Kondo Effect on Mesoscopic Scale (Review)

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(Received November 13, 2018)

Following the discovery of the Kondo effect the bulk transport and magnetic behavior of the dilute magnetic alloys have been successfully described. In the last fifteen years new directions have been developed as the study of the systems of reduced dimensions and the artificial atoms so called quantum dots. In this review the first subject is reviewed starting with the scanning tunneling microscope (STM) study of a single magnetic impurity. The next subject is the reduction of the amplitude of the Kondo effect in samples of reduced dimension which was explained by the surface magnetic anisotropy which blocks the motion of the integer spin nearby the surface. The electron dephasing and energy relaxation experiments are discussed with the possible explanation including the surface anisotropy, where the situation in cases of integer and half-integer spins is very different. Finally, the present situation of the theory of dynamical structural defects is briefly presented which may lead to two-channel Kondo behavior.

KEYWORDS: Kondo effect, Kondo resonance, size dependence, mesoscopic samples, spin-orbit-induced surface anisotropy, dephasing, energy relaxation, dynamical defects

1. Introduction

Following the pioneering work of Kondo¹ in the first decades the properties of bulk dilute magnetic alloy systems have been successfully studied. In the last fifteen years, however, the interest has turned to the systems of reduced dimensions and the single impurity problems. The latter is also represented by the very rapidly developing fields of quantum dots, where Kondo like impurities are manufactured. The goal of the present review to have an overview over the most interesting problems of the first kind, and especially, the connection between the phase coherence and energy relaxation, the surface anisotropy and the nature of the Kondo scatterers will be emphasized. The limited length of this review does not allow completeness, but it is restricted to some of the most important moments and phenomena.

2. Kondo resonance in the electron density of states measured by STM

In the original Kondo model based on the Kondo Hamiltonian the magnetic impurity is represented as a localized spin. The Kondo resonance is around the Fermi energy and frequently called Abrikosov-Suhl resonance. The more appropriate model is, however, the Anderson model, where the d-levels with finite width, Δ, are also included, and they are split due to the on-site Coulomb interaction. It was conjectured by Grüner and one of the authors² and first calculated by Yamada³ that the Kondo resonance is superimposed on the atomic d-level structure in the d-level density of states. Since that time it has been a great challenge to measure that directly. It was shown⁴ that the conduction electron density is suppressed nearby the impurity because the strong scattering by the impurity results in interference between the incoming and outgoing waves and that depression in the local density of states (LDOS) is the largest around the Fermi energy in the range of the Kondo temperature.⁴ That time a local probe of the density of states was not available. It was suggested, however, that a dilute layer of magnetic impurities has similar effect. That could be measured by placing that layer nearby the barrier in one of the electrodes of a metal-oxide-metal tunnel junction, where the resonance occurs as a zero bias resistivity maximum.⁵ Recently, by using scanning tunneling microscope (STM) the direct probe became possible. Concerning the experimental observation an unexpected difficulty appeared, namely the surface anisotropy for integer spins to be discussed later. The Mn impurity has very low Kondo temperature in Au, Ag and Cu, thus too high resolution would be required. The Fe and Cr impurities do not move freely because of having S = 2 which was not realized at the time of the first experiments, but were examined later in a systematic study of different transition-metal impurities on Au surfaces.⁶ The successful experiments were performed with single Ce atoms on Ag⁷ as well as with single Co atoms on Au⁸ and Cu⁹ surfaces by measuring the I-V characteristics of the tunneling current through the tip of a STM placed close to the surface and at a small distance R from the magnetic atom (see Fig. 1 (a)). In these experiments the electron tunnels from the tip into the metal, travels to the impurity and after scattering goes back to the tip, resulting in an interference between the unperturbed and scattered electron waves. There is also a possibility that the electrons tunnel from the tip directly into the d- or f-level of the magnetic impurity. However, the tunneling rate for the latter process is probably very small, especially for f-levels, which are deeply inside the atom. To explain the observed narrow asymmetric Fano resonance¹⁰ structure in the electronic LDOS the first proposed theory⁸,¹¹ took into account both processes. However, as it has been shown in Ref.,¹² the Fano resonance can develop even if
the density of states is calculated the final expression obtained for the tunnel-Kondo resonance, respectively. After a straightforward the scattering on the upper and lower d-levels and the approximated as a sum of three Lorentzian according to Fig. 1. (a) Schematic setup of the STM measurements. (b) Qualitative dependence of the calculated line shape of the tunneling DOS on the distance of the tip from the impurity using the first part of Eq. (1) and the 3-dimensional Au bulk Green’s functions. The results obtained by using the 2-dimensional free-electron like Au(111) surface band\textsuperscript{15} are quite similar.\textsuperscript{12}

