Surface-Induced Magnetic Anisotropy of Impurities

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We present theoretical and numerical studies of the magnetic anisotropy energy of an atomic-like impurity near the surface of a metallic host (Au). The valence band of the host metal is described in terms of a realistic tight-binding surface Green's function technique. We compare two models: *(i)* when spin-orbit coupling is taken into account in the d-band of the host and *(ii)* when the impurity's d-level experiences strong spin-orbit splitting. The level splitting of the impurity's spin-states is calculated in leading (first or second) order of the exchange interaction between the impurity and the host atoms. It is shown that the magnetic anisotropy constant is an oscillating function of the distance d of the impurity from the surface. For large distances, an asymptotic analysis implies that the period of these oscillations is determined by the extremal vectors of the host's Fermi Surface and the amplitude decays as $1/d^2$. Our numerical results clearly suggest that the host-induced magnetic anisotropy energy is by several orders smaller in magnitude than the one originating from a strong local spin-orbit coupling.

***Index Terms*—Anisotropy impurity surface.**

I. Introduction

In order to explain the thickness dependence of the amplitude of the Kondo resistivity in thin films of dilute magnetic alloys [1] the role of the spin-orbit (SO) interaction has been outlined which in the presence of a surface gives rise to a level splitting of an impurity [2], [20]. By using a suitable fit to the measured amplitude of the Kondo resistance, in case of a thin film of dilute Au(Fe) alloy, Újsághy *et al.* concluded that for impurities closer to the surface than about 180 Å the level splitting should be higher than or at least comparable to the energy-scale fixed by the Kondo temperature, $T_K = 0.3K \simeq 0.03$ meV [2], [20].

In the original model of Újsághy *et al.* [2], [20], [3], an impurity interacts with the conduction electrons of the host metal that experience SO scattering through hybridizing with the low-lying valence d-orbitals (HSO model). This model leads to an effective spin-Hamiltonian

$$H_{\text{anis}}^{\text{HSO}} = K(d)(\mathbf{n}\,\mathbf{S})^2 \tag{1}$$

where $\mathbf{n}$ is the normal vector of the surface and $\mathbf{S}$ is the spin-operator. For large distances, d, from the surface the magnetic anisotropy (MA) constant, $K(d)$, behaves as $\sin(2k_F d)/d^3$, where k_F is the Fermi wavenumber. It should be noted that this result refers to randomly distributed host atoms, while for the case of an ordered crystal a $1/d^2$ decay of $K(d)$ has been predicted [3].

Recently a new mechanism of the magnetic anisotropy has been proposed [4] that relies on a strong local SO coupling at the impurity (LSO model). The corresponding anisotropy appears already to first order of the exchange coupling J between the magnetic impurity and the conduction electrons. In the asymptotic regime this anisotropy depends on d as $\sin(Q_F d)/d^2$, with Q_F being the length of an extremal vector of the Fermi Surface (FS).

The aim of the present work is to provide a quantitative comparison of the above mechanisms. For this purpose, for both cases we employ the tight-binding Green's function method in treating the conduction and valence electrons of the host. Using Au as host metal we perform numerical calculations of the anisotropy constants as based on the asymptotic formulas. The oscillation periods are directly identified from the calculated FS. In the case of the LSO model we also numerically confirm the validity of the asymptotic expression of $K(d)$.

II. Theory and Computational Details

The tight-binding Hamiltonian of a two-dimensional (2-D) translational invariant non-magnetic host can be written as

$$H_{\lambda\sigma,\lambda'\sigma'}^{pn,p'n'} = (\varepsilon_\lambda\,\delta_{\lambda\lambda'}\delta_{\sigma\sigma'} + \xi(\boldsymbol{\ell}\cdot\mathbf{s})_{\lambda\sigma,\lambda'\sigma'})\delta_{pp'}\delta_{nn'} + V_{\lambda,\lambda'}^{pn,p'n'}\,\delta_{\sigma\sigma'} \tag{2}$$

where p and n label atomic layers parallel to the surface and sites within the layers, respectively, λ denotes canonical spd orbitals centered at the lattice positions and $\sigma = \pm 1/2$ is the spin-index. In (2) all the parameters are replaced by their bulk counterparts, i.e., we neglect the dependence of the on-site energies, ε_λ and of the SO parameter, ξ, with respect to the layers and so for the hopping matrixelements, $V_{\lambda,\lambda'}^{pn,p'n'}$ that are confined to the first and second nearest neighbors. This approach is suitable for our present study related to the asymptotic regime. For the same reason, in the vacuum region the on-site energies are taken to be infinity.

