Spin Anisotropy of Ferromagnetic Films

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We calculate the spin anisotropy of ferromagnetic monolayers of Fe, Ni, and V. We find that the easy direction of magnetization is perpendicular to the plane of the monolayer for Fe and V, but in the plane for Ni. The result for Fe explains why spin splitting but no spin polarization is observed in recent photoemission experiments on Fe overlayers.

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The effect of reduced coordination on ferromagnetism has been the subject of experimental and theoretical studies for a number of years.[1-20] Recent self-consistent spin-polarized electronic structure calculations predict enhanced moments at the {100} surfaces of Ni[6-9] and Fe.[10] These theoretical predictions are supported by photoemission experiments.[11,12] Experiment[13] and theory[14,15] indicate a transition from antiferromagnetism to ferromagnetism at the Cr{100} surface.

One may infer from the above results that reduced coordination at a surface generally increases the magnetic moment. This is in accord with the Slater-Stoner theory of itinerant-electron ferromagnetism[21,22] since the reduced coordination leads to narrowing of the *d* bands and increased density of states at the Fermi level. It is reasonable to anticipate that epitaxial films of ferromagnetic atoms grown on inert substrates will exhibit greater enhancement since the weak substrate-film interaction will effectively further reduce the coordination.

This has been confirmed by recent spin-polarized calculations[16-18] for a monolayer of Fe on Ag{100} where a 36% enhancement of the magnetic moment per atom over that of bulk Fe is found. In Ref. 17, results for a number of other overlayers, substrates, and sandwiches were presented including a prediction that a monolayer of V on Ag{100} will be ferromagnetic.

The local-density approximation which underlies the calculations of Refs. 16–18, when applied to bulk ferromagnetic materials, predicts magnetic properties that agree well with experiment.[6-15] Recent photoemission experiments[19,20] on overlayers of Fe grown epitaxially on Ag{100} are fully consistent with the band structure of Refs. 16 and 18. The spin-polarized data of Jonker *et al.*[19] for electrons photoemitted from $\bar{\Gamma}$ display spin splitting close to, but perhaps slightly larger than, the splitting predicted by this band structure.

However, as they stand, the calculations of Refs. 16–18 are incomplete because the total energy is entirely independent of the spin quantization axis. The calculations therefore do not determine the direction of the magnetic moment. While ferromagnetic resonance and torsion magnetometry methods[23] may be used to measure overlayer anisotropies, the experiments are difficult and experimental errors large.[23] It is therefore important to obtain an independent determination of the anisotropy theoretically. The calculation of the spin anisotropy of ferromagnetic monolayers based on accurate self-consistent electronic structures is the subject of this Letter.

It has been proposed for a long time that the source of spin anisotropy in a ferromagnet is the spin-orbit interaction.[24] However, the anisotropy is a sensitive function of the details of the electronic structure and early attempts[25,26] to calculate the anisotropy of bulk Fe and Ni gave uncertain results as a result of the necessarily approximate treatment of the electronic structure. Studies[27,28] of the surface anisotropy of Ni were similarly hampered by the lack of accurate surface electronic structures. A recent bulk calculation[29] is in close agreement with experiment for Fe, Co, and Ni.

The energy is independent of the direction of spin quantization in the above overlayer calculations because they do not include spin-orbit interactions for valence levels. However, the spin-orbit interaction is small for the valence levels and can be introduced as a perturbation of the spin-polarized electronic structure to calculate the spin anisotropy. We describe such a calculation when the electronic structure has been determined by the self-consistent local-orbital (SCLO) method.[30] Briefly, the SCLO method uses a slab geometry to represent a desired surface or interface. The self-consistent eigenstates of the slab are linear combinations of Bloch functions labeled by two-dimensional wave vectors, $\mathbf{k}_{\parallel}$, in the plane of the slab. The Bloch functions consist of functions constructed from the atomic orbitals of the constituent atoms plus certain polarization orbitals. Required for the anisotropy calculations are the matrix elements of the spin-orbit interaction between the eigenstates of the slab.

The spin-orbit interaction arises from the one-electron operator[31]

$$H_{\text{s.o.}} = \tfrac{1}{2}\alpha^2 \boldsymbol{\sigma} \cdot [\mathbf{F}(\mathbf{r}) \times \mathbf{p}], \tag{1}$$

where $\mathbf{F}(\mathbf{r})$ is the electric field at $\mathbf{r}$, and $\boldsymbol{\sigma}$ and $\mathbf{p}$ are the spin and momentum operators. α is the fine-structure constant. Equation (1) is in Hartree atomic units. The matrix elements of $H_{\text{s.o.}}$ will depend on the direction of spin quantization of the slab eigenstates relative to the spatial orientation of the slab. This is the source of the spin anisotropy.