one neglects the direct tunneling to the impurity. This assumption was supported also by the “quantum mirage experiments”\textsuperscript{9} where an elliptical corral was built from magnetic or non-magnetic atoms on a metal surface with a magnetic impurity in one of the foci’s and an attenuated Fano resonance was measured in the other foci as well. In that case the role of the direct tunneling is obviously negligible. That assumption was also justified later for the experimental situation by a microscopic theory of tunneling into a single impurity on a metal surface by Gadzuk et al.\textsuperscript{13}

In the theory of Ref.\textsuperscript{12} the physics is governed by the unperturbed one-electron Green’s function at the surface of the metal $G_{R,σ}^{(0)}(ω−iδ)$ and the scattering amplitude $t_σ(ω−iδ)$ due to the impurity. The latter, given by $\frac{Δ}{\pi ρ_0}G_{d,σ}(ω−iδ)$ in the Anderson model,\textsuperscript{12,14} can be approximated as a sum of three Lorentzian according to the scattering on the upper and lower d-levels and the Kondo resonance, respectively. After a straightforward calculation the final expression obtained for the tunneling density of states is

$$\delta ρ_R(ω) = \frac{[\text{Im} G_R^{(0)}(ω−iδ)]^2}{π ρ_0} \left\{ \frac{(q_R + ε)^2}{ε^2 + 1} - 1 + C_R \right\} \quad (1)$$

where the spin index $σ$ was dropped, $q_R = \text{Re} G_R^{(0)}(ω−iδ)/\text{Im} G_R^{(0)}(ω−iδ)$, $ε = (ω − ε_K)/T_K$, $T_K$ is the Kondo temperature, $ε_K$ is a shift with respect to the Fermi energy, and $ρ_0$ is the density of states at the Fermi level for one spin direction. $C_R$ arises from potential scattering on the d-level\textsuperscript{12} and corresponds to a weakly energy dependent Friedel oscillation.

The first part of Eq. (1) coming from the scattering by the Kondo resonance gives a Fano line shape in the tunneling LDOS, controlled by the parameter $q_R$. The fit on the experimental data for a Co atom on a Au (111) surface\textsuperscript{8} gave excellent agreement with fitting parameters being consistent with the predictions of an NCA calculation combined with band structure results.\textsuperscript{12}

To calculate the distance dependence of $q_R$ and $C_R$, i.e., of the line shape, the tunneling of electrons from the tip (1) into the 3-dimensional Au bulk states as well as (2) into the 2-dimensional Au(111) surface band\textsuperscript{15} was considered. In both cases a free electron-like band structure was assumed.\textsuperscript{12} Whereas the periodic changes of the line shape between Fano and Lorentzian ones and the decrease in the overall amplitude with increasing distance were demonstrated for both cases (see Fig. 1 (b)), the precise dependence of the line shape on $R$ is not reproduced by the simplifying assumption of a free electron band structure.\textsuperscript{12}

There is a question concerning the role of the bulk and surface states in the formation of the Kondo resonance and in the tunneling. According to novel examinations\textsuperscript{16,17} it seems that the bulk states have the dominating role in the former, and the surface states in the latter.

3. Size dependence of the Kondo effect

In the Kondo ground state the spin is completely screened by the conduction electrons, thus the impurity spin must move together with a compensation cloud in the conduction electron band and its scale is the only relevant scale, namely, the Kondo coherence length $ξ ∼ v_F/T_K$ which can be extremely large for lower Kondo temperatures, e.g., $ξ = 10^4 \text{Å}$ for $T_K = 1$K. In the mesoscopic samples that scale can be easily matched by the size of the sample and it was conjectured\textsuperscript{18} that, in that case, the full spin compensation cannot be developed, thus a suppression of the Kondo effect could be expected.

