Magnetic anisotropy of transition-metal thin films

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(Received 30 October 1992; revised manuscript received 25 June 1993)

The magnetic-anisotropy energy (MAE) versus the d-band filling is systematically studied for a number of high-symmetry free-standing transition-metal monolayers and bilayers. We show that a simple tight-binding model combined with the recursion method is very useful in the elucidation of the complicated MAE problem. A canonical MAE curve is proposed as the simplest one curve consistent with the oscillation theorem and is interpreted in electronic-band-structure terms. Departures from this simple picture found in calculations are discussed in detail based on a symmetry analysis and the generalized theory of Wigner and von Neumann describing the energy-band crossing geometry. Some of our conclusions seem to agree with recent theoretical results and may shed light on the existing controversies regarding the Fe(001) monolayer. Other topics such as the crystal-field splitting, magnetic orbital momentum, the applicability of perturbation theory for MAE evaluation, and the substrate role are touched upon.

I. INTRODUCTION

The unique magnetic properties of thin transition-metal films are presently the subject of intense investigations. Considerable effort has been devoted to the problem of the film magnetic anisotropy (MA), especially because of the possibility of preparing samples with perpendicular orientation of the magnetic moment.[1] The amount of information obtained in this area both by experimental[2–5] and theoretical methods[6] is rapidly growing. Nevertheless, a lucid and unifying interpretation of the rich spectrum of effects still presents a challenge. In most theoretical papers a free-standing monolayer or a monolayer adsorbed on a noble-metal substrate was studied by various methods.[6–14] The agreement between particular results is not very satisfactory, one of the reasons being of numerical origin. A number of studies[6,12–14] show that in contrast to the magnetic-moment value for $3d$ metals, MA can be strongly influenced by the noble-metal substrate.

A recent semiempirical study[10,11] has shown that the use of simple models combined with qualitative arguments enables one to pose new questions. Let us formulate some of them: (1) Is it possible to study MA within a simple perturbation theory approach? (2) If the answer to (1) is positive, what is then the origin of the numerical difficulties faced by other authors? (3) Is there a correspondence between magnetic-anisotropy energy (MAE) and magnetic orbital moment value? (4) Is MA enhanced by the thin-film crystal-field effects? By answering these questions one could progress further in understanding the problem. Pursuing this idea we have recently performed an analysis of the free-standing monolayer MA based on a simple tight-binding electronic Hamiltonian and employing the recursion method technique.[15,16] Here we gather and discuss in more detail the methodical problems and numerical results related to these studies.

The model is explained in Sec. II. The well-known uncertainty of semiempirical schemes is outweighed by the fact that we control the accuracy of most numerical procedures as well as by the possibility of obtaining an extended set of data helping us to draw conclusions about general trends.

Section III is devoted to a qualitative analysis of the principal aim of this study: to understand the dependence of the film MAE ΔE on the d-band occupation N_d. The moment theory enables us to find the minimum number of nodes of the $\Delta E(N_d)$ curve and to suggest a canonical behavior of MAE. We propose an explanation of this picture in terms of the electronic structure of the film. Departures from this scenario found in our calculations force us to seek also other, highly specific, contributions to MAE and to reconsider the validity of the perturbation theory approach at the same time. A generalization of the model of Sec. II is also introduced.

Finally, in Sec. IV we confront our qualitative analysis with numerical results and compare our conclusions with the available literature data. We also comment on the relevance of our results to other questions related to MA.

II. MODEL

We consider the electronic structure of free-standing high-symmetry ferromagnetic or antiferromagnetic transition-metal monolayers and bilayers. They are described by a tight-binding nearest-neighbor d-band Hamiltonian [for bcc (011) bilayers second-nearest-neighbor interactions are included as well assuming the R^{-5} distance dependence of the hopping elements],

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

Above, H^0 is the paramagnetic Hamiltonian. The sum runs over all lattice sites q and contains site-localized

operators only. The term $(\lambda/2)\sigma_\alpha$ yields the exchange splitting λ with magnetization along the direction α. σ_α is a 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. In structures with antiferromagnetic coupling, $A=-1$ at sites with the magnetization reversed, otherwise $A=1$. The value of the exchange splitting is assumed to be independent of the magnetic-moment orientation (see below). The last term in Eq. (1) describes the spin-orbit (SO) coupling. Throughout the paper, we use a coordinate system with the Z axis along the surface normal and the X axis oriented along a surface nearest-neighbor bond. Two possible directions of magnetization, $\alpha=X$ or Z are considered. We disregard, of course, a small in-plane MA. The mean value M_α of the magnetic orbital moment (i.e., the orbital moment in Bohr magneton units) projected on the magnetization direction is nonzero due to the SO coupling.[11] To find it, the real d-orbital basis commonly used is transformed to a complex spherical harmonics basis with the axis $\theta=0$ of spherical coordinates oriented along the X or Z axis, respectively. However, the choice of X axis does not reflect the spatial symmetry $Z\rightarrow -Z$ of the film and allows some unphysical mixing of noninteracting orbitals when termination of the continued fraction is made. The final effect is some smearing of sharp features in the local density of electronic states (LDOS), and the convergence slows down. (In other words, continued fractions converge more slowly when a poor basis is chosen). For this reason we orient the axis $\theta=0$ of spherical harmonics along the X axis only when M_x is to be calculated.