F can be decomposed into spherically symmetric atomic fields at each atomic site plus self-consistent corrections. It is a standard approximation to treat the contribution of the atomic field at a site as dominant in the vicinity of that site.[25-29] When this is done, the matrix elements of (1) between Bloch functions reduce to matrix elements between corresponding atomic functions at a single site of the operator

$$H_{\text{s.o.}} \cong \tfrac{1}{2}\alpha^2[F(r)/r]\mathbf{L}\cdot\boldsymbol{\sigma}, \tag{2}$$

where $F(r)$ is the atomic radial field of that site and L is the angular momentum operator.[32] Since the SCLO atomic orbitals are simple linear combinations of products of angular momentum and spin eigenfunctions times a radial function, the desired matrix elements of the spin-orbit interaction between eigenstates of the slab can be obtained from the properties of the spin and orbital angular momentum operators and the radial integrals

$$\int d^3r\, R_i(r)[F(r)/r]R_j(r), \tag{3}$$

where $R_j(r)$ is the radial function of the jth orbital. We calculate only matrix elements between d orbitals. This has proven sufficient in bulk calculations.[29] The resulting spin-orbit matrix is diagonal in $\mathbf{k}_\parallel$ but not in spin.

The spin anisotropy is obtained as the variation of the total energy of the slab with direction of spin quantization. Because the spin-orbit interaction is small, the charge-density change it induces is small. We rely on this to approximate the total energy change due to the spin-orbit interaction by the difference in the sum of one-electron energies with and without the interaction integrated over the first Brillouin zone of the slab. Conditions under which such an approximation is accurate have been discussed by Weinert, Watson, and Davenport.[33]

We note that the quantization direction need not be constant in space but may, for example, vary from layer to layer in the slab. Such variation will occur in a slab of ferromagnetic atoms when the bulk and surface directions of easy magnetization are different. In this first study, we consider only the simplest case of two-dimensional coordination: that of isolated monolayers in which the direction of quantization is constant. The spin anisotropy of isolated monolayers is of intrinsic interest and may not be significantly altered by interaction with inert substrates such as Ag and Au.[16-18] In the case of Fe on Ag{100},[18] the overlayer magnetic moment is only slightly reduced from the monolayer moment, and the Fe band structure is largely unaltered by the Ag. In the following we present calculations of the anisotropy for {100} monolayers of Fe, V, and Ni at the Ag lattice constant so that our results correspond as closely as possible to overlayers on Ag or Au{100}.

Even for a monolayer the anisotropy calculations are laborious. To obtain the spin-orbit energy for a given spin quantization, one has to diagonalize the spin-orbit matrix coupling the two spin polarizations at a number of $\mathbf{k}_\parallel$ points to approximate the integral over the Brillouin zone. Because there is a preferred direction, the arms of the star of $\mathbf{k}_\parallel$ are not in general equivalent. More serious is that the spin-orbit energy is slowly convergent in the number of $\mathbf{k}_\parallel$ vectors used to approximate the Brillouin zone integral.[34] This slow convergence has been noted in bulk anisotropy calculations.[29]

Symmetry considerations dictate that the anisotropy energy of a monolayer have the form

$$E_{\text{s.o.}} = E_{\text{s.o.}}^{(0)} + E_z^{(2)}\alpha_z^2 + E_{xz}^{(4)}(\alpha_x^2\alpha_z^2 + \alpha_y^2\alpha_z^2) + E_{xy}^{(4)}\alpha_x^2\alpha_y^2 + O(\alpha^6), \tag{4}$$

where α_x, α_y, and α_z are direction cosines along $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$. $\hat{\mathbf{z}}$ is perpendicular to the plane of the monolayer and $\hat{\mathbf{x}}$ is along a nearest-neighbor direction in the plane. Provided that the sixth-order corrections can be ignored, the parameters of Eq. (4) can be determined from the spin-orbit energy at four quantization directions. Figure 1 shows results for the monolayer of Fe. The spin-orbit energy per atom of the monolayer is plotted versus the number of $\mathbf{k}_\parallel$ vectors used to sample the Brillouin zone. The slow convergence with number of $\mathbf{k}_\parallel$ vectors is manifest. The easy direction of magnetization is unequivocally along $\hat{\mathbf{z}}$. Parameters

