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Monolayer magnetic anisotropy: A systematical tight-binding study

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The magnetic anisotropy of a free-standing transition-metal monolayer versus the band filling is systematically studied. By using a tight-binding Hamiltonian we show that it is possible to obtain an accurate description of the anisotropy energy. We show that the magnetic anisotropy energy versus d-band filling must exhibit a minimum number of nodes, with irregular oscillations imposed on this curve. Their origin, which is likely to be related to energy-band crossings, is discussed in detail. Our results are consistent with the available data. For Fe and Co (001) monolayers, a very small magnetic anisotropy is found, as well as for a Ni (001) monolayer. Moreover, the shape of the anisotropy energy curve might explain the controversial situation for iron.

I. INTRODUCTION

Very thin transition-metal magnetic layers have recently been the subject of many studies. Considerable attention has been paid to possible perpendicular orientation of the film magnetic moment.[1] The monolayer magnetic anisotropy energy (MAE) was studied theoretically by several groups[2–10] at different levels of sophistication. The agreement between different results is not satisfactory, one of the reasons apparently being of numerical character. Besides that, the recent studies[3,7,9,10] show that in contrast to the $3d$-metal magnetic moment value, the MAE can be strongly influenced by the noble-metal substrate. Recently a stimulating semiempirical study[5,6] has appeared. It suggests that the use of simple models combined with qualitative arguments can bring new insight to the problem.

In this paper we would like to point out the existence of general trends that can be related to the electronic structure. First, we derive the minimal number of nodes MAE displays versus the band filling. Then we perform a systematic study of thin-film magnetic anisotropy by using a tight-binding electronic Hamiltonian and employing the recursion-method technique.[11] The advantage of this approach is that we can be confident of the accuracy of approximations and numerical procedures. In the recursion method the local density of electronic states (LDOS) is expressed as a continued fraction. Convergence problems are critical at points where the LDOS is infinite and nonanalytic, i.e., near van Hove singularities. However, the situation is much improved by the known smearing properties of the integral operator when quantities such as energy or charge are computed. The choice of a poor orbital basis can slow down the convergence as well. To find the magnetic orbital moment value, the real d-orbital basis has to be transformed to spherical harmonics with the spherical coordinate axis $\theta=0$ parallel to the magnetization. The complex formalism represents no essential problem in the recursion method. It appears, however, that energy calculations converge better when the basis reflecting the film geometry is employed and the axis $\theta=0$ coincides with the sample normal even for in-plane magnetization. For the respective continued fractions the standard quadratic termination is used with the bandwidth negligibly larger than the minimal prescription of Ref. 12. For simplicity, a square lattice [(001) layer] with nearest-neighbor interactions is studied. Results for other geometries will be published elsewhere together with a more complete discussion of important points.

The ferromagnetic monolayer is described by the tight-binding d-band Hamiltonian

$$H_\alpha = H^0 + \sum_q [-(\lambda/2)\sigma_\alpha + \xi \mathbf{L}\cdot\mathbf{S}] \quad (\alpha = X, Z) . \tag{1}$$

Above, H^0 is the paramagnetic Hamiltonian. The sum over all lattice sites q contains atom-localized operators only. The term $-(\lambda/2)\sigma_\alpha$ leads to the exchange splitting λ with magnetization along the direction α (σ_α is the Pauli matrix). Note that $\sigma_\alpha = (p_\uparrow - p_\downarrow)$ in our model, where $p_\uparrow, p_\downarrow$ are orthogonal projectors on the subspace of majority and minority spins, respectively. Throughout the paper we use the coordinate system with the Z axis along the surface normal and the X axis oriented along a nearest-neighbor bond. The last term in Eq. (1) describes the spin-orbit coupling.

The energy difference ΔE associated with the change of magnetization orientation (the magnetic anisotropy energy) is computed taking the double counting of Coulombic and exchange terms into account and respecting strict local charge neutrality, although λ is kept independent of the magnetization orientation. The latter simplification affects the results in the second order of the perturbation theory only.