We construct the Hamiltonian H^0 using Slater-Koster parameters with the ratio $dd\sigma:dd\pi:dd\delta=-6:4:-1$.[17] Tests were performed showing that the results were not too sensitive to the parameter choice. A simple expression for the paramagnetic (001) monolayer bandwidth w that is equal to the distance between the X^2-Y^2 levels in M and Γ points of the Brillouin zone (BZ) reads in our parametrization,[17] $w=-38\ dd\delta$ (note that in Ref. 17 the coordinate system is rotated by 45° with respect to our choice). It is known that two distinct regimes exist for ferromagnetic films. The large exchange-splitting regime (LER) yields the maximum possible (saturated) magnetic moment. For smaller λ regime (SER), holes exist in the majority-spin bands. To study the first case, we chose the isolated Fe (001) monolayer with the Au nearest-neighbor distance as an example for which $\lambda\sim 2.9$ eV.[12] Both Ref. 12 and predictions based on scaling of tight-binding Fe models give $w\geq 2$ eV and we take $dd\delta=-0.055$ eV. The other possibility takes place for Ni (001); various estimates give $w=3-3.5$ eV and we take $dd\delta=-0.092$ eV, whereas $\lambda=0.9$ eV.[17] The same parameters are utilized for other structures. For the SO coupling parameter we use the value $\xi=0.05$ eV.[11]

Another problem crucial for understanding MA is the hypothesis of considerable crystal-field splitting in thin films.[7,10,11] To place E_F in the high-density LDOS peak for a Co (111) monolayer,[18] Bruno[10,11] assumed that the $(XY,\ X^2-Y^2)$ pair is stabilized by 0.5 eV with respect to other d orbitals and explained this as an electrostatic effect opposing the surface band narrowing. Note that the same idea was employed in Ref. 19. The correction improves the agreement of tight-binding energy bands with those of Ref. 18 near the K point of the Brillouin zone (BZ), spoiling the band structure at Γ at the same time.[10] In our parametrization no correction is necessary to get E_F in the LDOS peak for $N_d\sim 8$, although at the K point, the $(XY,\ X^2-Y^2)$ levels lie still too high in energy. In fact, the source of the crystal-field term is different. For the hexagonal (111) monolayer, the (X,Y) p bands are lowered in energy at the K point and they interact strongly with the $(XY,\ X^2-Y^2)$ levels. As a result, the latter d levels are stabilized considerably in this part of the BZ. This situation is characteristic for the (111) monolayer and is enabled by the fact that at K the above p and d orbitals belong to the same two-dimensional irreducible representation of the symmetry group. We have thoroughly checked this interpretation both by calculating energy levels at K and by comparing the tight-binding LDOS obtained for Hamiltonians with and without s and p orbitals. Hence, the crystal-field term is a model-dependent correction trying to compensate for simplifications in particular Hamiltonian parametrizations. In agreement with Ref. 17, we found no reason for similar corrections in the available literature data on the (001) monolayer.

The energy difference ΔE associated with the change of magnetization orientation (the magnetic anisotropy energy) is computed from the widely used expression

$$\Delta E=\sum_j \left[\Delta\int^{E_F} E\rho_j(E)dE-N_j\Delta\varepsilon_j\right]. \tag{2}$$

In Eq. (2), ρ_j is the partial LDOS associated with the spin orbital j and N_j is the corresponding electron occupation number. $\Delta\varepsilon_j$ is the change of the on-site Hamiltonian matrix element comprising both the Coulombic and exchange terms; the second term in Eq. (2) cancels the double counting of these contributions as discussed briefly in Ref. 20. Note that the one-electron energies are obtained by linearization of the energy functional around the ground state. As a result, all contributions from two-particle operators are counted twice when the one-particle energies are summed up. In our model, the change $\Delta\varepsilon_j$ is supposed to stem from the Coulomb interaction and is taken the same for all orbitals and found from the local charge neutrality condition. Supposing that the magnetic-moment value is calculated self-consistently, we could get slightly different values $\Delta\tilde{\varepsilon}_j$. It is known, however, that a correction of second order only in $(\Delta\varepsilon_j-\Delta\tilde{\varepsilon}_j)$ to the energy is introduced in this way. A simple reason for this is that the magnetization value follows from a variational principle which ensures the cancellation of all linear corrections to the energy.[21] The change of the magnetic moment due to the change of its orientation Δm is found to be a few $10^{-3}\mu_B$ in LER and can reach for some terms the value $2.10^{-2}\mu_B$ in SER. Since the resulting uncertainity in ΔE may be assessed to be smaller than $\sim J\Delta m^2$, where $J\sim 1$ eV is the exchange parameter, the error should not surpass a few 10^4-10^{-5} eV/atom. By adding the correction $\delta N_d\cdot E_F$ to the in-

tegral in Eq. (2), where δN_d is the *numerical* error in the postulated d-band occupation N_d, the inaccuracy of ΔE evaluation is reduced to the order $(\delta N_d)^2$. We conclude that there is *no trivial source of errors* in our calculations. Of course, some subtle numerical problems still remain as will be discussed below.