The Green's function (GF) matrix of the host has been calculated via a surface GF technique [5], [21] that allows for a perfect treatment of the semi-infinite geometry induced by the surface and for incorporating SO coupling non-perturbatively. In the presence of an impurity the hopping of the conduction electrons to the d-orbitals of the impurity has to be excluded. To this end, we choose the d-like on-site energies of the impurity far below the valence band and we solved the Dyson equation

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for the corresponding GF matrix by using the previously calculated GF matrix of the host. In terms of an asymptotic analysis it can be shown that for large d the local spectral density, $\varrho(\varepsilon)$, defined as the imaginary part of GF, is subject to Friedel-type oscillations [6], [22], [23] of the following form:

$$\varrho(\varepsilon, d) \simeq \varrho^0(\varepsilon) + \frac{1}{d}\sum_n g_n(\varepsilon)\cos[Q_n(\varepsilon)d + \theta_n(\varepsilon)] \qquad (3)$$

where $\varrho^0(\varepsilon)$ is the spectral function in the bulk, $Q_n(\varepsilon)$ is the length of an extremal vector of a constant-energy surface pointing normal to the geometrical surface, whereas $g_n(\varepsilon)$ and $\theta_n(\varepsilon)$ are the amplitude and the phase of the oscillations, respectively.

In our numerical calculations we used on-site energies as well as first and second nearest neighbor hopping parameters as given for Au in [7] and the experimental fcc lattice constant, $a = 4.078$ Å. We choose a spin-orbit parameter, $\xi = 0.64$ eV, obtained from the difference of the SO-split d-resonance energies, $\Delta E_d = E_{j=5/2} - E_{j=3/2}$, derived from self-consistent relativistic first-principles calculations [8] in terms of the approach, $\Delta E_d \simeq 5\xi/2$. In order to reduce the computational efforts in performing necessary surface Brillouin zone (SBZ) integrals we made use of the C_{4v} point-group symmetry of the fcc(001) surface and an adaptive uniform mesh refinement for sampling k-points in the irreducible (1/8) segment of the SBZ (ISBZ). In general, about 10^4 k-points in the ISBZ were sufficient to calculate all the spectral function matrixelements with a relative accuracy of 1%. We performed calculations for the spectral functions up to 50 monolayers (ML) below the surface which corresponds to a maximum of $d \simeq 100$ Å.

Within the *HSO model* [2], [20], [3] we considered an impurity with a half-filled d-shell treated as an $S = 5/2$ spin within Abrikosov's pseudo-fermion representation [9]. The interaction between the impurity's d-electrons and the host's conduction electrons is approached by [10]

$$H_J = J\sum_{\alpha,\sigma\sigma'}(c^\dagger_{\alpha\sigma}\boldsymbol{\sigma}_{\sigma\sigma'}c_{\alpha\sigma'})\cdot\mathbf{S} \qquad (4)$$

where $\boldsymbol{\sigma}$ denotes the Pauli matrices, $\mathbf{S}$ stands for the spin operator of the impurity, $c^\dagger_{\alpha\sigma}(c_{\alpha\sigma})$ create (annihilate) conduction electrons in state $|\alpha\sigma\rangle$ and J is an effective exchange coupling. As a feasible approach we allowed for hoppings only between the impurity's d-orbitals and the s-orbitals at the first neighbor sites of the impurity. For an fcc lattice this defines 12 valence orbitals from which only five d-like combinations have non-zero contributions to the sum in (4).

It can easily be shown that the first order contribution to the static ($\omega = 0$) self-energy of the impurity vanishes, while under tetragonal symmetry the anisotropic part of the second order contribution is of the form, (1), with an asymptotic expression for $K(d)$ that follows from (3)

$$K(d) = -\frac{4J^2\pi\varrho^0(\varepsilon_F)g(\varepsilon_F)}{|Q'(\varepsilon_F)|}\times\frac{\cos\left[Q(\varepsilon_F)d + \theta(\varepsilon_F)\right]}{d^2} \qquad (5)$$

where ε_F is the Fermi energy, $Q'(\varepsilon) \equiv dQ(\varepsilon)/d\varepsilon$ and, as justified by our numerical results, merely the most significant contribution of the off-diagonal spectral densities, $\varrho_{\alpha\sigma,\alpha'\sigma'}$, is considered. Since for free electrons $Q(\varepsilon_F) = 2k_F$ the result, (5), agrees qualitatively well with that derived by Újsághy *et al.* [3].

