Magnetic Anisotropy of an Impurity in a Semi-Infinite Host

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(Received 21 February 1997)

We investigate the interaction of a magnetic (Fe) impurity with the surface of a nonmagnetic (Au) semi-infinite host on the bases of fully relativistic spin-polarized first principles calculations. We show that the surface induces a magnetic anisotropy on the impurity, however, it is questionable whether the anisotropy coupling constant K is sufficiently large to explain the thickness dependence of the Kondo amplitude B in thin films of dilute Fe_cAu_{1-c} alloys. We also find that $K(d)$ is an oscillating function of the distance d between the impurity and the surface with an amplitude which falls as $1/d^2$ and a period which is determined by the shape of the Fermi surface of the bulk Au host. [S0031-9007(97)03192-X]

PACS numbers: 75.30.Gw, 75.30.Hx, 75.50.Bb

The recent discovery that the Kondo contribution, $B \ln T$ where T is the temperature, to the resistivity in thin films of dilute magnetic alloys depends on the thickness of the film [1,2] is attracting considerable current attention [3,4]. Of particular interest is the suggestion of Újsághy *et al.* [3] that a magnetic impurity, such as Fe in Au, near the surface of the host metal is subject to a magnetic anisotropy described by the interaction Hamiltonian

$$\delta H = K(d)\,(\hat{S}_i^z)^2, \tag{1}$$

where $\hat{S}_i^z$ is the z component (normal to the surface) of the impurity spin operator and $K(d)$ is the anisotropy constant which is a function of the distance d between the impurity and the surface as depicted in Fig. 1. They argue that impurities which are close enough to the surface to experience $K(d) \geq k_B T_K$, where T_K is the Kondo temperature, will have their spin rotations hindered by the fact that their states corresponding to large values of the magnetic quantum number m become inaccessible in the course of thermal fluctuations of the spin. As a consequence of this freezing out of spin degrees of freedom the $S(S+1)$ factor which enters B is reduced and this decrease appears to be the right order of magnitude to explain a variety of experimental observations [5]. Clearly, for this scenario to be tenable $K(d)$ must be large enough and it must fall off sufficiently slowly with d. However, in Ref. [3] the estimate of $K(d)$ is based on a simple, semiphenomenological Kondo-impurity model, which leaves their conclusions somewhat tentative. In this Letter we report on material specific, parameter free, first-principles calculations of $K(d)$ based on the local density approximation (LDA). We find a $K(d)$ which is roughly of the right size and decays fairly slowly with increasing d. However, our calculations imply an asymptotic behavior intriguingly different from that of Újsághy *et al.* [3].

As is well known, the electron spins interact with the geometry of the lattice via the spin-orbit coupling. Indeed, magnetocrystalline anisotropy energies, in particular, for metallic surfaces and interfaces have been calculated successfully from first principles (see Ref. [6] and numerous references therein). Our work builds on these developments and is a straightforward application of these methods to the novel problem at hand. Briefly, we applied the fully relativistic spin-polarized screened Korringa-Kohn-Rostoker (KKR) method [6] for calculating the magnetic anisotropy energy (MAE) for an Fe impurity "buried" in an Au(001) surface. To render the problem tractable we did not attempt a fully self-consistent calculation, but we were satisfied with a frozen potential approximation. That is to say, we took the crystal potential on all the Au sites to be the same as was obtained in a relativistic LDA calculation for an infinite bulk Au crystal [7] and the Fe potential was that from a corresponding impurity calculation. Relying on the force theorem [8], the

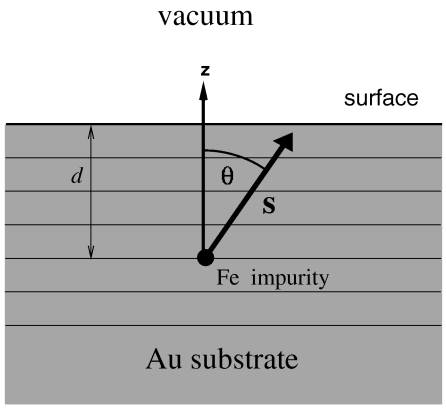

FIG. 1. Sketch of the geometry we use in the paper. Horizontal lines denote layers of the substrate.

