Spin-Orbit-Induced Magnetic Anisotropy for Impurities in Metallic Samples of Reduced Dimensions: Finite Size Dependence in the Kondo Effect

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We show that the conduction electron mediated interaction between a magnetic impurity and a nonmagnetic, semi-infinite host can lead to an impurity magnetic anisotropy with an easy plane parallel to the surface. Similarly, that anisotropy occurs in any mesoscopic sample. The effect is due to spin-orbit coupling and can lead to the freezing out of an $S = 5/2$ or $S = 2$ spin into an $S_z = 1/2$ or $S_z = 0$ state at low temperatures. We argue that this phenomenon provides a natural explanation for the anomalous behavior of the Kondo resistivity in a number of experiments involving thin films.

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In the past four years a number of groups have studied the Kondo resistance minimum as a function of the size of the samples [1–5]. The aim of the first experiments in this series was to observe the spin-compensation cloud of the impurity, which has never been observed experimentally before on the scale larger than ~1000 Å [6]. Surprisingly, the interpretation of these measurements is problematic to say the least. Some of them, on films of Au(Fe), Cu(Cr), and Cu(Fe) show a size dependent Kondo resistivity [2–4], while others do not [5], depending whether the thickness or width of the samples were varied or not. Moreover, in some experiments the Kondo resistivity increases when the sample is covered by a film of the host metal [3] and in all cases studied so far the Kondo temperature T_K shows no significant size effect. No theory, so far, is able to account for all these effects. As it has been known for a long time that the formation of the Kondo compensation cloud depends only on the local electron density [7,8], therefore, the geometry can influence only its shape and not the existence of the Kondo compensation cloud. In this Letter we present a simple model calculation which provides a coherent physical picture, based on spin-orbit interaction, which is consistent with all the observed phenomena.

Concerning magnetic films it has been known since van Vleck [9] that the spin-orbit interaction can result in magnetic anisotropy which hinders the motion of the spin. This has been widely applied for magnetic layers [10,11] but not for a single spin. In the present Letter we propose to our knowledge for the first time that for magnetic impurities in a nonmagnetic metallic host the conduction electrons interacting with the magnetic moment and having also a spin-orbit scattering on, e.g., the d levels of the host atoms can induce a spin anisotropy, which reflects the reduced dimensionality and the shape of the sample and may result in the suppression of the Kondo effect. In order to get this anisotropy the different angular momentum channels must be taken into account. The largest anisotropy is expected to occur in the vicinity of the surface of the sample and its direction $\mathbf{n}$ is perpendicular to the surface ($|\mathbf{n}| = 1$). The anisotropy is given by the Hamiltonian

$$H = K(\mathbf{nS})^2, \tag{1}$$

where $\mathbf{S}$ is the spin of the impurity and the strength of anisotropy is K which depends on the position of the impurity, the shape of the sample, etc.

The model is based on the interaction of the conduction electrons with the magnetic impurity, which is described by the simplest realistic Hamiltonian with orbital quantum numbers [12]

$$H_0 = \sum_{k,m,\sigma} \varepsilon_k a^\dagger_{km\sigma} a_{km\sigma} + J \sum_{\substack{k,k',m,m' \\ \sigma,\sigma'}} \boldsymbol{S}(a^\dagger_{km\sigma} \boldsymbol{\sigma}_{\sigma\sigma'} a_{k'm'\sigma'}) \delta_{mm'}, \tag{2}$$

where $a^\dagger_{klm\sigma}$ ($a_{klm\sigma}$) creates (annihilates) an electron with momentum k, angular momentum l, m, and spin σ, J is the effective Kondo coupling, $\boldsymbol{\sigma}$ stands for the Pauli matrices, and the origin is placed at the impurity site. Keeping only the $l = 2$ channels the index l is dropped. For the sake of simplicity spin $S = 5/2$ is chosen, in which case the Hamiltonian is diagonal in quantum number m because of Hund's rule (in any other case the Hamiltonian consists of several complicated terms [12]). For further simplification it is assumed that the free-electron-like conduction electrons move in the whole space and the shape of the sample is imitated by the positions of the atoms with spin-orbit interaction (see Fig. 1). The spin-orbit interaction is weak; therefore its effect will be considered as a perturbation. In order to make transparent that the spin-orbit interaction is mainly in the d channel and due to the Coulomb potential of the nuclei we introduce a simple model, where the spin-orbit interaction takes place on the d levels of the host, which hybridizes with the conduction electrons. The host atom orbitals are labeled by n referring to the position $\mathbf{R}_n$

