, R. Wu, and A. J. Freeman Bull. Am. Phys. Soc. **40**, 528 (1995).
[9] S. L. Cunningham, Phys, Rev. B **10**, 4988 (1974).
[10] M. Y. Kim, L. P. Zhong, X. D. Wang, and A. J. Freeman (unpublished).
[11] A. J. Freeman and R. Wu, J. Magn. Magn. Mater. **100**, 497 (1991).
[12] D. S. Wang, R. Wu, and A. J. Freeman, Phys. Rev. B **48**, 15 886 (1993).