Effect of Spin-Orbit Interaction on a Magnetic Impurity in the Vicinity of a Surface

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We propose a new mechanism for surface-induced magnetic anisotropy to explain the thickness dependence of the Kondo resistivity of thin films of dilute magnetic alloys. The surface anisotropy energy, generated by spin-orbit coupling *on the magnetic impurity itself*, is an oscillating function of the distance d from the surface and decays as $1/d^2$. Numerical estimates based on simple models suggest that this mechanism, unlike its alternatives, gives rise to an effect of the desired order of magnitude.

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The original observation that the amplitude of the Kondo resistivity in thin films of dilute magnetic alloys depends on the thickness L of the film, [1,2] has attracted considerable attention [3–7]. So far the most promising explanation of this phenomenon was given by Újsághy *et al.* [6,7]: They suggested that a magnetic impurity, such as Fe in Au, near the surface of the host metal is subject to a magnetic anisotropy that blocks the spin-dynamics responsible for the Kondo scattering within a given distance L_c to the surface, if the anisotropy is larger than the Kondo temperature T_K of the magnetic impurities. As a consequence, the Kondo resistivity $R_K(L)$ of a thin film relative to that of a ''bulklike'' thick film, $R_K^{\text{bulk}}(L)$, can be estimated for $L \gg L_c$ as

$$\frac{R_K(L)}{R_K^{\text{bulk}}(L)} = 1 - \frac{2L_c}{L}, \tag{1}$$

where the factor 2 on the righ-hand side accounts for the two surfaces of the film. Fitting the experiments with this formula yields $L_c \simeq 180$ Å in case of Au(Fe) thin films [6].

Újsághy *et al.* [6,7] based their arguments on calculations for a $5/2$ Kondo impurity embedded in a semi-infinite host with spin-orbit interaction on the host atoms only. They found a surface-induced anisotropy energy,

$$H_{\text{anis}} = K(d)\hat{S}_z^2,$$

where $\hat{S}_z$ is the z component of the impurity spin operator and the anisotropy constant $K(d)$ is a function of the distance d of the impurity from the surface. Using lowest order perturbation theory in both the spin-orbit coupling constant λ and the effects of the surface, they derived an expression for $K(d)$ which for large d decayed as $1/d$. Moreover, their quantitative estimates of $K(d)$ gave sufficiently large values to explain the experimental facts in their more detailed calculations [8].

Subsequently, Szunyogh and Györffy [9] studied the problem using a material specific, parameter-free first-principles approach, namely, spin-polarized relativistic calculations based on the local density approximation (LDA). In these calculations, the semi-infinite host was taken into account without significant approximations. Consequently, the spin-orbit coupling on the host atoms and electrons' scattering between the impurity and the host atoms were treated on equal footing and to all orders in the coupling strength. They found $K(d) \approx \cos(2k_F' d)/d^2$, where $2k_F'$ is the length of a spanning vector of the host's Fermi surface. Moreover, the size of the anisotropy energy turned out to be too small by orders of magnitude. Clearly, the LDA results would eliminate the whole idea of explaining the size dependent Kondo effect by ''surface-induced magnetic anisotropy,'' if they did not suffer from the well-known weakness of the LDA in describing spin fluctuations on the impurity. LDA calculations also underestimate ''Hunds rule correlations'' systematically.

In this Letter we present calculations which include dynamical spin fluctuations at the same level as Refs. [6,7], but go beyond their approach in that here we treat the spin-orbit coupling in the semi-infinite host nonperturbatively, and we also incorporate the effects of spin-orbit coupling on the impurity. We find that, while the host-induced anisotropy, as proposed in Ref. [6], is negligible, an improved treatment of correlations and the strong (typically ~ 1 eV) spin-orbit coupling *on the magnetic impurity* can lead to a dramatic enhancement of the surface-induced magnetic anisotropy for impurities with partially filled d shell. As it turns out it is large enough to explain the experiments. Furthermore, this anisotropy has a simple physical origin: for partially filled d shells each spin state has also an *orbital structure*. In a given spin state, electrons on the deep d levels lower their energy by hybridizing with the conduction electrons through virtual fluctuations. However, in the vicinity of a surface, Friedel oscillations appear and, therefore, the density of states available for the d electrons to hybridize with depends on the *orbital state*, and, thus, on the spin of the impurity (see Fig. 1). This