III. QUALITATIVE ANALYSIS

In this study, the Hamiltonian (1) is treated by the recursion method. Since an implicit evaluation of moments $\mu_k = \mathrm{Tr} H^k$ is made in this method, it is natural to apply the oscillation theorem[22,23] linking the ΔE behavior to the change of moments. The theorem gives the minimum number of nodes of the ΔE curve when the latter is considered as a function of the Fermi energy E_F or the d-electron occupation N_d. Moments for the two choices $\alpha = X, Z$ differ due to the noncommutativity of the three terms in the right-hand side of Eq. (1). The lowest moment for which the above difference is nonzero is of the sixth order, the respective contributions being of the form

$$\mathrm{Tr}\xi^2 \sum_P H^0_{pq} H^0_{qp} \left[\frac{\lambda}{2}\sigma_\alpha\right]\left[\frac{\lambda}{2}\sigma_\alpha\right](\mathbf{L}\cdot\mathbf{S})(\mathbf{L}\cdot\mathbf{S}) , \qquad (3)$$

where the sum is taken over all the permutations P of the six terms shown. In Eq. (3), H^0_{pq} is the paramagnetic Hamiltonian block connecting a neighbor pair (p,q). To derive the result let us decompose H^k into products of k factors similar to Eq. (3). It is easy to see that the trace is zero if the number of Pauli matrices in the product is odd. The time-reversal antiunitary transformation changes the sign of spin and orbital momentum which, together with the previous remark, shows that the number of SO-coupling operators must be even. The product has nonzero matrix elements diagonal in the site index p only for favorable combinations of the Hamiltonian blocks H^0_{pq} $(p \neq q)$; the simplest one is given in Eq. (3). It is possible to show that the trace can be L dependent only if all three types of operators shown explicitly in Eq. (3) are present. Equation (3) contains the simplest product consistent with these rules. A lengthy but elementary evaluation for the (p,q) pair in the (100) direction proves that the result is really different for $L = X$ and Z. Intuitively, Eq. (3) reflects the fact that the simplest unit showing MA is the atom pair (p,q). The oscillation theorem tells us that ΔE changes its sign, at least four times. An explicit calculation reveals that the expression (3) is positive and is larger for a perpendicular polarization of the magnetic moment. According to the generalized Hückel rule[24] the latter orientation should be preferred in the roughly half-filled $(N_d \sim 5)$ d-band case. Since this heuristic rule assumes a symmetric energy spectrum, it applies to the (001) monolayer only. In this case, taking the number of nodes into account, we expect switch to the parallel magnetization for an off-central position of E_F, changing its direction once more as the bands become yet more filled (empty). Below, such a hypothetical behavior is referred to as canonical. For geometries different from the (001) monolayer, an asymmetric deformation of the canonical curve is expected.

MA is controlled by the SO coupling between occupied and empty electronic states. To assess the strength of this coupling, let us remind the reader of several points. (1) The selection rule $\Delta\mathbf{k} = 0$ for quasiwave vectors is to be obeyed. (2) Selection rules for the orbital symmetry can be readily derived (Table I); they are especially effective for systems of high symmetry. (3) High-density peaks in LDOS are of importance assuming that they lie close together in energy and conform to (1) and (2). Although the interaction between states around E_F is generally decisive only for particular positions of the Fermi level, it can be responsible for some specific features in the MAE curve and it is instructive to consider such a possibility. For periodic structures similar peaks correspond to van Hove singularities (VHS) in LDOS. VHS are stronger for two-dimensional systems than for three-dimensional ones. For extrema of a band we obtain the Heaviside step function behavior whereas for a saddle point one has a logarithmic singularity. An explicit analysis, which is essentially independent of the Hamiltonian parametrization can be performed for the (001) monolayer.[17] (Note, however, that due to the competition of effects (1)–(3), the spin-orbit interaction need not be most intense precisely at the high-symmetry BZ points that we mentioned below.) The bonding combinations of the (XZ, YZ) orbitals form high-density features in the LDOS having their origin in the region near the X-M line of the BZ and in particular, comprising the two above kinds of VHS. An analogous situation takes place for antibonding states near the Γ-X line. The two peaks define in a certain sense limits of the playground of our model, since for ferromagnetic Fe, E_F lies slightly above the lower peak in the minority bands[12] whereas it falls just into the region of the antibonding states for Ni.[17] Another peak worth mentioning is the logarithmic singularity lying between the two LDOS features described. It corresponds to XY states near the point X of BZ. We do not mention here VHS due to $3Z^2$ and X^2-Y^2 orbitals, which seem to be of lesser importance for the (001) layer. For other geometries, the analysis is less straightforward. We note only that the nearest-neighbor triangles contribute to the third moment and bring about asymmetry pushing LDOS peaks to higher energies.[18] The above considerations, although quite general, are consistent

TABLE I. Symmetry-allowed spin-orbit interactions between various orbitals. Spin orbitals A-B or spin-orbital groups (A)-(B) are given for which the matrix element $\langle A/\mathbf{L}\cdot\mathbf{S}/B\rangle$ is nonzero. The Y^2-Z^2 orbital is a linear combination of $3Z^2-R^2$ and X^2-Y^2 functions. See the text for the coordinate system used.

