Effect of Magnetic Impurities on Energy Exchange between Electrons

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In order to probe quantitatively the effect of Kondo impurities on energy exchange between electrons in metals, we have compared measurements on two silver wires with dilute magnetic impurities (manganese) introduced in one of them. The measurement of the temperature dependence of the electron phase coherence time on the wires provides an independent determination of the impurity concentration. Quantitative agreement on the energy exchange rate is found with a theory by Göppert *et al.* that accounts for Kondo scattering of electrons on spin-1/2 impurities.

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In diffusive metals, it is expected that the dominant inelastic electron scattering process at low temperature is the Coulomb interaction [1,2], leading to a power law increase of the electron phase coherence time τ_φ with decreasing temperature T. However, in the presence of a small concentration of magnetic impurities with low Kondo temperature, τ_φ can be limited by spin-flip scattering, resulting in a nearly temperature independent phase coherence time over a broad temperature range [3]. As shown in Ref. [3], this mechanism could explain the apparent low-temperature saturation of τ_φ observed in many experiments, which caused a controversy in recent years [4,5]. It was recently proposed that magnetic impurities also affect the energy exchange rate between electrons [6], which could explain the anomalous interaction rate observed in a series of experiments [7,8]. A first hint that this proposal is relevant was the observation of a magnetic field dependence of the rate [9,10], in a manner consistent with a theory taking into account the Kondo effect [11]. In those experiments, however, the nature and amount of magnetic impurities were not controlled. Assuming that the impurities were Mn, the concentrations needed to explain energy exchange experiments in silver wires were up to 2 orders of magnitude larger than the concentrations deduced from τ_φ measurements on similar samples [9,10]. It was proposed that the samples for energy exchange rate measurements could have been contaminated during fabrication [9,10]. Another hypothesis is that impurities other than Mn, which affect energy exchange rates more drastically then phase coherence, were present [12,13]. Comparison of these proposals with existing experimental results is difficult because it requires dealing with more involved theories (large spin, surface anisotropy, large Kondo temperature), and pointless because it requires uncontrolled extra parameters. In order to overcome these difficulties and investigate quantitatively the mechanism proposed by Ref. [6], we have performed a comparative experiment described in this Letter, in which we probe the specific effect of the addition of 0.7 ppm (parts per million) of Mn atoms on the energy exchange rate between electrons. We measured the temperature dependence of τ_φ on the same samples, accessing interactions in a complementary manner.

The scattering of electrons by magnetic impurities in metals is a many-body problem known as the Kondo effect: electrons tend to screen the spin of the impurity, leading to a renormalization of the scattering rate. The characteristic energy scale for this process is the Kondo temperature T_K. At $T \gtrsim T_K$, screening is incomplete, and spin-flip scattering takes place, whereas, at $T \ll T_K$, the impurity and the electrons form a singlet state, leading to potential scattering only. As far as electron dephasing is concerned, the Kondo effect results in a maximal dephasing rate at T_K [14]. The Kondo effect also provides a channel for efficient energy exchange between electrons scattering from the same magnetic impurity [6,15,16]. The rate of such a process depends on the energy of the states of the magnetic impurity, and is therefore sensitive to the magnetic field because of the Zeeman effect [11]. The spin states of the magnetic impurities can furthermore be split in the presence of spin-orbit scattering near an interface [17], which also modifies the rate. Further complications arise when the concentration of magnetic impurities is so high that the RKKY interaction between magnetic impurities constrains the spin dynamics [18,19].

In order to test quantitatively the impact of magnetic impurities on the energy exchange between electrons, we have compared the energy exchange rate and $\tau_\varphi(T)$ in two wires that differ only by the intentional addition of manganese impurities in one of them, with concentrations low enough so that interactions between Mn impurities can be neglected [18]. To observe specifically the influence of the Mn impurities, the two samples were fabricated simultaneously on the same wafer. In a first step, a set of wires and their contact pads were patterned by e-beam lithography and evaporation of silver from a nominally 6N-purity source (99.9999% Ag from Alfa Aesar®). Mn^+ ions were implanted at 70 kV in half of them, using the ion implanter IRMA at CSNSM Orsay. The neutralization current from the sample holder to ground was monitored during the implantation, leading to a direct measurement of the number of implanted atoms. Monte Carlo simulations