In the 90’s several experiments\textsuperscript{19–23} were performed on thin films and narrow wires of dilute magnetic alloys to measure the Kondo compensation cloud. In most of the cases\textsuperscript{19–21} a suppression of the Kondo resistivity amplitude and no essential change in the Kondo temperature were observed for small sample sizes. Covering a thin layer of magnetic alloys by another pure metal layer (see Fig. 2 (a)), a partial recovery of the Kondo signal was found\textsuperscript{24,25} which was even smaller for more disordered overlayers. These cannot be attributed to the reduced size of the Kondo screening cloud due to the size of the sample as only the energy separation of the metallic electron levels are relevant. As far as the level separation is smaller than $T_K$ only the shape and size of the Kondo cloud is modified.\textsuperscript{27,28}

The experiments in ballistic samples were explained by the theory of the spin-orbit-induced surface anisotropy.\textsuperscript{29–32} According to that theory a magnetic impurity in a metallic host with strong spin-orbit interaction experiences a surface anisotropy having the following
form for flat surfaces:

$$H = K_d (\mathbf{nS})^2$$  \hspace{1cm} (2)

where \(\mathbf{n}\) is the normal direction of the experienced surface element and \(\mathbf{S}\) is the spin of the impurity, and \(K_d > 0\) is the anisotropy constant. The most slowly decaying contribution is non-oscillating, and inversely proportional to the distance \(d\) measured from the surface, and is in the range of \(0.01 \left(\frac{d}{A}\right) eV < K_d < 1 \left(\frac{d}{A}\right) eV\). \(^{29,30}\)

The surface contribution to the self-energy was calculated on basis of diagram Fig. 3 \(^{29,30}\) which is second order in the exchange coupling and the spin-orbit (SO) scattering as well, both calculated for \(l = 2\) scattering. For the spin-orbit scatterers an Anderson type model is taken with spin-orbit interaction on the d-level of the scatterer and an average was taken over the sample. \(^{29,30}\) The surprising \(1/d\) dependence can be explained in the following way. One of the two spin-orbit scatterers in diagram Fig. 3 must experience of the finite size by missing the scatterers in the area indicated on the figure Fig. 4 as region I, while the other one can be very nearby the impurity (region II on Fig. 4). The number of the most effective missing scatterers can be estimated as proportional to \(d^3\), while of the second type as the number of scatterers in the neighborhood of the spin which is calculated to be between 100-1000. That large number appears as a prefactor. The transition concerning the angular momentum can be treated in a frame, where the z axis connects the certain scatterer and the impurity. The magnetic quantum number changes e.g. as \(m \rightarrow m \pm 1\). The overlap of those localized d-states with the conduction electrons must be taken. The amplitude of the electron spherical wave function centered at the impurity on an atomic scale \(a (a \ll d)\) nearby the axis is \(1/r(a/r)^{|m|}\) at distance \(r \sim d \gg a\), \(r^{-1}\) comes from the radial amplitude of a spherical wave, while \(r^{-|m|}\) from the angular dependence \(Y_{lm} \sim (\sin \theta)^{|m|}\). Namely, the scattering atom of size \(a\) is seen from the spin inside the angle \(\theta \sim a/r\). Therefore the largest contribution is due to the states \(m = 0\) and \(m = \pm 1\). The overlap of the radial wave function with the atomic orbital of the scatterer is, however, oscillating, thus it contains an extra factor in the form \(\sum_{n=0} (S_k^n \sin k_F r (k_F r)^{-n} + C_m^n \cos k_F r (k_F r)^{-n})\) (see Eq. (13a-c) in Ref. \(^{30}\)), where the amplitude \(S_k^n\) and \(C_m^n\) are zero for even and odd \(n\), respectively, and \(k_F\) is the Fermi wavelength. In the product of the incoming and outgoing waves the non-oscillating parts arise from terms proportional to \(\sin^2(k_F r)\) or \(\cos^2(k_F r)\). In the case of combination \(m = 0\), \(m = \pm 1\) waves the terms proportional to \(C_m = 0\) \(C_m = \pm 1\) and \(S_k = 0\) \(S_k = \pm 1\) contribute and that results in an extra \((k_F r)^{-1}\) factor. Thus the contribution from the missing scatterers is \((d/a)^3 |d^2(a/d)|^{||m|}\). In that way the largest contribution for \(m = 0, \pm 1\) is proportional to \(1/d\). Similar contribution arises when the incoming and outgoing waves have identical \(|m| = 1\).