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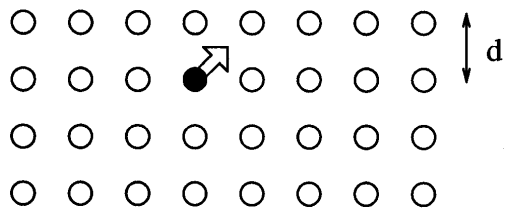

FIG. 1. The positions of the orbitals with spin-orbit interaction are shown by circles which are placed into an infinite electron gas. The position of the magnetic impurity is also indicated.

and also by the quantum numbers l, m, σ (e.g., $l = 2$ for the Cu and Au host and the index l is dropped again). The Hamiltonian of these extra orbitals is

$$H_1 = \varepsilon_0 \sum_{nm\sigma} b_{m\sigma}^{(n)\dagger} b_{m\sigma}^{(n)} + \lambda \sum_{\substack{nmm' \\ \sigma\sigma'}} \langle m|\mathbf{L}|m'\rangle \langle \sigma|\boldsymbol{\sigma}|\sigma'\rangle b_{m\sigma}^{(n)\dagger} b_{m'\sigma'}^{(n)} + \sum_{nkmm'\sigma} [V_{kmm'}(\mathbf{R}_n) b_{m\sigma}^{(n)\dagger} a_{km'\sigma} + \text{H.c.}], \quad (3)$$

where $b_{m\sigma}^{(n)\dagger}$ ($b_{m\sigma}^{(n)}$) creates (annihilates) the host atom orbital at site n, $V_{kmm'}(\mathbf{R}_n)$ is Anderson's hybridization matrix element, which depends on $\mathbf{R}_n$ since spherical wave representation with origin at the magnetic impurity is used, λ is the strength of the spin-orbit coupling, and $\mathbf{L}$ is the orbital momentum at site n. For each host atom the Hamiltonian can be simplified by using the local coordinate system where the $z_{(n)}$ axis is directed parallel to $\mathbf{R}_n$. In that system m is conserved and the spherical wave with origin at $\mathbf{R}_n$ is created by $a_{klm}^{(n)\dagger}$. The overlap between these spherical waves can be evaluated analytically. In the local system the matrix elements are different for different m, as the spherical waves disappear along that axis for $m \neq 0$ and they show different power behaviors in the distance measured from that axis $z_{(n)}$. In this way, the calculated $V_{km'=m}(R_n)$ matrix elements ($R_n = |\mathbf{R}_n|$) at $k = k_F$ also exhibit different power dependence. The local host atom propagator in first order of the spin-orbit coupling is proportional to λ/ε_0^2 for low frequencies $\omega \ll \varepsilon_0$.

The diagrams for the self-energy for the impurity spin are shown in Fig. 2. Because of the structures in the spin factors only the diagram (b) contributes to the anisotropy constant K in Eq. (1). The diagrams for the electron propagator leaving and arriving at the impurity are shown in Fig. 2(d). In the local system the propagator has the following matrix form:

$$\frac{\lambda V^2}{\varepsilon_0^2} \sum_{kk'} \frac{1}{\omega - \varepsilon_k} \times \left(B^+\sigma^- + B^-\sigma^+ + B^z\sigma^z\right)_{mm'\sigma\sigma'} \frac{1}{\omega - \varepsilon_{k'}}, \quad (4)$$

where $B^{\pm}$ and B^z are 5×5 matrices in the quantum number m and V is the hopping amplitude of a spherical