MAE was then calculated by considering the band energy only. It is central to our concerns here that we have dealt with the spin polarization and the spin-orbit coupling on equal footing and we took full account of the semi-infinite geometry of the host. Although the interesting values of MAE are very small ($\sim 10\ \mu$eV), we demonstrate that the calculated results are robust to changes in numerical procedure.

First we calculated the MAE of the Fe impurity in bulk Au. For the energy difference $E(100) - E(110)$, where the Miller indices (100) and (110) refer to the orientation of the magnetization, we got $1.2\ \mu\text{eV} \simeq 0.01$ K. Reassuringly, this is much smaller than the relevant energy scale set by $T_K \simeq 0.3$ K and hence will not complicate the foregoing discussion. Repeating these calculations in the presence of a surface, the orientation dependence of the energy was found to be well described by $E(\theta) = K\cos^2(\theta) + E(\frac{\pi}{2})$, where $K \equiv E(0) - E(\frac{\pi}{2})$ is the anisotropy constant and θ denotes the angle between the magnetic moment and the surface normal (see Fig. 1). We also investigated the MAE with respect to directions in the plane, however, since the cubic symmetry parallel to the planes is not broken, it was found to have approximately the same value as the MAE in the bulk.

Our results for $K(d)$ are presented in Fig. 2. Note that the lattice spacing, d_0, of the Au(001) planes equals 2.04 Å. Since here we are interested in the MAE of Fe impurities buried fairly deep below the surface, $K(d)$ for $d < 10$ Å are not shown in Fig. 2. As was noted in Ref. [6], the numerical accuracy of the calculated MAE ultimately depends on an accurate evaluation of certain Brillouin zone (BZ) integrals. To assess the accuracy of our results, in Fig. 2 we displayed MAE's as calculated for different numbers of the $\mathbf{k}_\parallel$ points in an irreducible segment of the surface BZ (IBZ). Evidently, our results are well converged.

The first thing to note about the above results is that in the range of d under consideration the magnitude of $K(d)$ is below 0.01 meV $\sim$ 0.1 K. While this is the right order of magnitude, it is too small to be a convincing vindication of the arguments by Újsághy *et al.* [3]. However, there are a number of reasons to suggest that our calculations underestimate the MAE. These we shall enumerate later.

Let us now turn to other features of the MAE in Fig. 2. Evidently, $K(d)$ oscillates as a function of d. Therefore, the LDA ground state orientation of the spin moment of Fe switches alternatingly between perpendicular and parallel positions with respect to the surface. This remarkable behavior is distinctly different from that expected by Újsághy *et al.* [3], who found asymptotically a monotonous $1/d$ decay. Inferring from Fig. 2, the decay of the amplitude of the oscillations seems also to be faster than $1/d$.

In search for an explanation of these unexpected oscillations of $K(d)$ we recall the well-studied fact that the abrupt change in the potential at the surface results in Friedel oscillations in the charge density deep inside the bulk [9]. Significantly, the period of these oscillations is governed by the Fermi surface. To ascertain that such Friedel oscillations do occur in the present problem we calculated the cell-integrated charges of the semi-infinite Au host. The results are shown in Fig. 3. Although these calculations are not as well converged with respect to the BZ integration as those of the MAE, the oscillations are