According to the anisotropy there are different splitting schemes for integer and half-integer spins (see Fig. 5). For integer spins the ground state is a singlet, whereas for half-integer spins it is a Kramer’s doublet. Thus for integer spins the anisotropy causes size effects \(^{31}\) in mesoscopic samples in agreement with the early experiments. \(^{19-23}\) The surface anisotropy was tested later also by new kind of experiments, measuring other spin dependent quantities (e.g. the magnetoresistance, \(^{33,34}\) the thermopower, \(^{35}\) and impurity spin magnetization \(^{37}\)), or in samples with half-integer spins \(^{32,38,39}\) which could be all explained with the theory of surface anisotropy.

The thermopower of a homogeneous sample is zero even if the diameter of the measured wire is changing along its length. In case of surface anisotropy the percentage of blocked spins are higher in a narrow region of the wire than in the broader one. Thus having nominally the same impurity concentration, the concentration of the effectively free spins are different, therefore measurable thermopower occurs. \(^{35}\)

The most exciting experiment probably was performed by Giordano and coworkers \(^{36}\) (see Fig. 2 (b)) where different multilayer structures composed of Au and Au(Fe) films were examined positioning the overlayer only on
one side or on both sides of the film. The results gave a good agreement with the theory of surface anisotropy also quantitatively.

4. Dephasing and non-equilibrium transport

The magnetic impurities play an important role in transport properties of mesoscopic systems in cases of implanted impurities and contamination like small amount of Fe impurities or oxidation of copper with forming copper oxide ($S = 1^{40}$).

4.1 Dephasing

The dephasing at low temperature has recently attracted considerable interest and also intensified by the debate over the saturation at low temperature. Magnetic impurities with degenerate spin states can always contribute to the dephasing by spin flip processes. The non-elastic scattering rate has a maximum at the Kondo temperature and freezes out at low temperatures where the Kondo singlet ground state is formed, which do not exhibit dynamical feature. The most appropriate study of that is a recent one, where the numerical renormalization group has been applied.\textsuperscript{41} Such dephasing rate with Fe doped samples has been observed by e.g. Hae-sendorck et al.\textsuperscript{42} showing maximum at $T_K$. The surface anisotropy can reduce and even block the spin-flip processes for integer spin (e.g. Fe, Cr, CuO) if the anisotropy constant $K_D$ is comparable to or dominating over the $T_K$, respectively. On the other hand, for half-integer spin the anisotropy has only minor role by freezing the spin into a degenerate Kramer’s doublet and only some prefactors can be modified. The dephasing is usually measured in equilibrium situation as magnetoresistance,\textsuperscript{43–46} universal conductance fluctuation,\textsuperscript{47} and Aharonov-Bohm oscillation in mesoscopic rings in magnetic fields.\textsuperscript{46} In case of out-of-equilibrium situation where the distribution of electrons is broadened by applying larger voltages on short wires, dephasing becomes even possible if that broadening dominates the anisotropy. Non-equilibrium measurements\textsuperscript{48} were also carried out but were there no direct evidences for the presence of magnetic impurities, however, classical two-level systems with energy splitting can play a role similar to the integer magnetic impurities with anisotropy.

The size dependence of dephasing was observed in PdAu nanowires\textsuperscript{45} with large spin-orbit scattering. As the diameters of the wires were reduced the dephasing time increases. That is consistent with the concept of surface anisotropy as in that case in smaller wires the integer spins can be blocked. That effect is just the opposite to the case where extra dephasing scatterers are assumed at the surface, e.g. due to copper-oxide.