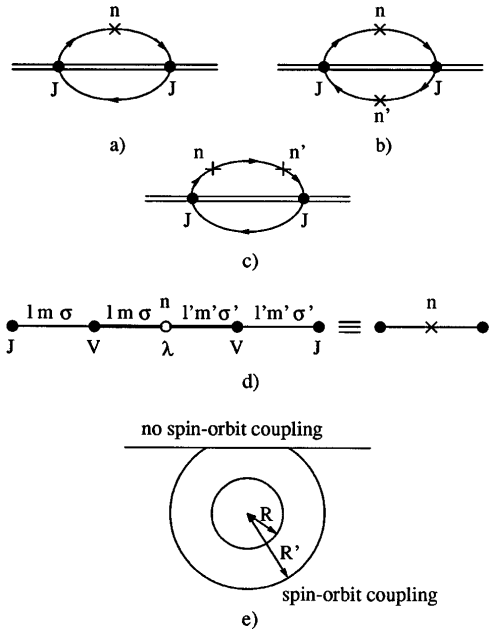

FIG. 2. (a)–(c) The self-energy diagrams of the impurity spin. The double line represents the spin, the single one the conduction electrons. The solid circles stand for the exchange interaction and the × labeled by n for the spin-orbit interaction on the orbital of the atom at $\mathbf{R}_n$. (d) The conduction electron propagator which contains hybridization V with the localized orbital where the heavy lines are the localized d-electron propagators and λ indicates the spin-orbit interaction. The indices are according to the local system. (e) Carrying out the average over the sites of localized orbitals, the different shells are shown which can be restricted by the surface.

wave with origin at the host atom to the local orbital. The scattering amplitude in Eq. (4) could also be introduced phenomenologically by taking the d wave character granted.

As the diagram Fig. 2(b) contains two host atoms with indices n and n', the summation over those must be carried out. For the sake of simplicity an infinite half space is considered for the host atoms and the impurity is placed in a distance d (see Fig. 1) from the surface; furthermore, the homogeneous average over the host atom positions is taken (no crystal structure effect). The most tedious part of the calculation is to rotate the local system back to the system of the sample, where the z axis is perpendicular to the surface. Turning to the average over the positions of the diagram Fig. 2(b) first the shells with constant R_n and $R_{n'}$ are considered [see Fig. 2(e)] and the integration with respect to the angles must be performed. If, e.g., $R_n > d$ then the presence of the surface appears as a limit in these integrals. It turns out that the dominant contribution arises from those terms where $R_n > d > R_{n'}$ or the opposite. A long but rather straightforward calculation which will be published elsewhere gives K_d for $k_F d \gg 1$ as

$$K_d = 4D(J\rho_0)^2 \frac{\Delta^2\lambda^2}{\langle\varepsilon^2\rangle^2} f\left(\frac{\omega}{D}\right) \frac{1}{(k_F a)^6} \frac{P(k_F r_0)}{k_F d} > 0, \quad (5)$$

where r_0 is a short distance cutoff in range of the atomic radius and the numerical factor depending strongly on r_0 is $P(k_F r_0) \sim 1 - 100$ if $k_F r_0 \sim 1$. The function f gives the analytical part of the diagram which is a slowly varying function and $f(\omega/D) \sim 2$, ρ_0 is the density of the states of the conduction electrons for one spin direction and D is its bandwidth. In the case of realistic Kondo temperature $T_K \sim 0.1-1$ K, $J\rho_0 \sim 0.1$. Furthermore, a^3 is the size of the volume per host atom which appears in the normalization of the average over the host atoms. A realistic value for the spin-orbit coupling is $\lambda \sim 1$ eV, the width of the host d band is $\Delta = 2\pi V^2 \rho_0$, and the average of the square of the energy ε of the d resonance is $\langle \varepsilon^2 \rangle \sim \max\{\varepsilon_0^2, (\Delta/2)^2\}$. Using the parameters $\Delta \sim D \sim 5$ eV, $\varepsilon_0 \sim 2$ eV $k_F a \sim 3$, the final estimation of order of magnitude is

$$\frac{3}{d/\text{Å}}\, 10^{-4}\ \text{eV} < K < \frac{3}{d/\text{Å}}\, 10^{-2}\ \text{eV}. \qquad (6)$$