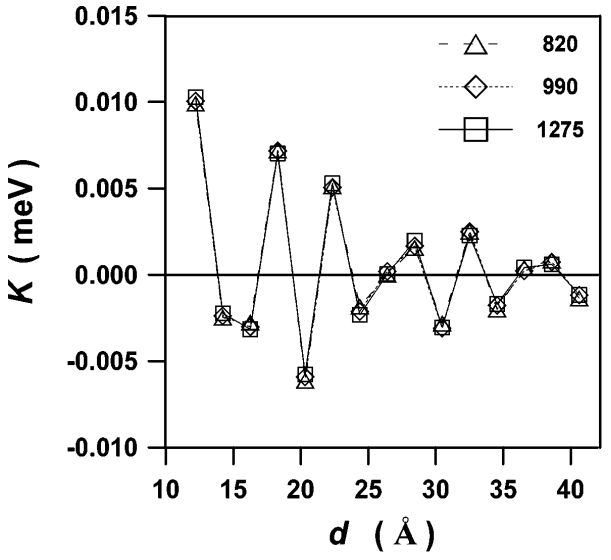

FIG. 2. Calculated anisotropy constant K for an Fe impurity as a function of the distance d from the (001) surface of the Au substrate. Different symbols refer to different numbers of $\mathbf{k}_\parallel$ points in the IBZ (see text) as denoted in the legend. Lines serve as guides for the eye.

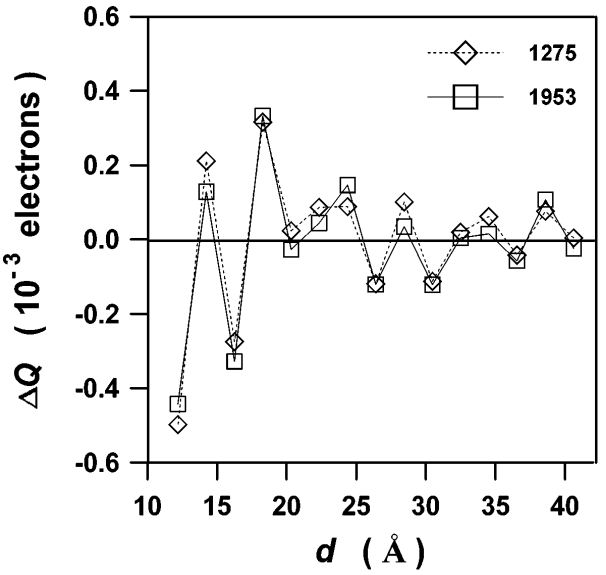

FIG. 3. Excess charges $\Delta Q = Q - Q_{\text{bulk}}$ on Au atoms near the (001) surface. Different symbols refer to different numbers of $\mathbf{k}_\parallel$ points in the IBZ as denoted in the legend. Lines serve as guides for the eye.

clearly seen. Interestingly, their period appears to be the same as that of $K(d)$. This suggests that the oscillations of $K(d)$ are the consequences of such Friedel oscillations.

To develop this idea further we studied analytically the interaction of an impurity with a surface (or interface) based on Lloyd's formula for the integrated density of states [10]. The corresponding contribution to the grand potential Ω_{iS} can be written as

$$\Omega_{iS} = \frac{1}{\pi}\,\mathrm{Im}\int d\varepsilon\, f(\varepsilon)\,\mathrm{Tr}\ln[\mathbf{I} - \mathbf{\Delta}^{i}(\varepsilon)\boldsymbol{\tau}^{b}(\varepsilon) \times \mathbf{\Delta}^{S}(\varepsilon)\boldsymbol{\tau}^{b}(\varepsilon)], \quad (2)$$

where $f(\varepsilon)$ denotes the Fermi distribution and Tr stands for the trace of a matrix in a composite site-angular momentum space. In Eq. (2) $\boldsymbol{\tau}^{b}(\varepsilon)$ is the inverse of the real-space KKR matrix of the unperturbed bulk, whereas the perturbation caused by the impurity and the surface is described by the interactors $\mathbf{\Delta}^{i}(\varepsilon)$ and $\mathbf{\Delta}^{S}(\varepsilon)$, respectively. Since we are interested in a situation when the impurity is rather far from the surface, after expanding the ln in Eq. (2) it is sufficient to keep the first nonzero term only. One can then easily make use of the translational symmetry properties of $\boldsymbol{\tau}^{b}(\varepsilon)$ and $\mathbf{\Delta}^{S}(\varepsilon)$ to transform each summation over sites into integrals in the Brillouin zone, ending up with