In our numerical investigations of the HSO model we used the asymptotic form, (5), of the MA constant after having fitted the spectral function matrixelements to the function in (3). As our results clearly indicate, even beyond about 10 atomic layers ($d > 20$ Å) the calculated matrixelements followed the asymptotic form, thus, the parameters, $g(\varepsilon)$, $\theta(\varepsilon)$ and $Q(\varepsilon)$ could be fitted with a high accuracy.

As the simplest realization of the *LSO model* [4] an impurity with a d^1 configuration, such as a V^{4+} or Ti^{3+} ion, is considered. According to Hund's third rule, a strong local spin-orbit coupling leads to a $J = 3/2$ multiplet that is separated from the $J = 5/2$ multiplet typically by about 1 eV. Under a cubic crystal field the $J = 3/2$ multiplet remains degenerate (Γ_8 double representation). The impurity's $J = 3/2$ multiplet strongly hybridizes with those d-type linear combinations of s-orbitals centered at the nearest neighbor atoms (see above) which transform according to the Γ_8 representation, $|d_m\rangle$ ($m = -3/2, \ldots, 3/2$). In lowest order of the hybridization, a Coqblin-Schrieffer transformation leads to the following effective exchange interaction, [11]

$$H_J = J\sum_{m,m'} d^\dagger_m d_{m'}|\frac{3}{2}m'\rangle\langle\frac{3}{2}m| \qquad (6)$$

where $|(3/(2)m\rangle$ stand for the four states of the $J = 3/2$ impurity multiplet, $d^\dagger_m(d_m)$ are creation (annihilation) operators acting on the host states, $|d_m\rangle$, while J is again an effective strength of the exchange coupling. Due to the different orbital structure of the $|(3)/(2), \pm(3)/(2)\rangle$ and $|(3)/(2), \pm(1)/(2)\rangle$ states, in the presence of a surface the first order contribution to the self-energy gives rise to a magnetic anisotropy

$$\begin{aligned} K &= \frac{1}{2}\left(\Sigma^{(1)}_{\pm 3/2} - \Sigma^{(1)}_{\pm 1/2}\right) \\ &= \frac{J}{2}\int_{-\infty}^{\varepsilon_F} d\varepsilon\Delta\varrho(\varepsilon) \end{aligned} \qquad (7)$$

with $\Delta\varrho(\varepsilon) = \varrho_{\pm 3/2}(\varepsilon) - \varrho_{\pm 1/2}(\varepsilon)$. Employing (3) for $\Delta\varrho(\varepsilon)$ in the asymptotic regime and noting that $\varrho^0_{\pm 3/2}(\varepsilon) = \varrho^0_{\pm 1/2}(\varepsilon)$ we obtain

$$K(d) = \frac{J\,\Delta g(\varepsilon_F)}{2|Q'(\varepsilon_F)|}\frac{\sin[Q(\varepsilon_F)d + \theta(\varepsilon_F)]}{d^2}. \qquad (8)$$

Interestingly, the asymptotic d-dependence of the MA constants is described by very similar functions, (5) and (8), within the two models.

In case of the LSO model we followed a similar procedure as for the HSO model to calculate the MA constant in the asymptotic regime, see (8). Making use, however, that the spectral functions are analytic in the complex plane, it is quite feasible to calculate the MA constant from (7) in terms of a contour integration. Indeed, only 12 energy points along a semicircular contour in the upper complex semiplane was sufficient for a very accurate evaluation of the corresponding integral.

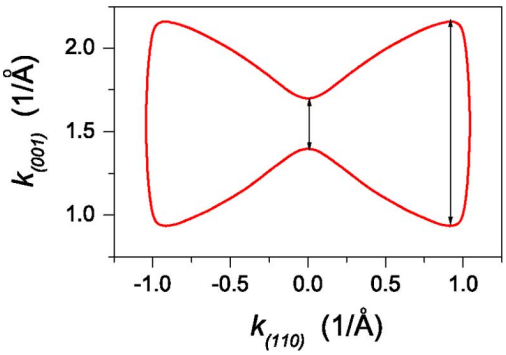

Fig. 1. Calculated plane cut of the FS of Au perpendicular to the $(1\ -1\ 0)$ direction. The arrows denote the extremal vectors of the lengths, $Q_{\min} = 0.298$ Å^{-1} and $Q_{\max} = 1.228$ Å^{-1}.