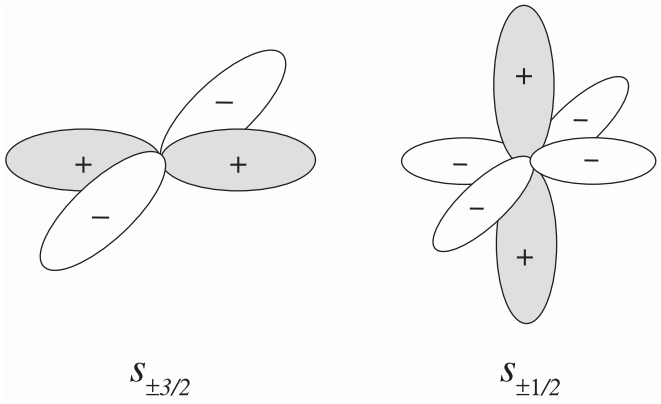

FIG. 1. Sketch of the orbital structures of the d-type Γ_8 combinations formed by s orbitals at the nearest-neighbor sites around an impurity in a simple cubic host. The $s_{\pm 3/2}$ combinations are composed from orbitals located at neighbors within the same plane, whereas the $s_{\pm 1/2}$ combinations have significant out-of-plane contributions.

mechanism gives rise to an anisotropy that already appears to first order of the exchange coupling J between the magnetic impurity and the conduction electrons, decays as $1/d^2$ and is orders of magnitude larger than the similar anisotropy induced by spin-orbit coupling on the host sites [6].

We shall first analyze the simplest possible model that captures all important aspects of the problem, and start with a magnetic impurity in a d^1 configuration such as a V^{4+} or Ti^{3+} ion embedded into a simple cubic (sc) lattice. In this case, by Hund's third rule, strong local spin-orbit coupling will lead to a $J = 3/2$ multiplet that is separated from the $J = 5/2$ state typically by an energy of the order of ~ 1 eV. The advantage of this model is that under a cubic crystal field the $J = 3/2$ multiplet remains degenerate (Γ_8 double representation), and no anisotropy is generated when the surface is absent. For the sake of simplicity, we assume that the host atoms form a (001) surface of a simple cubic lattice. We also assume that the conduction band of the host is dominated by s electrons, which we describe in terms of a single-band nearest-neighbor tight-binding model.

The impurity's $J = 3/2$ multiplet can only hybridize with those linear combinations of s states on the nearest-neighbor atoms which transform according to the Γ_8 representation. Within the full twelve-dimensional subspace, spanned by orbitals on six neighbors and two spin states per site, two such (four-dimensional) sets can be constructed. One of these has p-type orbital structure and, therefore, hybridizes only weakly with the impurity's d level. The d-type set, s_m ($m = -3/2, \ldots, 3/2$), which hybridizes strongly with the $J = 3/2$ multiplet, splits into combinations with two different orbital characters as depicted in Fig. 1: the combinations $s_{\pm 1/2}$ couple to the impurity states $J_z = m = \pm 1/2$, while $s_{\pm 3/2}$ couple to $J_z = m = \pm 3/2$.

Assuming that the impurity-host interaction is mainly dominated by quantum fluctuations to the (nondegenerate) d^0 state, in lowest order of the hybridization, a Coqblin-Schrieffer transformation leads to the following effective exchange interaction [10],

$$H_J = J \sum_{m,m'} s_m^\dagger s_{m'} \left| \frac{3}{2} m' \right\rangle \left\langle \frac{3}{2} m \right|, \tag{2}$$

where $|\frac{3}{2} m\rangle$ stands for the four states of the Γ_8 impurity multiplet, $s_m^\dagger$ and s_m are creation and annihilation operators acting on the host states, respectively, and J denotes the effective strength of the coupling. We then employed Abrikosov's pseudofermion representation [11] to calculate the splitting of the four states up to second order in J [6]. The first and second order contributions to the self-energy at $T = 0$ are given by

$$\Sigma_{mm'}^{(1)} = J \int_{-\infty}^{E_F} d\epsilon \varrho_{mm'}(\epsilon), \tag{3}$$