II. OSCILLATION THEOREM

Since an implicit evaluation of moments, $\mu_k = \mathrm{Tr} H^k$, is performed in the recursion method, it is natural to apply the oscillation theorem[13] connecting the ΔE behavior with the change of moments due to the magnetization reorientation. It can be shown that moments for the two values $\alpha = X, Z$ differ due to the noncommutativity of the $(\lambda/2)\sigma_\alpha$ term with Pauli matrices present in the $\mathbf{L}\cdot\mathbf{S}$ operator. The lowest moment for which the above

difference is nonzero is of the sixth order, the α-dependent contributions being of the form

$$\mathrm{Tr}\xi^2 \sum_P PH^0_{pq}H^0_{qp}[(\lambda/2)\sigma_\alpha][(\lambda/2)\sigma_\alpha](\mathbf{L}\cdot\mathbf{S})(\mathbf{L}\cdot\mathbf{S}) , \quad (2)$$

where the sum is taken over all the permutations P of the six terms shown. In Eq. (2), H^0_{pq} is the paramagnetic Hamiltonian block connecting the nearest-neighbor pair (p,q). According to the oscillation theorem, ΔE will change its sign at least four times. It is usually assumed that the change of higher-order moments is less important, since they bear information mainly on details of the energy-band structure. As we show below, however, such features are probably essential in our case.

III. (001) MONOLAYER MAGNETIC ANISOTROPY

An enormous number of semiempirical calculations of transition-metal properties have been performed based on the idea of a simple general tight-binding Hamiltonian constructed from a few independent parameters. For a particular metal, linear rescaling of universal parameters to obtain the correct bandwidth is performed. We use the d-band Hamiltonian H^0 with the ratio of the Slater-Koster parameters $dd\sigma:dd\pi:dd\delta=-6:4:-1$. This parametrization is supported by the analysis of d-orbital behavior and by the linear-muffin-tin orbital (LMTO) theory; we refer the reader to Ref. 14, where a similar model for the (001) paramagnetic monolayer is discussed to detail. Particularly, the width of the d-band w is -38 $dd\delta$. It is known that two distinct regimes exist for ferromagnetic films. The first one with large exchange splitting [large exchange regime (LER)] yields the maximal possible (saturated) magnetic moment. For smaller λ [small exchange regime (SER)], holes exist in the majority spin bands. To study the first case, we chose the Fe (001) monolayer with Au nearest-neighbor distance as an example, with $\lambda\sim 2.9$ eV, and $dd\delta=-0.055$ eV.[7] The other possibility takes place for Ni (001);[14] we take $\lambda=0.9$ eV and $dd\delta=-0.092$ eV. For the spin-orbit coupling parameter we take the value $\xi=0.05$.[6]

Perusal of our numerical results shows that the MAE curves consist of the superposition of two contributions: the regular one can be understood more or less in simple terms, whereas the rapidly oscillating contribution has an irregular character. The interplay between the two components depends both on the film geometry and the d-band occupation studied.

A possible source of the oscillations [which are very dense, e.g., for the (111) fcc monolayer] may be the energy-band crossings.[15] A full qualitative analysis of this effect is rather involved and will be given elsewhere. The symmetry arguments show that a crossing of two bands is usually strongly perturbed by the spin-orbit interaction only for one of the two orientations of magnetic moment considered. However, in two-dimensional systems according to the Wigner–von Neumann theorem,[16] an isolated crossing point (and possibly also some crossings along a curve caused by the symmetry) is a stable feature, and it may move to a close Brillouin-zone (BZ) point having no symmetry. The two crossings (removed and created) represent the negative and positive component, respectively, of a "crossing dipole" introduced by the spin-orbit perturbation. It is obvious that a related dipole-like feature (oscillation) should appear on the MAE curve. Naturally, our simple model is capable of giving only qualitative information on similar effects. The lack of correspondence between gross LDOS features and oscillations does not support the suspicion that the oscillations represent an artifact of the recursion method.

MAE is expected to scale as ξ^2 (Ref. 6) on the grounds of perturbation theory arguments. However, terms linear in ξ due to the (quasi)degeneracy of levels near energy-band crossings might appear. Our numerical tests show linear rather than quadratic scaling for the oscillatory component of MAE providing thus another support to our interpretation. Also the van Hove singularities in the LDOS due to (XZ,YZ) states near the X-M and Γ-X directions of the Brillouin zone (BZ) need a careful treatment. Another important (logarithmic) van Hove singularity due to XY states at point X falls in the middle of the band.