Magnetization orientation	Mutual A-B spin orientation	
	Parallel spins	Antiparallel spins
Z	XZ-YZ (X^2-Y^2)-XY	(XZ, YZ)-$(XY,$ $X^2-Y^2, 3Z^2-R^2)$
X	XY-XZ (Y^2-Z^2)-YZ	(XY, XZ)-$(YZ,$ $X^2-Y^2, 3Z^2-R^2)$

with second-order perturbation theory,[11] suggesting the ξ^2 scaling of ΔE. It is seemingly only for E_F falling near the degenerate (XZ, YZ) levels in high-symmetry points of BZ that the quadratic scaling might be an overestimate. As will be seen below, this picture is partly justified but it is distorted by the presence of oscillating features which are clearly associated with moments of high order. At first sight one might be afraid that the oscillations arise from the inability of the recursion method to reproduce accurately the nonanalytic character of VHS or from the approximate termination of LDOS continued fractions by a quadratic terminator. Subsequent analysis does not confirm this suspicion and show that the oscillations do not correspond to VHS. Besides that similar oscillations are found both well inside the band and close to the spectrum edges of the quadratic terminator which allows us to rule out another source of error. Finally, let us discuss a possible reduction in the integration accuracy for unfavorable mutual positions of the integration grid points and unspecified LDOS singularities. We use a standard Gaussian integration scheme in which the integration step is refined until a convergence of 10^{-6} is reached. The integration grid points and the set of integrand dangerous points are different for different values of E_F and hence, the error should show a random character. Let us consider the MAE curve for LER (001) layer [Fig. 1(a)], where in comparison to Refs. 15 and 16, results for a practically full (empty) band are included. Due to the symmetry of the paramagnetic LDOS the curve is roughly symmetric around its center and both its left and right parts are again almost symmetric. This brings some symmetry to the MAE curve. In particular the rapid oscillations for quasi empty or full bands are very similar. The same is true for the oscillations just below or above the center of the curve. The symmetries of the computed MAE curve, in turn, rule out the random errors described above. In the light of the bulk MA study,[25] the oscillations are likely to originate from energy-band crossings. Implicit support for this idea is also provided by Ref. 9. In this situation the SO interaction enables for appropriate positions of E_F, a kind of Fermi surface nesting with zero quasiwave vector or solid-state Jahn-Teller effect.

To proceed further, let us consider for a while the SO coupling as a perturbation and let us apply a generalization of the theory of Wigner and von Neumann[26] for band crossings. This theory states that for r-parametric energy surfaces, $(r-2)$-dimensional crossings generally exist. If there are global symmetry constraints, however, the crossing is a $(r-1)$-dimensional manifold. Since the system is two dimensional, the crossings can occur in isolated points some of which correspond to symmetry points in the BZ. The crossing geometry has the form of a double elliptic cone.[26] In addition, some unperturbed bands cross along curves. This is enabled by constraints forbidding interaction between up and down spins (A) and between states transforming differently under the $Z \rightarrow -Z$ reflection (B). The third kind of one-dimensional crossing (C) takes place for the XY bands of the (001) monolayer if interactions between more distant neighbors are neglected: The nearest-neighbor matrix elements between XY and other d orbitals are zero. The SO coupling reduces the crossings (A) and (C) to isolated-point crossings or removes them completely. On the other hand, for the perpendicular orientation of the magnetic moment, the $Z \rightarrow -Z$ symmetry is conserved (the magnetic momentum is an axial vector) and the crossing (B) is but slightly modified by interactions with other bands. The (quasi)degenerate perturbation theory gives corrections to energy levels linear in ξ instead of quadratic ones, which follow from standard arguments.[11] Since the neighborhood of the crossing point where the linear dependence holds is itself ξ dependent, it is not trivial to predict the magnitude of the contribution to MAE. An isolated crossing can (but need not) still exist when the perturbation is introduced;[26] for example the X orientation of the magnetic moment does not violate the $X \rightarrow -X$ symmetry and band crossings are allowed for the directions of BZ invariant with respect to this symmetry. Generally, the perturbation of the crossing is different for $\alpha = X$ or Z, which can easily introduce narrow peaks into the MAE curve. The width of a particular oscillation should be $\sim\xi$ on the energy scale, i.e., $\sim\xi\rho$ when the N_d variable is used (ρ is the value of the LDOS at given energy). The predicted widths of the oscillations, a few $10^{-1}e$ with a compression for small