and

$$\Sigma_{mm'}^{(2)} = J^2 \sum_{m''} \int_{-\infty}^{E_F} d\epsilon \int_{E_F}^{\infty} d\epsilon' \frac{1}{\epsilon' - \epsilon} \varrho_{mm'}(\epsilon) \varrho_{m''m''}(\epsilon'), \tag{4}$$

respectively. Here $\varrho_{mm'}(\epsilon)$ denotes the local spectral function of the host computed in the absence of the exchange interaction, i.e., $J = 0$, and E_F is the Fermi energy [12]. To compute $\varrho_{mm'}(\epsilon)$, we made use of the so-called surface Green's function matching procedure [13] that completely accounts for the semi-infinite geometry of the host. Note that Eqs. (3) and (4), in addition to incorporating quantum fluctuations of the spin at the same level as Ref. [6], also take into account the semi-infinite nature of the host nonperturbatively through the spectral functions [14].

In this simple case, tetragonal symmetry of the sc(001) surface implies that $\varrho_{mm'}(\epsilon)$, consequently, $\Sigma_{mm'}$ are diagonal in m, m'. From time reversal symmetry it further follows that the states $|\frac{3}{2} \pm \frac{1}{2}\rangle$ and $|\frac{3}{2} \pm \frac{3}{2}\rangle$ remain degenerate. Thus the fourfold degeneracy of the $J = 3/2$ multiplet is split by an effective anisotropy term,

$$H_{\text{anis}} = K J_z^2, \tag{5}$$

with $K = (\Sigma_{3/2} - \Sigma_{1/2})/2$.

A clear understanding of the level splitting due to the vicinity of a surface obviously emerges from Fig. 1: the spectral density related to $s_{3/2}$ orbitals extending in a single atomic plane differs from that corresponding to $s_{1/2}$ orbitals that in fact take an average over three adjacent atomic planes. This is demonstrated in Fig. 2, where $\varrho_{3/2}(\epsilon)$ and $\varrho_{1/2}(\epsilon)$ are plotted at the fifth atomic plane counted from the surface. In our numerical implementation a layer spacing of 2.6 Å (that corresponds to the atomic volume of fcc Cu), and a hopping parameter $V = -1.4$ eV were chosen. Evidently, $\varrho_{3/2}(\epsilon)$ oscillates strongly within the energy

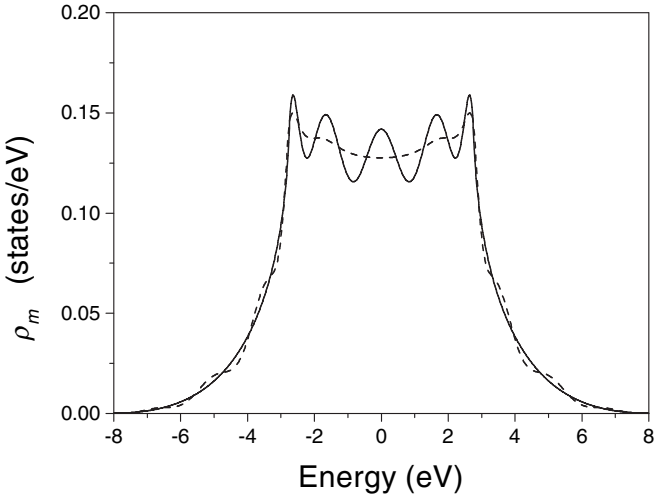

FIG. 2. Spectral density functions corresponding to orbitals $m = \pm\frac{3}{2}$ (solid line) and $m = \pm\frac{1}{2}$ (dashes), see also Fig. 1, at the fifth layer below the (001) surface of a sc single-band host metal. The lattice parameter was chosen to 2.6 Å and the hopping to 1.4 eV.

range $-2|\mathrm{V}| < \epsilon < 2|\mathrm{V}|$ (the center of the valence band is set to zero), while $\varrho_{1/2}(\epsilon)$ behaves smoothly.