We do not include any crystal-field correction.[5,6] An analysis shows that the crystal field in Ref. 5 compensates artifacts in the LDOS and in the band structure of the (111) monolayer near point K of the BZ arising from the omission of p orbitals. In agreement with Ref. 14, a similar problem seems to be absent in the (001) case.

As is clear from the above results, at least six moments of the Hamiltonian are to be included to get any information on the anisotropy energy. Our tests show that for 16 moments the MAE curve is strongly distorted, whereas for about 30 moments the gross features seem to be correctly reproduced. Below, we present the results evaluated including 50 moments.

In Figs. 1 and 2, we display the MAE curves together with results for the orbital magnetic moment M_α. Since the ΔE curves are almost symmetric with respect to the $N_d=5$ point, and the $M_{X,Z}$ curves are approximately odd functions of (N_d-5) for the (001) layer and zero crystal field, only the results for $N_d\geq 5$ are displayed. The most striking features are related to specific LDOS features described above. We expect that the spin-orbit interaction contributes essentially to the magnetic anisotropy when it couples high-density peaks that lie close together in energy and are separated by E_F.[6] The selection rule $\Delta\mathbf{k}=0$ reduces the number of possible interactions, and analysis of the energy-band structure[14] allows us to suggest a more complete interpretation. The two above conditions stress the role of Fermi surface effects[7,15,17] which, in turn, can lead to abrupt changes in the ΔE behavior. To corroborate our interpretation, we made test calculations for different values of crystal-field splitting. The correlation between the LDOS peak shifts and changes in the ΔE curve shape gives us some confidence in the picture we propose.

As an example, consider the LER [Fig. 1(a)]. In this case, the oscillations are less numerous than for, e.g., the (111) film. The region $N_d\gtrsim 7$ is dominated by interactions between minority spin electrons. The negative value of ΔE at $N_d\sim 8.5$, which corresponds to a preferred perpendicular magnetic moment orientation is re-

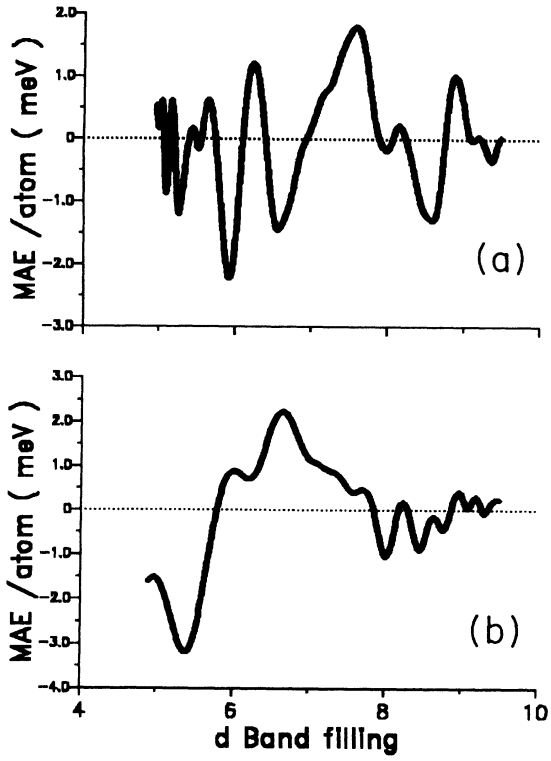

FIG. 1. Magnetic anisotropy energy (MAE) per atom (meV) versus the d-band filling for (001) monolayer. Negative values correspond to favorable perpendicular direction of the magnetization. (a) Large exchange splitting regime. (b) Small exchange splitting regime.