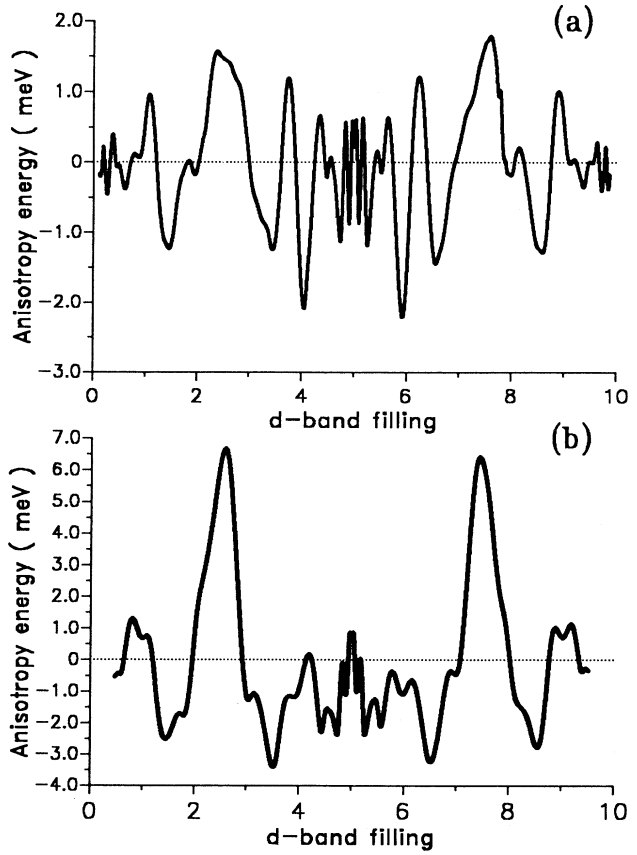

FIG. 1. Magnetic-anisotropy energy (MAE) per atom (meV) versus the d-band filling for (001) monolayer in the large exchange-splitting regime. Negative values correspond to favorable perpendicular direction of the magnetization. (a) $\xi = 0.05$ eV. (b) $\xi = 0.10$ eV.

LDOS at band edges and for LER also in the band center, are fully consistent with our numerical results. The general discussion presented above remains also valid if s- and p- electrons are included. Most crossings of d bands are changed quantitatively rather than qualitatively by this interaction and so should be the MAE curve. Some other remarks will be given in the discussion; it is, however, beyond the scope of this paper to give a more complete elucidation.

Another important conclusion is drawn from the numerical test presented in the next section. Namely, the scaling of ΔE against ξ is different for the canonical curve component and for the oscillations. Whereas the former obeys roughly a quadratic scaling, the latter features grow more slowly with ξ. It is clear that these effects depend strongly on the dimensionality and symmetry of the system.

Let us here only shortly mention the approximate relation[10,11]

$$\Delta E \sim \pm \frac{\xi}{4\mu_B}(M_Z - M_X) . \tag{4}$$

It is easy to see that the above expression is exact in the second order of the perturbation theory when the $\uparrow$-$\downarrow$ spin interaction is neglected. Similarly as in Ref. 11, our results show that this approximation for systems with E_F lying well away from the $N_d = 5$ value is often a satisfactory, although not completely reliable, guess. Since hybridization with the substrate creates holes in the majority spin bands by reducing the film magnetization,[6] the spin-up–spin-down interaction at E_F may be more important in realistic systems and Eq. (4) is to be used with caution. At $N_d \sim 5$, M_α changes its sign from negative to positive in analogy to the switch from normal to inverted multiplets in free atoms. The maximum values of the magnetic orbital moment are typically $\mp(0.1-0.3)\mu_B$ in SER and $\mp(0.3-0.4)\mu_B$ in LER although essentially bigger values appear in a few cases with MAE anomalously large (see the next section).

Finally, to get some insight into the possible role of noble metals in the MAE problem, we modified the monolayer Hamiltonian (1) by adding another layer to it (cf. Ref. 12) with atoms bearing only s orbitals. The two layers are arranged in the fcc (001) or (111) geometry. The nearest-neighbor interaction among s orbitals is given by the Slater-Koster parameter $ss\sigma = -0.9$ eV, which is a reasonable guess for Au or Ag.[27] To assess the s-d adlayer-substrate matrix elements, we use the Shiba-like approximation $sd\sigma = -(ss\sigma \times dd\sigma)^{0.5} \sim -0.55$ eV for LER d-d interactions. To find the s-orbital "atomic" level ε_s^0, care is necessary, since the latter quantity is known to shift downwards considerably for atoms with a low coordination to avoid depletion of free-electron-like bands.[28] From comparison with first-principles LDOS calculations[29,30] we find $\varepsilon_s^0 \sim 3$ eV with the energy zero placed in the common center of gravity of the d bands. Note, however, that the E_F positions we obtain, e.g., for Fe or Co lie a bit too high, which may be due to an underestimation of the amount of bonding d states due to a reduced number of interactions in our model. Nevertheless, as we document in the next paragraph, the model is sufficient to demonstrate some important qualitative changes introduces by the substrate.