Departing from the surface, the oscillations of $\varrho_{3/2}(\epsilon)$ get more and more rapid while decreasing in magnitude. For large d, $\varrho_{1/2}(\epsilon)$ approaches $\varrho_{3/2}(\epsilon)$ and both tend to $\varrho^{\mathrm{bulk}}(\epsilon)$. Interestingly, at a given energy, they also display Friedel oscillations [15],

$$\varrho_m(\epsilon; d) \simeq A_m \cos[2k_z(\epsilon)d + \phi]/d, \tag{6}$$

where $k_z(\epsilon)$ is the length of the extremal wave vector parallel to the surface normal of the constant-energy surface in reciprocal space and $\phi = 0$ or $\pi/2$. Performing the energy integrations in Eqs. (3) and (4), both self-energy contributions yield oscillations with a period of $\pi/k_z(E_F)$ for large d and an amplitude $\sim 1/d^2$, as also follows from an asymptotic analysis analogous to Ref. [9].

The impurity's first and second order level splittings, $\Sigma_{3/2} - \Sigma_{1/2}$, are plotted in Fig. 3 for $E_F = \mathrm{V} = -1.4$ eV. Here we used $J = 1$ eV, a typical exchange coupling for Kondo impurities with a Kondo temperature of the order of a few Kelvins. As can also be obtained from analytic calculations, the period of the oscillations is 3 atomic layers (7.8 Å) in this case. Remarkably, the second order self-energy diagram contributes about the same amount to the level splitting as the first order one.

Note that the present theory also predicts that there will be impurities with nearly vanishing level splittings. However, for incommensurate Friedel oscillations the distribution of $\Delta \equiv |\Sigma_{3/2}(d) - \Sigma_{1/2}(d)|$ within an interval $[d - \delta d, d + \delta d]$ of a few atomic layers is *peaked* around the maximum values of the anisotropy within that interval, $\Delta_{\max}(d)$. Therefore, for large values of $\Delta_{\max}(d) \gg T_K$ (i.e., in the vicinity of the surface) only a very small fraction of the impurity spins will experience an anisotropy-induced splitting, $\Delta < T_K$. As can be read off Fig. 3, beyond $d \sim 100$ Å the amplitude $\Delta_{\max}$ is still in the range of few tenths of a meV (1 K $\sim$ 0.09 meV), and the typical level splitting is close to the values needed to suppress the Kondo effect in thin films of alloys with $T_K \sim 0.1$–1 K such as Au(Fe).

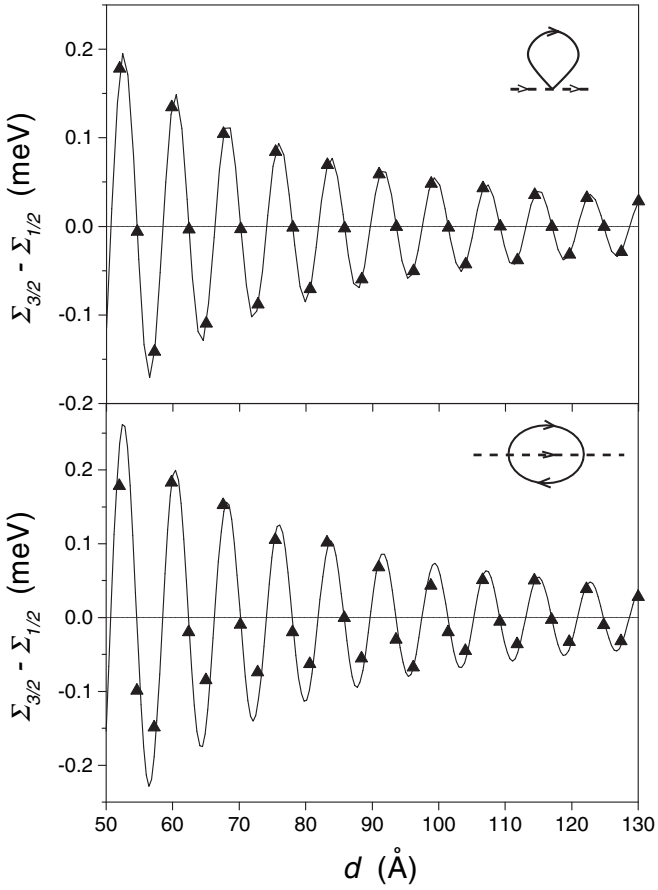

FIG. 3. First order (upper panel) and second order (lower panel) contributions to the level splitting of a d^1 impurity with strong on-site spin-orbit interaction as a function of the distance d from a sc(001) surface. See numerical parameters in the text. For both cases the solid lines depict functions $A \sin(2\pi d/d_0)/d^2$ ($d_0 = 7.8$ Å) fitted to the calculated values.