[20] yield the concentration of Mn atoms that stop inside the silver wire, $c = 0.7 \pm 0.1$ ppm. In order to measure the energy exchange between electrons [9], a long and thin electrode forming a tunnel junction with the middle of the wire is used as a probe. This electrode was patterned on individual chips in a second lithography step followed by evaporation of 3.5 nm of aluminum, oxidation, and evaporation of 16 nm of aluminum. We focus here on the results obtained on two wires, one without manganese added (labeled "bare" in the following), one with manganese added ("implanted"). For both samples, the wire length and cross-section area are $L = 40\ \mu$m and $S_e = 230\ \text{nm} \times 42\ \text{nm}$. The samples were measured in a dilution refrigerator with base temperature of 20 mK. The low-temperature wire resistance ($R = 55\ \Omega$) was identical for both wires, which yields the diffusion constant of electrons $D = 0.029\ \text{m}^2/\text{s}$.

For each wire, we have first measured the magnetoresistance at temperatures ranging from 20 mK to 7 K. Following Refs. [3,21], magnetoresistance curves are fit using the theory of weak localization, resulting in evaluations of the phase coherence time τ_φ. In the bare wire, it was important to take into account finite length corrections because τ_φ is comparable to the diffusion time $\tau_D = L^2/D \approx 56$ ns below 1 K [22], leading to a reduction of the predicted magnetoresistance by $\approx 30\%$ below 1 K. Reproducible conductance fluctuations were visible, so that the uncertainty in the determination of τ_φ becomes large below 60 mK in the bare sample. The spin-orbit time $\tau_{\text{so}} \approx 8$ ps was extracted from the data above 1 K. The temperature dependence of τ_φ is shown in Fig. 1 for both wires. Below 1 K, τ_φ is smaller by nearly 1 order of magnitude in the implanted wire than in the bare one. In none of the samples does τ_φ increase as $T^{-2/3}$ when temperature is lowered, as would be expected if the electron-electron interaction was the dominant dephasing process (solid line labeled "pure" in Fig. 1). The apparent saturation of τ_φ is attributed to the presence of magnetic impurities [3]. This effect is quantified by a fit of the data with a sum of three terms:

$$\frac{1}{\tau_\varphi} = \mathcal{A}T^{2/3} + \mathcal{B}T^3 + \gamma_{\text{sf}}(T), \tag{1}$$

with $\mathcal{A} = \frac{1}{\hbar}\left(\frac{\pi k_B^2}{4\nu_F L S_e}\frac{R}{R_K}\right)^{1/3}$ describing Coulomb interaction [21], $\mathcal{B}$ the electron-phonon interaction [5], and

$$\gamma_{\text{sf}}(T) = \frac{c}{\pi\hbar\nu_F}\frac{\pi^2 S(S+1)}{\pi^2 S(S+1) + \ln(T/T_K)^2} \tag{2}$$

the spin-flip (sf) scattering rate, according to the Nagaoka-Suhl formula [3,23]. The density of states in silver is $\nu_F \approx 1.03 \times 10^{47}\ \text{J}^{-1}\,\text{m}^{-3}$ (2 spin states), the resistance quantum $R_K = h/e^2$, and the spin of the magnetic impurities S. Assuming that the only magnetic impurities present are Mn atoms, with $S = 5/2$ and $T_K = 40$ mK [24] and that $\mathcal{A}$ is fixed at its theoretical value $\mathcal{A} = 0.19\ \text{ns}^{-1}\,\text{K}^{-2/3}$, the best fits are obtained for $c_b = 0.10 \pm 0.01$ ppm and $\mathcal{B}_b \approx 3.7 \times 10^{-2}\ \text{ns}^{-1}\,\text{K}^{-3}$ for the bare wire, and $c_i = 0.95 \pm 0.1$ ppm, $\mathcal{B}_i \approx 5.5 \times 10^{-2}\ \text{ns}^{-1}\,\text{K}^{-3}$ for the implanted one [25]. The difference between the implanted and bare samples, $c_i - c_b = 0.85 \pm 0.1$ ppm, is in reasonable agreement with the estimated amount of implanted ions. The value of c_b is significantly larger than found in previous experiments [3], indicating a lesser quality of the source material or a slight contamination during fabrication.