IV. RESULTS AND DISCUSSION

As is clear from the previous discussion, at least 6 moments of the Hamiltonian are to be taken into account to get any information on MAE. Our tests show that for about 30 moments the overall shape of the MAE curve is correctly reproduced although the oscillatory features "breathe" slightly as the number of moments varies. Below we present the results for a variety of structures including evaluation of 48–50 moments [36 moments for (111) bilayers] for each orbital. The accuracy we reach is sufficient for our semiquantitative purposes.

For methodical reasons we present in Fig. 1(b) the situation for LER (001) monolayer with an exaggerated value $\xi = 0.1$ eV of the SO coupling. It is immediately seen that apart from departures at the ends and in the center the curve agrees well with the canonical hypothesis; let us note that in the middle, the MAE curve shifts essentially to negative values as predicted by the sixth moment analysis. Since the curve is almost symmetric we describe only its right-hand part. For $N_d \gtrsim 7$ interactions between minority-spin electrons dominate. The negative value of ΔE at $N_d \sim 8.5$ pointing to a preferred perpendicular magnetic-moment orientation is related to the higher (XY, YZ) LDOS peak and can be tentatively associated with the splitting of degenerate levels at the Γ point of the BZ (cf. Table I). When these states become filled ($N_d \sim 9$), their interaction (probably near the X point) 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 LDOS peak near X. At $N_d \lesssim 7$ we find a perpendicular MA with origin similar to the feature at $N_d \sim 8.5$ but the degeneracy of (XZ, YZ) levels at the point M is not important. In the center of the d bands, interaction of states with opposite spins is to be considered as well. Coupling between (XZ, YZ) and $X^2 - Y^2$ orbitals favors the perpendicular magnetization but other interactions give rise to oscillations. Let us now turn to $\xi = 0.05$ eV [Fig. 1(a)]. A comparison of Figs. 1(a) and 1(b) reveals that near the oscillation-free maxima the quadratic scaling with ξ is approximately obeyed, some departures being tentatively explained by the inadequacy of the second-order perturbation theory at the VHS coming from degenerate levels. In the center, the MAE values shift down with growing ξ. The behavior is consistent with the idea that there is a negative (canonical) component in this region which scales with ξ more quickly than another, oscillating, component which is positive. After finishing the paper we have become aware of a recent analysis of MAE.[31,32] The authors ascribe the oscillations to errors due to a particular numerical scheme (which is quite different from ours) and argue that the contribution to MAE from band crossings at E_F is of order ξA, where A is the area in the two-dimensional Brillouin zone where the energy separation between the two bands remains about ξ. Assuming linear dispersion near an isolated crossing[32] one

has $A \sim \xi^2$ with a small ξ^3 MAE correction. The bands cross, however, along curves as well, on which the energy attains at least one minimum and one maximum, in symmetry points of the Brillouin zone. In appropriate coordinates the energy separation is now $\Delta E = (ax^2 + by)$ which yields $A \sim \xi^{3/2}$ and the variation of the MAE $\sim \xi^{5/2}$. This simplistic guess gives a non-negligible contribution which, nevertheless, scales still more quickly than the canonical part. In SER, the most important features described above are found again although they are now shifted to somewhat lower values of N_d because of the holes in the majority-spin bands.[15] To summarize the above discussion, a marked perpendicular MA 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. These remarks give hope that some gross MA trends can be understood by performing an orbital decomposition of LDOS rather than by demanding MAE calculations.

To illustrate the role of the hypothetical crystal-field splitting we show in Figs. 2 results for LER (001) monolayer with the value $\Delta = 0.5$ eV advocated in Refs. 10 and 11. It is clear that MA is sensitive to this effect;[11] a striking result is the splitting of $M_{X,Z}$ curves [Fig. 2(b)] in agreement with the approximate Eq. (4); the curve for the magnetic orbital moment without crystal-field effects is given in Ref. 15.