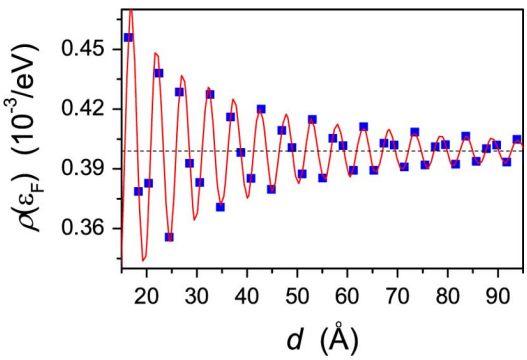

Fig. 2. Asymptotic fit, (3) (solid line), as function of the distance d from a Au(001) surface of the calculated off-diagonal spectral function, $\varrho(\varepsilon_F)$ (squares), giving rise to the most significant contribution to $K(d)$ within the HSO model. The dashed line denotes the bulk value of $\varrho(\varepsilon_F)$.

III. Numerical Results

Since the asymptotic analysis of the MA constants highlighted the role of the extremal vectors of the FS, we investigated the plane cut of the FS perpendicular to the $(1\ -1\ 0)$ direction. This cut is depicted in Fig. 1 from which the length of the (001) extremal vectors can easily be read off: the absolute minimum of the width of the FS, $Q_{\min}$, can be found at $k_{(110)} = 0$, whilst the maximum width of the corresponding cut, $Q_{\max}$, is related to saddle-points of the FS. The calculated values $Q_{\min} = 0.298$ Å $^{-1}$ and $Q_{\max} = 1.228$ Å $^{-1}$ correspond to periods of 21.07 Å and 5.11 Å (10.34 ML and 2.51 ML) that agree fairly well with the periods calculated by Bruno and Chappert, 8.6 ML and 2.6 ML [12], [24] respectively.

In Fig. 2 the calculated values of that off-diagonal spectral function that gives rise to the largest contribution to $K(d)$ is displayed together with a function fitted to the asymptotic form, (3). As can be observed in this figure, the asymptotic function quite surprisingly applies in the range of $d > 20$ Å, therefore, in practical terms there is no need to perform a "preasymptotic" analysis as suggested in [3]. The fitted parameters of (3) are as follows: $\varrho^0(\varepsilon_F) = -3.99 \cdot 10^{-4}$ eV^{-1}, $g(\varepsilon_F) = -1.484 \cdot 10^{-3}$ Å eV^{-1}, $Q(\epsilon_F) = 1.223$ Å $^{-1}$, and $\theta(\epsilon_F) = 1.324$ rad. In particular, $Q(\epsilon_F)$ agrees within a relative accuracy of 0.5% with the length of the extremal vector, $Q_{\max}$, of the Au Fermi Surface.

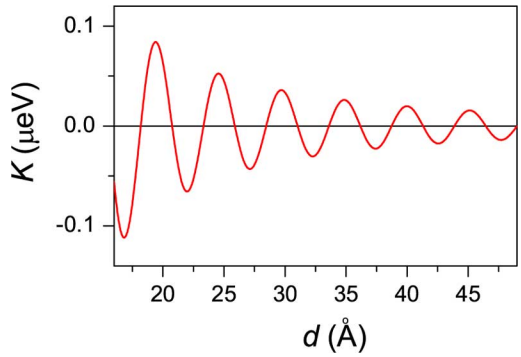

Fig. 3. MA constant within the HSO model as calculated from the asymptotic expression, (5).

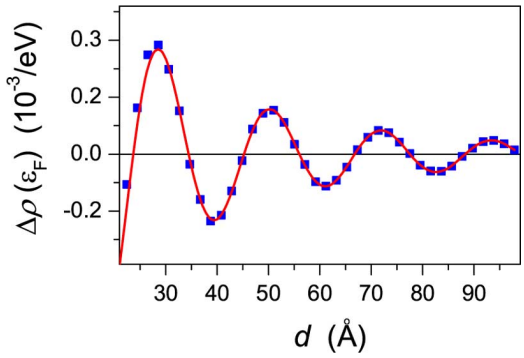

Fig. 4. Calculated difference of spectral functions, $\Delta\varrho(\varepsilon_F)$, (squares) with a corresponding asymptotic fit (solid line) as a function of the distance from the (001) surface of Au.