$$\Omega_{iS} = -\frac{d_0^2 A_0}{\pi(2\pi)^4}\,\mathrm{Im}\int d\varepsilon\, f(\varepsilon)\int d^2k_{\parallel} \times \iint dk_z\, dk_z'\, e^{-id(k_z - k_z')}\mathrm{tr}[\Delta^{i}(\varepsilon)\tau^{b}(\varepsilon;\mathbf{k}_{\parallel},k_z) \times \Delta^{S}(\varepsilon;\mathbf{k}_{\parallel},k_z,k_z')\tau^{b}(\varepsilon;\mathbf{k}_{\parallel},k_z')], \quad (3)$$

where A_0 is the volume of the 2D unit cell and tr denotes the trace of a matrix in angular momentum space only. In what follows, we only sketch the steps of the asymptotic analysis of Eq. (3) and the details will be published in a forthcoming paper.

Our analysis rests on three basic assumptions, each of which makes use of the presence of a rapidly oscillating function in the integrand of Eq. (3). First, we suppose that for a fixed ε and $\mathbf{k}_{\parallel}$ the main contribution to the integrals over k_z and k_z' comes from poles, k_z^{*} and $k_z'^{*}$, of $\tau^{b}(\varepsilon;\mathbf{k}_{\parallel},k_z)$. Second, the $\mathbf{k}_{\parallel}$ integral is evaluated using the stationary phase method by finding the stationary points $\mathbf{k}_{\parallel}^{\nu}$ of the function $q(\varepsilon,\mathbf{k}_{\parallel}) = k_z^{*} - k_z'^{*}$. Finally, the energy integral is carried out by using, e.g., Lighthill's theorems [11]. Our result for $T = 0$ can be summarized as

$$\Omega_{iS}(d) = \left(\frac{d_0}{d}\right)^2 \sum_{\nu} \sin(q_{\nu}d + \phi_{\nu})I_{\nu}, \quad (4)$$

with

$$I_{\nu} = \frac{A_0}{8\pi^4} D_{\nu}\,\mathrm{Im}\,\mathrm{tr}[\Delta^{i}(\varepsilon_F)\tau^{b}(\varepsilon_F;\mathbf{k}_{\nu}) \times \Delta^{S}(\varepsilon_F;\mathbf{k}_{\parallel}^{\nu},k_z^{*},k_z'^{*})\tau^{b}(\varepsilon_F;\mathbf{k}_{\nu}')], \quad (5)$$

where ε_F is the Fermi energy, $\mathbf{k}_{\nu} = (\mathbf{k}_{\parallel}^{\nu}, k_z^{*})$, $\mathbf{k}_{\nu}' = (\mathbf{k}_{\parallel}^{\nu}, k_z'^{*})$, $q_{\nu} = q(\varepsilon_F, \mathbf{k}_{\parallel}^{\nu})$ $(0 \le q_{\nu} \le \pi/d_0)$, the phase ϕ_{ν} takes the values $-\frac{\pi}{2}$, 0, or $\frac{\pi}{2}$ for minimum, saddle-point, or maximum of $q(\varepsilon_F,\mathbf{k}_{\parallel})$ at $\mathbf{k}_{\parallel}^{\nu}$, respectively, while D_{ν} is related to the curvatures of the Fermi surface and the Fermi velocities at $\mathbf{k}_{\nu}$ and $\mathbf{k}_{\nu}'$. Indeed, this asymptotic analysis predicts an oscillatory behavior of the impurity-surface interaction as a function of d with an amplitude falling off as $1/d^2$.