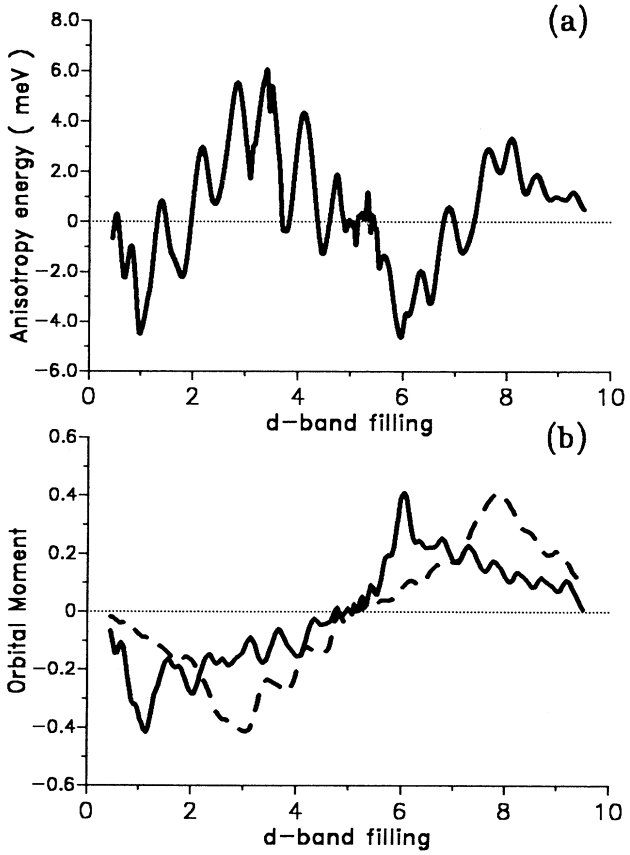

FIG. 2. (001) monolayer in the large exchange-splitting regime with a value of the crystal-field parameter of 0.5 eV. (a) Magnetic-anisotropy energy per atom (meV) versus the d-band filling. Negative values correspond to favorable perpendicular direction of the magnetization. (b) Magnetic orbital moment per atom (in Bohr magnetons) versus the d-band filling. Full (dashed) line corresponds to the perpendicular (in-plane) direction.

The results for the (111) monolayer show yet a more oscillatory behavior[16] and are in some respect similar to our results for the LER and SER bcc (011) monolayers. [Note that energy band crossings seem to be more numerous for the (111) monolayer than for the (001) one, especially if p orbitals are not included.] Now curves are not symmetric with respect to their center and parallel magnetization is usually preferred for transition metals from the right part of the Periodic Table.

Let us glance on MAE curves obtained for a number of mono- and bilayers. As a rule, one is able to discover the canonical features with a positive parallel magnetization peak for E_F well inside either majority or minority bands, and with negative lobes as one moves towards the band edges. The origin is undoubtedly similar to the situation described above: For E_F situated in pronounced (XZ, YZ) LDOS features, perpendicular magnetization is favored whereas interaction of the latter states with XY states (and generally perhaps also with other d states) leads to the change of direction. In many cases, however, the irregular features distort the simple picture. The fact that the oscillations persist for bilayers does not mean inevitably that they would not be quenched for thicker specimens. Due to the existence of the symmetry glide plane interchanging the first and the second layer, properties of free-standing bilayers are in most respects analogous to those of monolayers.

Recently, speculations about large MAE of monolayers (1–2 meV/atom) appeared,[11] although values essentially smaller than 1 meV are quoted in the latest calculations.[6] In our model, the amplitude of MAE curves does not exceed 1–3 meV/atom in most cases. These large values can be reached but for quite specific positions of E_F. Among the few exceptions admitting yet bigger MAE's let us mention the hypothetical antiferromagnetic $c(2\times2)$ (001) monolayer in LER.[33] The reason for the large MAE values is that because of the large exchange splitting, the interaction between neighboring atoms with opposite magnetization is weak leading to a "quasiatomic" situation. The MAE value is reduced by the competing interactions between different spin orbitals. By "isolating" some orbitals from the rest (also, e.g., by an appropriate crystal-field splitting) MA as well as the magnetic orbital moment can be enhanced.[11] In the abovementioned example of the antiferromagnetic monolayer, the magnetic orbital moment can acquire a magnitude as large as about $2.3\mu_B$, and for the same structure in SER we find a value of about $0.6\mu_B$. Finally, the bcc (001) bilayer with antiferromagnetic coupling between layers in the LER admits a magnetic orbital moment magnitude of about $0.8\mu_B$. On the other hand, it seems that the conditions such as the E_F position leading to very high MAE values are too special to be easily obeyed for elemental metals. As an interesting possibility in this respect we suggest to consider magnetic bimetallic systems.

Several particular cases are of interest for comparison

with the literature data. For Fe and Co (001) (LER, $N_d \sim 7$ and 8, respectively) we find very small MAE but the ΔE curve is very steep making the prediction unreliable. For Ni (001) (SER, $N_d \lesssim 9$), the prediction is also difficult, although MAE remains small in this region. For Co (111), we predict parallel MA for both regimes and the corresponding energy can be, in principle, rather large ($\sim$meV/atom). The comparison with the theoretical data[6–14] shows an overall agreement with the results of Refs. 6, 12, and 14 and the controversial situation in the iron case[8–13] is consistent with the rapid change of our MAE curve.