4.2 Energy relaxation

The out-of-equilibrium transport in short wires with large bias voltage has attracted great interest following the crucial experiments at Saclay.\textsuperscript{49} The distribution of electron energies were measured between the contacts at different position by attaching extra tunnel junction to the side of the wire (see Fig. 6). The wires were in the diffusive limit. The measured electron distribution in many cases shows a step-like distribution due to the electrons coming and accelerated from one of the contacts and decelerated from the other one. Even at very low temperature the distribution, however, does not show sharp steps but they are smeared due to a finite relaxation rate of the electrons. Altshuler, Aronov et al.\textsuperscript{50} predicted an energy relaxation rate due to the electron-electron scattering with $\varepsilon^{-3/2}$ dependence on the energy and well defined amplitude where the energy $\varepsilon$ is measured from the Fermi energy.

Some of the experiments can be explained by that but in other cases other relaxation mechanisms must exist. The Saclay group phenomenologically introduced an extra interaction between the electrons which has a $1/\varepsilon^2$ singularity where $\varepsilon$ is the energy transfer. Several authors suggested\textsuperscript{51–56} that the energy exchange is mediated by Kondo impurities (magnetic and structural defects) which was supported later also by experiments in magnetic field.\textsuperscript{57} It has been known since a long time\textsuperscript{58} that such interaction is singular in the energy transfer and recently Kaminski and Glazman\textsuperscript{51} called the attention to similar $1/\varepsilon^2$ singularity suggested by the Saclay group. Using that mechanism the electron transport is determined by the diffusive Boltzmann equation and compared with the experimentally determined electron distributions and the impurity concentrations were adjusted.\textsuperscript{52–56} In some cases the estimated magnetic impurity concentrations using that method are much larger than those determined from the dephasing rate, even by two orders of magnitude.

There are additional features. In the case of split Fermi energy due to the bias, Kondo resonances appear at both Fermi energies, but as the steps in the occupation numbers are reduced the Kondo temperature is also reduced assuming that the bias voltage $e|V| < kT_K$. In those cases the weak coupling Kondo theory (logarithmic approximation) can be applied. Furthermore, the
the non-equilibrium distribution of the electrons makes possible spin flip relaxation by creating electron-hole pairs with almost zero energy like in the Kondo relaxation processes. That relaxation rate is proportional to \( |eV| (e|V| \gg kT) \) and that results in an infrared cutoff smearing and even blocking the Kondo effect.

The effect of the spin-orbit-induced anisotropy on the energy relaxation in mesoscopic wires was examined recently.\(^6\) There the non-equilibrium distribution function of a wire with length \( L \) (see Fig. 6) was determined by solving the diffusive Boltzmann equation

\[
\frac{\partial f(\varepsilon, x)}{\partial t} = \frac{1}{\tau_D} \frac{\partial^2 f(\varepsilon, x)}{\partial x^2} + I_{\text{coll}}(\{f\}) = 0
\]

\[
I_{\text{coll}}(\{f\}) = \int dE \{ f(\varepsilon)[1 - f(\varepsilon - E)]W(\varepsilon, E) - [1 - f(\varepsilon)]f(\varepsilon - E)W(\varepsilon - E, -E) \}
\]

taking into account in the scattering rate due to magnetic impurities \( W(\varepsilon, E) \) the surface anisotropy, as well. In Eq. (3) \( \tau_D = \frac{L^2}{D} \) is the diffusion constant, \( f \) is assumed not depending on the spin, and \( x \) denotes the position in the wire in the units of \( L \). Similar to the case of finite magnetic field\(^5\) there are also first order processes contributing to the scattering rate and the spin occupation numbers \( p_{\text{M+S}} \) depend also on the voltage. Calculating the latter from the first order processes the Boltzmann equation was solved self-consistently starting with the solution without inelastic scattering mechanism

\[
f^{(0)}(\varepsilon, x) = (1 - x)n_F(\varepsilon - \frac{\Delta}{2}) + xn_F(\varepsilon + \frac{\Delta}{2})
\]