Thus for a considerable large distance $d \sim 30$ Å we obtained that $K \sim 10^{-3}$ eV (10^{-5} eV) = 10 K (0.1 K), which is for the Au (Fe) system about $50T_K$ ($0.5T_K$), then the splitting between the states $S_z = 5/2$, $S_z = 3/2$, and $S_z = 1/2$ is $300T_K$ ($3T_K$) and $100T_K$ ($1T_K$). The largest ambiguity comes from the function P which is very sensitive on the choice of $k_F r_0$. Obviously these estimates are very rough, but clearly show the correct order of magnitude to freeze the spin states in the lowest states at $T = T_K$.

The result shows that the term dominating at larger distances does not contain oscillation contrary to the next correction. The calculation can be carried out for different geometries.

It is important that no randomness is taken into account; thus the calculation is valid only in the ballistic region. The essence of the calculation is the angular dependence, as keeping only s-wave scattering the spin-orbit coupling cannot influence the dynamics of the impurity [13]. Thus the mean free path limits the number of the effective host atoms and that reduces the influence of geometry by restricting it to the ballistic region.

The strength of the anisotropy is determined by the distance d of the surface and occurs as a low-energy cutoff in the logarithmic terms where it may replace the temperature. At a given place lowering the temperature for spin $S = 5/2$, e.g., first at $T = T_{3/2}$, the $S_z = \pm 5/2$ states are frozen out, leaving the spin states $S_z = \pm 3/2$, $\pm 1/2$ and at $T = T_{1/2}$ the spin is further reduced to $S_z = \pm 1/2$. Thus it may happen that at the surface for a given temperature $S_z = \pm 1/2$ and going inside the states with $S_z = \pm 3/2$ and $S_z = \pm 5/2$ recover gradually.

The form of the impurity spin Hamiltonian given by the second term in Eq. (2) is more complicated for $S \neq 5/2$ ($l = 2$), as Hund's rule does not forbid the change of m during the scattering (the ground state of the spin is not $L = 0$ [12]). The formation of the anisotropy must be, however, general, but in the case of integer S the impurity ground state must be not a doublet, but a singlet ($S_z = 0$). In that case in the region $K > T \geq T_K$, where T_K is the bulk Kondo temperature, the spin flip electron scattering cannot occur; thus the Kondo resistivity anomaly cannot be manifest for $S = 2$.

If for the bulk Kondo temperature $T_K \gg K$ then obviously the Kondo temperature is not affected. If $T_K \sim K$ then the anisotropy cannot have an essential effect on T_K, as no extra logarithmic terms arise from the energy region $\varepsilon < K$. Thus for those impurities where the resistivity anomaly is formed the Kondo temperature must have the bulk value.

The principal implications of the present theory concerning the Kondo resistivity amplitude in thin films and wires are the following.

(i) The Kondo temperature experimentally determined as the position of the largest slope in the resistivity is practically unchanged for Cr and Fe impurities [3–5]. For $S = 2$ only those impurities contribute to the resistivity anomaly for which $T_K \geq K$ where T_K is the bulk Kondo temperature and the resistivity increase is only slightly affected compared to the bulk. On the other hand, if $K > T_K$ then the Kondo anomaly is drastically reduced; thus their contribution is negligible. For $S = 5/2$ the situation is more complex as the states with $S_z = \pm 1/2$ play a role even for $T_K < K$ and it will be discussed elsewhere.