We mentioned on several occasions the importance of the noble-metal substrate. Let us consider now the results provided by the rudimentary model described in the previous section. Below we show the results for $\varepsilon_s^0 = 3.5$ eV. By comparing them with figures shown in Ref. 16 for ε_s^0, the reader will check that qualitatively the conclusions do not depend strongly on the parametrization although some quantitative changes may be rather large. In Figs. 3 we give the MAE curve for the (001) and (111) adlayers. In the monolayer case we have found the occupation of the d band $N_d \sim 7, 8, 9$ for Fe, Co, and Ni, respectively, by comparing our data with the literature results for E_F in these systems. In s-d models, N_d is usually somewhat reduced with respect to the d-band model value, one of the reasons being transfer of a certain amount of d states to higher binding energies due to the s-d hybridization. For the (001) overlayer this effect does not change the qualitative conclusions. In a reasonable range of parameters we find perpendicular MAE for iron (001) [Fig. 3(a)] in qualitative agreement with Ref. 12. The stabilization of this orientation can be traced to a fine reduction of the $3Z^2 - R^2$ partial LDOS (cf. Table I) at the Fermi level. The prediction of the in-plane MA for Co (111) is at variance with Ref. 14 if $N_d(\mathrm{Co}) \sim 8$ is taken. However, when the LDOS is considered we find that we get E_F placed well in a high-density peak whereas according to Ref. 14, E_F falls just below it. Hence the above-mentioned N_d reduction for the Co (111) overlayer takes place which might bring us closer to the point where the MAE changes sign [Fig. 3(b)]. The most striking feature of Figs. 3 is, however, a drastic reduction of the MAE oscillation suggestion that problems arising in MAE calculations are less severe for systems with reduced symmetry. In the light of our previous analysis, the substrate breaks the $Z \rightarrow -Z$ symmetry, which removes a number of band crossings and may at some energies reduce the high sensitivity of the SO interaction to the magnetic-moment direction. Similar effect may be caused by a nonideal interface geometry as well.

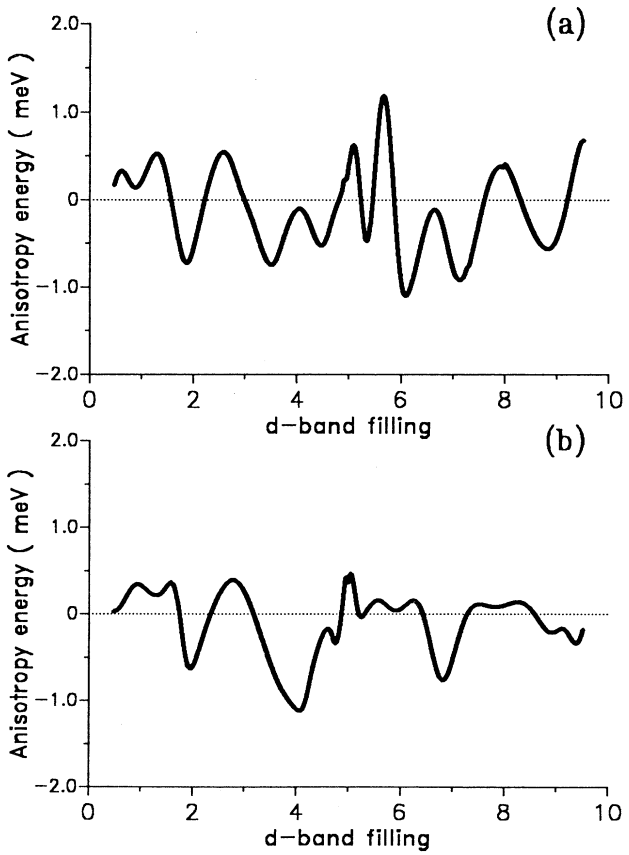

FIG. 3. Magnetic-anisotropy energy per atom (meV) versus the d-band filling for monolayer in the large exchange-splitting regime with a model substrate. Negative values correspond to favorable perpendicular direction of the magnetization. (a) (001) monolayer. (b) (111) monolayer.

Very recently $X(2ML)/\mathrm{Co}(111)$ (X=Pd, Pt, Cu, Ag, and Au) multilayers have been studied by using first-principles linear muffin-tin orbitals scheme.[34] The general shape of the MAE curves is very similar to our curve reported in Fig. 3(b). The details strongly depend on the choice of the spacer X. However it is striking that extrema on Fig. 3 of Ref. 33 are significantly larger than those of Fig. 3(b).

To summarize, we present an interpretation of the MA behavior in very thin free-standing transition-metal films that is based on an analysis of LDOS and on the moment theory. Free-standing films have specific properties which complicate an accurate calculation and partly invalidate arguments based on perturbation theory. For the free-standing Fe and Co films that are of great present interest, even the prediction of the MA direction is difficult. There is some evidence that some of these flaws are healed by interaction with the substrate or by other mechanisms breaking the high symmetry of isolated layers. One such mechanism might be departures from the ideal layer growth.[35] If this is indeed so, there is hope that more about the gross MA trends might be learned from the LDOS analysis. Large values of the MAE (several meV/atom) are found for hypothetical systems. Nevertheless, the MAE in realistic systems is expected to have more modest values.

ACKNOWLEDGMENTS

Š. Pick would like to thank the Laboratoire de Physique du Solide for kind hospitality and the French Ministry of Research and Technology for financial support. The Laboratoire de Physique du Solide de Nancy is Unité Associée au CNRS 155.

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