and using the following collision integral

\[
f^{(2)}_{\text{coll}}(\{f\}) = \int \int d\varepsilon'K_{M'M}^S(E, \varepsilon, \varepsilon', K_d) \times
\]

\[
\times \{ p_Mf(\varepsilon)f(\varepsilon')[1 - f(\varepsilon - E)];
\]

\[
\cdot [1 - f(\varepsilon' + E + K_dM^2 - K_dM'^2)];
\]

\[
- p_M'[1 - f(\varepsilon)][1 - f(\varepsilon')][f(\varepsilon - E)];
\]

\[
f(\varepsilon' + E + K_dM^2 - K_dM'^2)\}
\]

where the kernel \( K_{M'M}^S \) describes electron-electron interaction mediated by Kondo impurities with surface anisotropy. For simplicity, the case \( S = 1 \) (i.e. for CuO in the Körnigga lifetime\(^6\) of the impurity spin the value for \( K_d = 0 \) according to diagram Fig. 7 (b) was used.\(^5\)

At each step of the self-consistent numerical calculation, both the spin occupation numbers and the Körnigga lifetime were updated from the actual \( f \).

In Fig. 8 (a) the dependence of the distribution function on the strength of the anisotropy is illustrated. Increasing \( K_d \) first the energy transfer is getting larger but for larger \( K_d \) the ground state is frozen in, similar to the magnetic field dependence discussed in Ref.\(^5\). We can conclude that the contribution of magnetic impurities is enhanced or unchanged in case when for the strength of the anisotropy \( K_d < eU \). For \( K_d \approx 0.1 - 0.2K \) which is a good estimation for the strength of the anisotropy for the wires with width of \( \sim 45\text{nm} \) and thickness of \( \sim 85 - 110\text{nm} \) used in the experiments, the energy relaxation is only slightly affected by the anisotropy.

\[\text{Cu wires}\](40) was considered and an appropriate constant value \( J \) was used instead of the renormalized Kondo couplings depending on \( M, M' \).\(^5\) The kernel \( K_{M'M}^S \) was calculated in the Kondo model with anisotropy\(^3\) according to the diagram on Fig. 7 (a). As the weak dependence on

Cu wires\(^4\) was used instead of the renormalized Kondo couplings depending on \( M, M' \).\(^5\) The kernel \( K_{M'M}^S \) was calculated in the Kondo model with anisotropy\(^3\) according to the diagram on Fig. 7 (a). As the weak dependence on

[Fig. 7. The diagrams used for calculating (a) the kernel and (b) the Körnigga lifetime of the impurity spin. The solid lines denote the conduction electrons, the dotted lines the impurity spin, and the blob is the Kondo coupling.]

In Fig. 8 (b) fits on the experimental data of Cu wires\(^5\) can be seen for different \( K_d, p_0J, \) and \( c \) triads. We can see that equally good fit can be achieved with different \( K_d, p_0J \) (corresponding to the Kondo temperature) and \( c \) triads. That uncertainty is further increased if a distribution in \( K_d \) is also included. At fix \( p_0J \), the larger the \( c \) is the smaller the necessary \( K_d \).

The half-integer case must be very similar to the case without surface anisotropy because of the degeneracy in
the ground state, and only the spin dependent prefactors are different.

Thus the role of surface anisotropy in electron dephasing and energy relaxation is very different for integer and half-integer spins having a singlet and a Kramer’s doublet ground state, respectively. In the first case for low temperature and thermal equilibrium the spin dynamics and therefore the dephasing are frozen out while in the out-of-equilibrium metallic wire experiments that can reenter. That suggests a pronounced size dependence and very different concentration for the dynamically active impurities in the dephasing and the out-of-equilibrium wire experiments. In the case of half-integer spin that cannot be expected. Further careful experiments for the size dependence and implanted impurities are required.