(ii) Decreasing the thickness of the film the percentage of the hindered spins is increased and the Kondo amplitude is reduced compared to the bulk [see Fig. 3(a)] in agreement with experiments [1–4]. If the thickness t of a film is large enough [1–4] then the Kondo resistivity of the sample is reduced by a factor of $1 - 2\lambda_0/t$, λ_0 being the effective thickness of the surface layer where the Kondo effect is absent due to surface anisotropy. A fit of the data of Ref. [1] with this simple formula is shown in Fig. 3(d). The fitted value, $\lambda_0 = 180$ Å, is still in the ballistic regime [1] and is consistent with our theory. For sample sizes comparable with λ_0 the dependence is more complex.

In this way the contradiction between experiments [1–4] and [5] seems to be resolved as well. In Ref. [5] thin stripes with thickness t kept constant but varying width $w \gg t$ have been measured. In this case the relative Kondo contribution is practically unaffected by the change of the width w of the wire [see Fig. 3(c)] as only t is a relevant parameter concerning the anisotropy for $w \gg t$.

(iii) In a film covered by an extra layer of the host material with long mean free path the impurities at the interface have no magnetic anisotropy [see Fig. 3(b)]; thus the Kondo amplitude increases (see Ref. [4]).

(iv) If the covering is made by a material with short mean free path then the asymmetry survives near to the interface and the previous effect is much less effective [3].

(v) Covering a film with different materials of negligible spin-orbit interaction, the asymmetry effect must be unaffected.

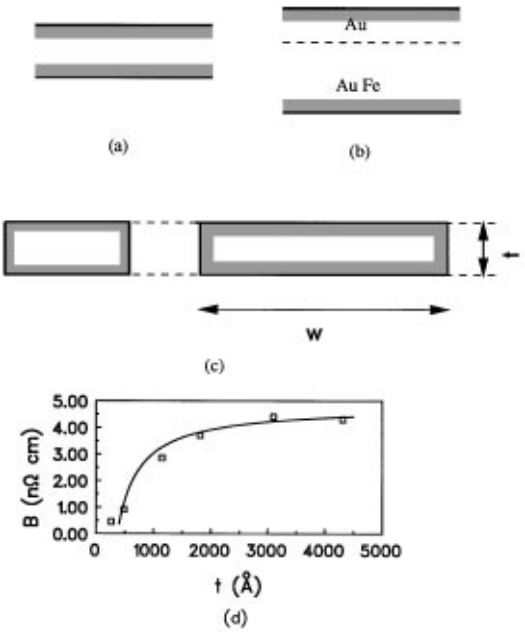

FIG. 3. (a)–(c) Cross sections of the samples used in the different experiments. The shaded regions indicate the domains where the anisotropy is strong. The axis of the anisotropy is perpendicular to the surface. (a) Simple film. (b) Au(Fe) film covered with a clean film. (c) Quasi-one-dimensional wires with thickness t and width w. (d) Fit of the measured amplitude B of the logarithmic contribution to the resistivity by the simple formula $B = \alpha(1 - 2\lambda_0/t)$ with the experimental results of Ref. [1]. The effective thickness and the coefficient α were chosen to be $\lambda_0 = 180$ Å and $\alpha = 4.7$, respectively.

The agreement between theory and experiments is remarkable for (i)–(iv) while the experiment for (v) has not been carried out yet.

Finally, we wish to stress the general, model independent nature of the above surface induced magnetic anisotropy. A similar effect occurs in the case of the RKKY interaction, and as was illustrated by Staunton *et al.* [14], in a relativistic treatment such coupling is, quite generally, anisotropic in spin space. Furthermore, the main idea presented should not be drastically influenced by the fact that in the model treated the conduction electrons are moving in the whole space and only the distribution of the host atom orbitals with spin-orbit interaction are characterizing the shape of the samples.

The main conclusions of the present Letter are that in any sample with strong spin-orbit interaction a magnetic impurity has a strong spin-orbit induced magnetic anisotropy nearby the surface inside the ballistic mean free path and that must show up in the spin dynamics at low temperature. The spin-orbit induced anisotropy explains all the experimental facts related to Kondo resistivity anomalies in quasi-one and -two dimensions.

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