By using the asymptotic fit of the corresponding spectral function we calculated the MA constant in terms of (5). For that reason we numerically determined the energy derivative of the magnitude of the extremal vector, $Q'(\varepsilon_F)$, by repeating the fit of the spectral functions at two additional energy points close below and above ε_F. We thus calculated a value of $Q'(\epsilon_F) = 0.235$ (Å eV)$^{-1}$. Using a typical value of $J = 1$ eV for the effective exchange the obtained function $K(d)$

$$K(d) = \frac{31.66}{d^2}\cos[1.223 \cdot d + 1.324]\,\mu\text{eV} \qquad (9)$$

where d is measured in Å, is displayed in Fig. 3. The main comment we should make is the surprisingly small, $\sim 0.1\ \mu$eV, range of K even for small distances ($d \sim 20$ Å) from the surface. As we checked the spectral function scaled linearly with the SO parameter, ξ, thus, the MA constant scaled with ξ^2. Since in our tight-binding approach we treated the SO interaction non-perturbatively, this result fairly justifies the first-order perturbation treatment of the Green's function with respect to ξ used by Újsághy *et al.* [2], [20], [3].

Next we turn to numerical studies of the magnetic anisotropy within the LSO model. In Fig. 4 we plotted the difference of the spectral functions, $\Delta\varrho(\varepsilon)$, as a function of d. Remarkably, the amplitude of the oscillations is about by one order larger than for the off-diagonal spectral function relevant to the HSO model, see Fig. 2. This can be attributed to the fact that the origin of the oscillations of $\Delta\varrho$ is a tetragonal crystal field splitting which is present even without SO interaction in the host. In addition, the

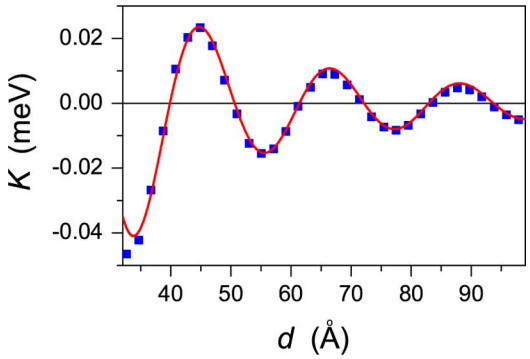

Fig. 5. MA constant within the LSO model calculated by using the asymptotic formula, (8), as a function of the distance d from the Au(001) surface (solid line). Squares stand for the MA constants calculated directly from (7).

oscillations exhibit a much larger period as compared to those in Fig. 2. A fit to the asymptotic function, (3), shown also in Fig. 4 resulted to the values $\Delta g(\varepsilon_F) = 1.16 \cdot 10^{-2}$ Å eV^{-1} and $Q = 0.292$ Å^{-1}. The latter one is in a very good agreement with the small extremal vector, $Q_{\min}$, of the Fermi Surface.

In Fig. 5 the MA constants are displayed as calculated by using (8) with the parameters from the fit of $\Delta\varrho(\varepsilon_F, d)$. Here we calculated the parameter, $Q'(\epsilon_F)$, in a similar way as for the off-diagonal spectral function relevant to the HSO model and obtained a value of 0.245 (Å eV)$^{-1}$. By choosing again $J = 1$ eV we got an amplitude of the oscillations of $K(d)$ decaying as $0.0237/d^2$ eV, d is being measured in Å. In Fig. 5 we also show the MA constants as derived from (7) in terms of a contour integration. Apparently, for $d > 35$ Å these values lie almost perfectly on the asymptotic curve. This nice agreement fairly proves both the validity of the asymptotic formula, (8), and the accuracy of our numerical procedure in calculating the MA constant.

IV. Summary and Conclusion

We performed comparative studies of two mechanisms for surface induced magnetic anisotropy of impurities based on spin-orbit interaction either in the host's d-band (HSO model) or on the impurity itself (LSO model). For the description of the host's valence and conduction electrons we used a tight-binding Green's function technique that allowed for a perfect treatment of the semi-infinite geometry of a surface. In addition, for the case of the HSO model a non-perturbative treatment of the SO interaction was possible. By using an asymptotic analysis we derived explicit expressions for the MA constants, K, showing in both models a very similar oscillatory dependence on the distance d from the surface: the periods of the oscillations are identified as the lengths of the extremal vectors of the Fermi Surface, while the amplitude of the oscillations decay as $1/d^2$.

By using realistic tight-binding parameters we performed numerical studies for impurities near a Au(001) surface. Our calculations revealed that, by using the same theoretical and computational background, the MA constants are by about three orders larger in case of the LSO model. In terms of direct calculations, in this case we also confirmed the validity of our asymptotic analysis of the MA constant. Our numerical studies, therefore, strongly indicate that a strong local SO coupling can be regarded as the primary mechanism for the magnetic anisotropy of an impurity near a surface and this anisotropy seems to be large enough to explain the experimentally observed size dependence of the Kondo resistance in thin films.

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