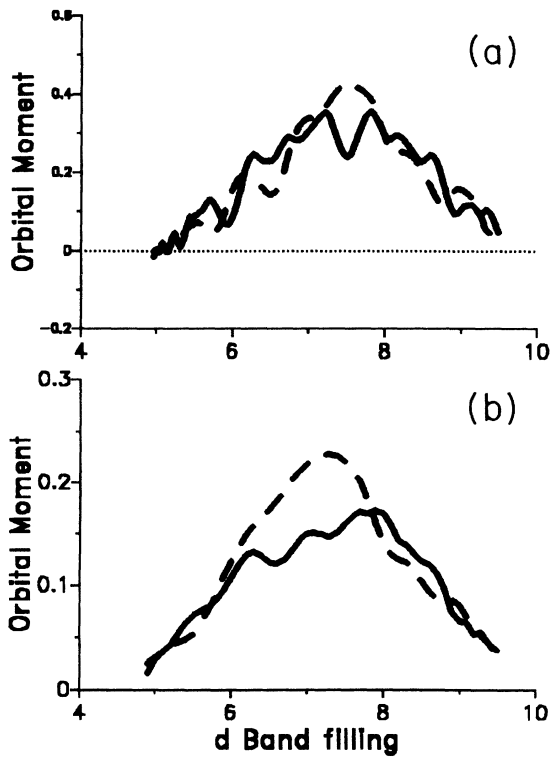

FIG. 2. Magnetic orbital moment per atom (in Bohr magnetons) versus the d-band filling for (001) monolayer. Full (dashed) line corresponds to the perpendicular (in-plane) direction. (a) Large exchange splitting regime. (b) Small exchange splitting regime.

lated to the higher (XZ, YZ) LDOS peak and may be associated with splitting of degenerate levels at the Γ point of the BZ. When these states become filled ($N_d \sim 9$), their interaction (probably near X) with empty states based on different orbitals leads to a change of the anisotropy sign. The prominent ΔE peak at $N_d \sim 7.5$ is due to the interaction between the XY and the lower (for lower position of E_F) or the upper (XZ, YZ) LDOS peak near X. At $N_d \lesssim 7$ we find a perpendicular anisotropy with origin similar to the feature at $N_d \sim 8.5$, but the degeneracy of (XZ, YZ) levels at point M is now important. In the center of d-bands interaction of states with opposite spins must be considered as well, giving a more complicated picture. We note only that here also the (XZ, YZ) pair plays an important role. In the SER, the most important features described above are found again [Fig. 1(b)], although they are now shifted to somewhat lower values of N_d because of the holes in the majority spin bands. Besides that, the quantitative changes are rather large.

To summarize the above discussion, pronounced perpendicular anisotropy for the (001) layer is expected for E_F in one of the two (XZ, YZ) LDOS peaks, and parallel magnetization takes place for E_F placed well between these peaks.

Figure 2 confirms the proportionality between the magnetic orbital moment anisotropy and the magnetic anisotropy energy[5,6] well away from the $N_d = 5$ value.

Several particular cases are important for comparison with existing data. For Fe and Co (001) (LER, $N_d \sim 7$ and 8, respectively), we find very small magnetic anisotropy, although the ΔE curve is very steep in this region, making any prediction unreliable. For Ni (001) (SER, $N_d \lesssim 9$), the prediction is also difficult, although anisotropy energy values remain small in this region. The comparison with available theoretical data[2-10] shows an overall agreement with Refs. 7, 9, and 10 although the controversial situation concerning the sign and magnitude of magnetic anisotropy of iron monolayer is consistent with the rapid change of our anisotropy curve.

A comment should be made on the pronounced perpendicular magnetic anisotropy found experimentally[1] for very thin transition-metal films on noble-metal substrates. Despite the "inert" character of noble metals the monolayer van Hove singularities, and especially those associated with nonsaturated (XZ, YZ) orbitals, are sensitive to perturbation. Theoretical results[7,9] show that they hybridize with noble metal s and/or $3Z^2$ orbitals. It seems possible that widening of the corresponding LDOS peaks can lead to preferred perpendicular anisotropy under less restrictive conditions on the E_F position than in the free-standing monolayer case.

In summary, we have determined the magnetic anisot-

ropy energy ΔE of a free-standing (001) cubic monolayer versus the band filling. This systematical study suggests that the oscillatory behavior of ΔE is not a numerical artifact: the ΔE curve must present a certain minimum number of nodes versus the band filling and some oscillations have been related to finer effects. More complete study of the influence of the geometry, the crystal-field and the thickness of the film is now in progress.

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