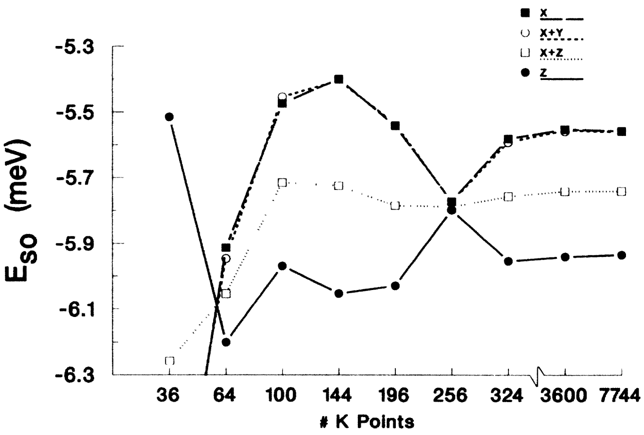

FIG. 1. Spin-orbit energy $E_{\text{s.o.}}$ of an Fe monolayer for four directions of spin quantization, as a function of the number of $\mathbf{k}_\parallel$ points used to approximate the integral over the first Brillouin zone.

TABLE I. Magnetic moment per atom and energy anisotropy coefficients for various monolayers of Fe, Ni, and V at the lattice constant of Ag, 5.449 bohr. The anisotropy coefficients were derived from calculations at 7744 $\mathbf{k}_{\parallel}$ points in the first Brillouin zone.

	Magnetic moment (μ_B)	$E_{\mathrm{s.o.}}^{(0)}$ (meV/atom)	$E_z^{(2)}$ (meV/atom)	$E_{xz}^{(4)}$ (meV/atom)	$E_{xy}^{(5)}$ (meV/atom)
Fe	3.20	−5.56	−0.38	0.018	−0.012
Ni	1.04	−16.65	4.00	0.210	0.620
V	3.00	−1.07	−0.06	−0.002	0.004

for the Fe, Ni, and V monolayers are given in Table I.

From the table we see that, like Fe, the easy direction of magnetization of V is perpendicular to the monolayer (since $E_z^{(2)} < 0$) but with a smaller anisotropy. For Ni the anisotropy is larger and the easy direction is along a cubic $\{100\}$ direction in the layer (since $E_z^{(2)} > 0$ and $E_{xy}^{(4)} > 0$). The anisotropy evidently arises from subtle details of the nature and filling of a given monolayer electronic structure. In terms of energy per atom, the monolayer anisotropies are large. For example, the anisotropy of the Fe monolayer ($\sim$ 0.4 meV/atom) is 100 times the anisotropy of bulk Fe (4 μeV/atom). This is a consequence of the reduced symmetry of the monolayers which allows the anisotropy to enter in second order. We note that our anisotropies are larger by over an order of magnitude than measured surface anisotropies[23] or earlier calculated anisotropies.[27,28] The classical dipole interaction energy favors alignment in the plane of the monolayer. It thus opposes the spin-orbit anisotropy for Fe and V but is less (0.3 meV/atom) than the spin anisotropy for Fe.

As in bulk ferromagnets the spin-orbit interaction is the major source of spin anisotropy in ferromagnetic monolayers. Theoretical determination of the easy direction of magnetization is essential in characterizing ferromagnetic overlayers and in interpreting experimental results. As an example, in the experiments of Jonker *et al.*[19] a magnetic field was used to align the film moment along a nearest-neighbor direction in the plane of the Fe overlayer and then removed to do the photoemission experiments. Despite the observation of spin-polarized bands, no imbalance of spin up and spin down was observed for quantization along the nearest-neighbor direction. Because of the form of Eq. (4) and the values of the anisotropy constants for Fe there is no barrier to rotation of the magnetization out of the plane. Our calculation predicts, therefore, that the moment would instantaneously revert to the perpendicular direction. Since the experiment does not detect spin polarization in this direction, our result provides an immediate explanation for the fact that spin-polarized bands but no spin polarization was observed for monolayer films of Fe.

The dipole interaction energy of a uniformly polarized film is proportional to the volume of the film whereas the anisotropy energy is proportional to its area. Consequently, the dipole energy will quickly overwhelm the anisotropy energy when the film is made thicker than a monolayer. When this happens the moment will lie in the plane of the film. This is an explanation of why Jonker *et al.* observe spin polarization for films thicker than 2.5 monolayers.

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