5. Point contacts with magnetic impurities

In point contact (PC) the magnetic impurities in the contact region cause very strong electron scattering in the energy region of $T_K$ around the Fermi energy. Thus they strongly influences the I-V characteristics at zero bias. The reduction in the current flowing through the contact is due to the electron backscattering (see Fig. 9) thus at zero bias there is resistivity increase. A thorough study of the Kondo effect in ultra small CuMn PCs has been carried out.\textsuperscript{61, 62} Rather surprisingly, in this case not a suppression but an orders of magnitude increase of the Kondo temperature has been reported.

![backscattering](image)

Fig. 9. The dominating backscattering process by the magnetic impurity in the PC.

As shown in Ref.\textsuperscript{63, 64} these anomalies can be well explained by the presence of LDOS fluctuations. For a small PC, even a weak channel quantization induces huge LDOS fluctuations\textsuperscript{63, 64} which become larger and larger with decreasing contact sizes. $T_K$ depends on the inverse of the LDOS exponentially ($T_K \sim \exp(-2\rho_0 J)$). The LDOS has a weak dependence on the energy, thus the change at the Fermi energy is dominating, that may produce an extremely wide distribution of the Kondo temperatures for impurities in the contact region. The zero bias anomaly of the PC, however, turns out to be dominated by impurities with the largest $T_K$, while those with very small $T_K$ do not show up at larger voltages. Indeed, in Ref.\textsuperscript{63, 64} the effect of these fluctuations was taken into account through a modified renormalization procedure, and a perfect agreement was found between the calculated and experimentally determined anomalous amplitude of the Kondo signal.

It was also predicted by the theory\textsuperscript{63, 64} that this effect should be much less pronounced for alloys with large $T_K$ as $T_K$ is less sensitive to the change in $\rho_0$ in that case. That has been later confirmed by the experiments studying Cu(Fe) alloys.\textsuperscript{65}

6. Orbital Kondo effect due to dynamical defects

In many different experiments typical Kondo logarithmic temperature dependence (see Ref.\textsuperscript{66}) has been observed and it was argued that is not due to the electron spin. It has been suggested many years ago\textsuperscript{67} that dynamical defects where an atom is sitting in a double well potential can be described by a quasispin and the electron-defect interaction depends on that quasispin and also on the angular momenta of the electron. The Hamiltonian is very similar to the spin Kondo Hamiltonian.\textsuperscript{1} In that model the dominating processes are the electron screening and electron assisted tunneling of the atom between the two wells. The corresponding couplings are non-commuting, thus logarithmic terms are expected. The variables in the couplings are of orbital origin, while the real electron spin is a silent conserving one. In that case if the region below the Kondo temperature could be reached, the ground state has a complicated structure due to the spin degeneracy. The main consequence is that the Fermi liquid behavior at $T < T_K$ is replaced by non-Fermi liquid behavior showing $T^{1/2}$ temperature dependence.

Several experiments have been reported where the observed low temperature anomalies were attributed to TLS Kondo defects,\textsuperscript{67–72} namely to dynamical structural defects: they disappear under annealing and did not, or only slightly depended on magnetic field.

There is an easy way to distinguish between slow TLS and Kondo-like scatterers.\textsuperscript{73} As it has been discussed concerning the point contact with magnetic impurities, the dominating dynamical processes are the backscatterings of the electrons resulting in an increase of resistivity. In case of slow, classical TLS at low temperature the electron must have large enough energy to excite the TLS, thus that processes have a lower threshold voltage different for different scatters. Thus the resistivity increases with the voltage. On the other hand, as it was discussed earlier in the case of Kondo scattering, the resistivity maximum is at zero bias.