As was stressed in the introduction, the above mechanism is a combined consequence of "spin-orbit coupling" and "Hunds rule" correlations at the magnetic impurity. Since the latter does not occur on the host sites, we expect a much reduced contribution to the total anisotropy energy from these. In fact we would expect that, though the "impurity spin" is treated classically, the host-induced anisotropy is described reasonably well by the first-principles LDA calculations, hence, the results for the anisotropy energy in Ref. [9] can be regarded as of the correct order of magnitude. This suggests that in models, such as that of Újsághy *et al.*, [6–8], where the spin-orbit interaction is restricted to the host atoms, the "surface-induced magnetic anisotropy" should be negligibly small.

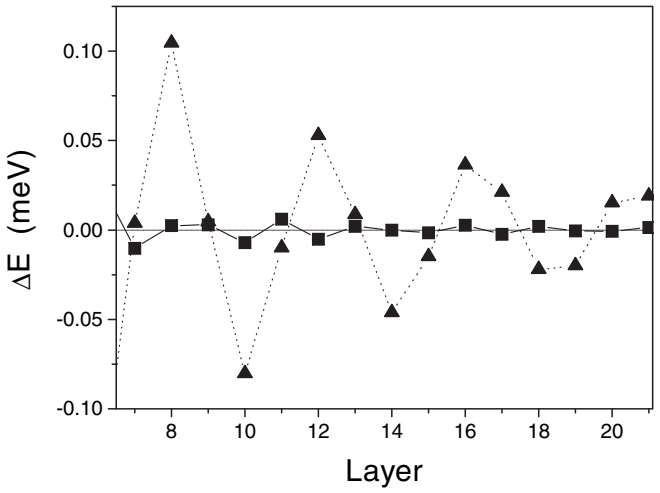

FIG. 4. LDA magnetic anisotropy energies for an Fe impurity in Au host as a function of its layer position measured from the (001) surface. Squares refer to the experimental lattice constant (7.68 Å), while triangles refer to the case when this lattice constant has been uniformly expanded by 50%.

From this point of view, the fact that they find a level splitting sufficiently large to explain the experimental data ought to be taken probably as a result of their largely analytic approximations. In fact, we also studied a somewhat modified version of our model where only host-induced spin anisotropy appears and found, as in the first first-principles calculations [9], that the obtained anisotropy was orders of magnitude smaller than the one discussed above.

To lend further credence to the new mechanism of surface-induced anisotropy, we have attempted to simulate the effects of Hunds rule correlations on the first-principles calculations in Ref. [9]. In calculations based on model Hamiltonians, one can manipulate the parameters of the theory, like the hopping integrals or the impurity-electron interactions parameter, J, to desirable ends. Evidently, there is no such freedom in first-principles calculations, however approximate. Nevertheless, in order to investigate correlations between different effects one can constrain the outcome of such calculations in other ways. As a quite crude device, we increased the lattice spacing of the Au host to mimic the band narrowing effects of correlations not included in LDA. In Fig. 4 we compare the surface-induced anisotropy energies of an Fe impurity as calculated for the experimental lattice spacing with those for a lattice constant artificially enhanced by 50%. Note that because of the different lattice constants this comparison is made in terms of the impurity's position measured in the layer index rather than in physical distances from the surface. As expected from the considerations above, increasing the lattice spacing resulted in a dramatic, order of magnitude increase of the predicted anisotropy. Reassuringly, this result is quite robust since it occurs in spite of the fact that, beside the band narrowing required to increase the effect of the on-site spin-orbit coupling, such an increase of the distance between the atoms should also reduce the coupling between the impurity and the conduction electrons (J) and, hence, the anisotropy energy. Clearly, the observed overall enhancement supports our contention that the origin of the large anisotropy energy and long critical length, L_c, is, indeed, the electron-electron correlations which are correctly captured by the basic ansatz of our d^1 model but are neglected in the first-principles LDA calculations.

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