In view of the above asymptotic form we can now reinterpret our results in Fig. 2. In Fig. 4 we depict the calculated values of $K(d)d^2$ and compare them to $I\,\sin(2\pi d/d^{*} + \pi/2)$ for $I = -2.8$ meV Å^2 and $d^{*} = 5$ Å $\sim 2.5d_0$. Evidently, the asymptotic form is in excellent agreement with the points derived from full calculations. As predicted by our asymptotic analysis, the period d^{*} corresponds to the extremal vector of the Fermi surface of bulk gold along the (001) direction at the "dog-bone" [12].

It is illuminating to mention that the form of Eq. (4) closely resembles the magnetic interaction between two interfaces in metallic multilayers [13,14]. The period d^{*} has indeed been quantitatively confirmed in the magnetic interface coupling investigations of the Fe/Au/Fe sandwich system both experimentally [15] and theoretically [16]. It should be stressed that the physical phenomenon of a magnetic impurity interacting with a nonmagnetic surface is very different from that of an interaction between magnetic layers separated by a nonmagnetic spacer metal. The fact that the same oscillations turn up in both cases lends support to our analysis as well to that of others who studied the multilayer case [13,14]. Moreover, it helps to identify the Friedel oscillations as the physical mechanism behind

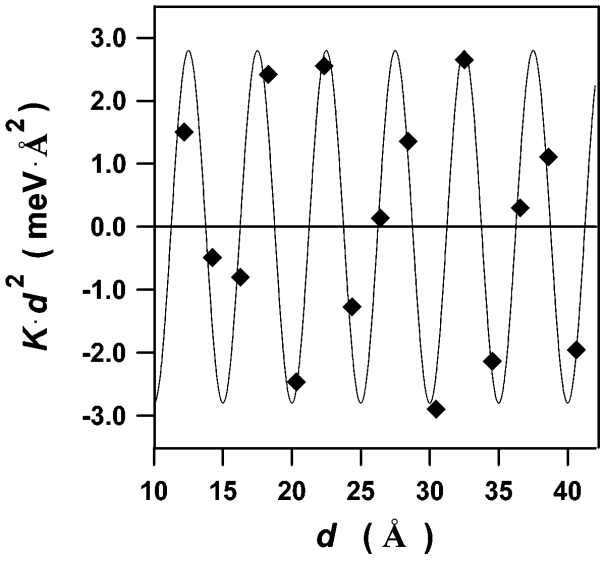

FIG. 4. $K(d)d^2$ (diamonds) as deduced from the data of Fig. 2. The solid line depicts the function $-2.8\sin(2\pi d/5.0 + \pi/2)$.

both effects. Thus, the point defect-planar defect interaction studied in this Letter should be regarded as an intermediate phenomenon between RKKY-like interactions [17] between point defects and the interface-interface interaction [14] mentioned above.

Given these general arguments it is quite surprising that the perturbation theory of Újsághy *et al.* [3] yields a nonoscillatory $K(d) \sim 1/d$ asymptotic behavior. We attribute the difference between this and our present results to dynamical scattering of the conduction electrons off the impurity spin not treated in LDA. However, the details of how this comes about are still subjects of further research.

Returning to the thickness dependence of the Kondo amplitude in thin films we have two comments to add. Concerning the size of the effect we observe that the MAE is expected to increase considerably if the symmetry parallel to the surface is broken by surface roughness. Furthermore, the inclusion of orbital contribution to the exchange-correlation potential [18] could also increase the MAE. Finally, direct observation of the oscillations of the impurity-surface interaction in some appropriately designed experiments, where the distance d between the impurity and the surface is controlled, could conclusively confirm or reject the hypothesis of Újsághy *et al.* [3].

Enlightening discussions with A. Zawadowski, O. Újsághy, G. Zaránd, and B. Újfalussy are gratefully acknowledged. This paper resulted from a collaboration within, and partially funded by, the TMR Network on "Ab initio calculations of magnetic properties of surfaces, interfaces and multilayers" (Contract No. ERB4061PL951423). One of the authors (L.S.) is also grateful for the financial support of the Hungarian National Scientific Research Foundation (OTKA No. F14378 and No. T21228).

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