The most of zero-bias anomalies\textsuperscript{73} are surprisingly Kondo-like. A logarithmic increase of the resistivity attributed to the presence of dislocations or substitutional tunneling impurities has been observed in various systems.\textsuperscript{67, 68} The most spectacular experiments were carried out in Cu and Ti PCs where a two-channel Kondo-like $\sim \sqrt{T}$ and $\sqrt{V}$ non-Fermi liquid scaling behavior due to non-magnetic scatterers has been observed in the dynamical resistance,\textsuperscript{69, 70} however the nature of the scatterers are still unknown. The widths of the zero-bias anomalies were associated with the Kondo temperature, $T_K \sim 5K$. In another beautiful experiment a repeated switching of the zero-bias anomaly between two curves in the presence of some slow TLSs has been observed in amorphous PC\textsubscript{8},\textsuperscript{71} which could be consistently explained assuming that a slow fluctuator influences the splitting of one or two fast Kondo TLSs close to it\textsuperscript{72} and that causes the change in the zero-bias anomalies.
There is a further set of experiments\textsuperscript{74} where an alternating voltage was superimposed on a constant bias $V_0$, $V(t) = V_0 + V_1 \cos(\omega t)$. As far as the characteristic frequency (e.g., Kondo temperature) of the mechanism responsible for the zero-bias anomaly is large compared to $\hbar \omega$, the measured $I-V$ characteristic is just the time average of the current: $\langle I(t) \rangle = I(V_0) + \frac{1}{2} \left( \frac{\partial^2 I}{\partial V^2} \right)_{V=V_0} V^2$.

The experiments agree with that, but those are far from being conclusive. In case of slow TLS when the actual voltage is in the range of the TLS energy $\Delta$ rectification occurs as current starts to flow when the actual voltage exceeds $\Delta$.\textsuperscript{73} That is also frequency independent. Thus the earlier expectation that in case of slow TLS strong frequency dependence is expected is not correct.

The model known as orbital two-channel Kondo model was strongly criticized by Kagan and his coworkers\textsuperscript{75} and later by Altshuler et al.\textsuperscript{76} Kagan’s argument was that the tunneling rate of the atom between the two wells is drastically reduced as the atom is moving with the electron screening cloud and logarithmic terms survive only in much lower energy region than the electronic band with cutoff. The actual range is determined roughly by the third excited state of the atom in the well. That argument has recently made more transparent\textsuperscript{76} using a simplified model where the atom is moving in an infinitely tall potential tower with a double potential at the bottom (see Fig. 10). Thus the atom does not become free well above the Debye temperature.

That model was treated numerically in the logarithmic approximation, and it was shown that including more than the first six levels the Kondo temperature is drastically reduced due to the reduction in the tunneling rate. That problem can be avoided by assuming that the second level is just above the barrier\textsuperscript{77} (see Fig. 10), thus tunneling does not occur. The question remained open, whether the Kondo temperature can be large enough to explain zero-bias anomalies in the energy range of 10K and also that the renormalized energy separation $\Delta$ between the two lowest levels can allow the scaling to reach the temperature range $T < T_K$. Assuming an intermediate atomic mass as 50 proton mass, the Kondo temperature is in the range of 0.2 K for very strong coupling, but the role of the energy separation is far from being clear. In this way the observed large zero-bias anomalies cannot be explained, but dephasing and energy relaxation rate can be influenced. The experimental situation concerning the role of structural defects in dephasing in metallic glasses and strongly disordered systems is still subject of debates.\textsuperscript{47,78,79}

As in the tower model the relevant energy scale is the level spacing, that and also the Kondo temperature can be increased by considering light atoms like H which can be present in atomic form or e.g. as water. Then the requested $T_K$ ($T_K \sim 10 K$) can be reached and also the coupling is also strong, because the phase shift of the electron scattering is nearby $\delta = \pi/2$ according to the Friedel sum rule. The energy separation $\Delta$ should be studied by numerical renormalization group valid even in that very strong coupling region. Recent experiment\textsuperscript{80} in Hungary strongly indicates the role of atomic hydrogen in Pd and Pt contacts where the H content is systematically changed.

7. Conclusions

In the coming years the identification of Kondo scatterers in the phenomena of dephasing and energy relaxation will be a very important task. Theoretically the possibility of the structural Kondo scatterers must be clarified. These problems are very closely related and they should be studied considering different samples containing different impurities and prepared in different ways.

Acknowledgements

We are grateful to N. O. Birge, V. M. Fonin, H. Grabert, J. Kroha, H. Pothier, and G. Zaránd for useful discussions. This work was supported by Hungarian grants OTKA F043465, T046303, T034243, TS040878, T038162, and grant No. RTN2-2001-00440.

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