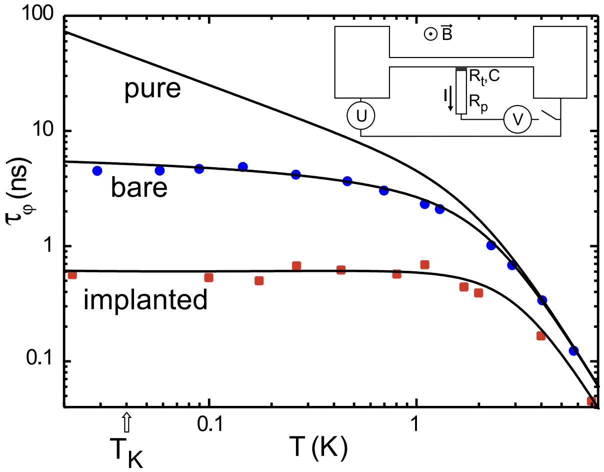

FIG. 1 (color online). Symbols: measured phase coherence time in the two wires. Solid lines: best fits with Eq. (1), obtained with $c_b = 0.10 \pm 0.01$ ppm (bare wire) and $c_i = 0.95 \pm 0.1$ ppm (implanted wire). The upper line is the prediction without spin-flip scattering ($c = 0$). Inset: layout of the circuit. The switch is open for magnetoresistance measurements, closed for energy exchange measurements.

We have then measured the energy exchange rate between electrons and its dependence on magnetic field B on the same two wires. The principle of the experiment is to drive electrons out of equilibrium with a bias voltage $U \gg k_B T/e$. The distribution function $f(E)$ of the electrons in the middle of the wire depends crucially on energy exchange between electrons [7]. The differential conductance $dI/dV(V)$ of the tunnel junction between the wire and the probe electrode (inset of Fig. 1, switch closed; see also Ref. [9]) is a convolution product of $f(E)$ with a function $q(E)$ describing inelastic tunneling [9]:

$$R_t\frac{dI}{dV}(V) = 1 - \int f(E)q(eV - E)dE \tag{3}$$

where R_t is the resistance of the tunnel junction. The information on $f(E)$ is therefore contained in $dI/dV(V)$ *via* the q function. The experiment is performed at $B \geq 0.3$ T, and the aluminum probe electrode is in its normal state. The q function is obtained from $dI/dV(V)$ at $U = 0$, where $f(E)$ is a Fermi function. In this situation, $dI/dV(V)$ displays a sharp minimum at zero voltage (sometimes called "zero bias anomaly"), due to dynamical Coulomb blockade of tunneling [26]. The environmental impedance responsible for Coulomb blockade is the resistance R_p of the probe electrode. The conductance is reduced at $V = 0$ by a factor of 0.78 in the bare sample and 0.62 in the implanted one. A slight (3% at most), unexpected dependence on B of $dI/dV(V)$ was observed on the implanted sample. In practice, we therefore derived a q function at each value of B from $dI/dV(V)$ taken at $U = 0$. Fits of $dI/dV(V)$ [27] give the resistance of the environment $R_p = 0.95$ kΩ (respectively, 1.3 kΩ), the capacitance of the tunnel junction $C = 4.4$ fF ($\approx$0.7 fF), the tunnel resistance $R_t = 16.5$ kΩ (96.9 kΩ), and the temperature $T_0 = 45$ mK for the bare (implanted) sample. The differences in those parameters are essentially due to geometry, and do not interfere with the measurement of energy exchange between electrons in the wires. When electrons are driven out of equilibrium ($U \neq 0$), $f(E)$ is not a Fermi function any longer. In the absence of energy exchange, $f(E)$ presents two steps at $E = -eU$ and $E = 0$, resulting in a splitting of the dip in $dI/dV(V)$ into two dips. In the opposite limit of a very high energy exchange rate, $f(E)$ approaches a Fermi function at a temperature $T \approx \frac{\sqrt{3}}{2\pi}\frac{eU}{k_B}$, and $dI/dV(V)$ presents a broad dip [9].

In Fig. 2, we show the measured $dI/dV(V)$ characteristics of the tunnel junctions on the bare and implanted wires, for $U = 0.1, 0.2,$ and 0.3 mV, and for B ranging from 0.3 to 2.1 T by steps of 0.3 T. At $B = 0.3$ T, the measurements on the bare sample show two clear dips at $V = 0$ and $V = U$, whereas the measurements on the implanted sample show a single, broad dip around $V = U/2$. The addition of 0.7 ppm of Mn has therefore significantly increased the energy exchange rate between electrons, resulting in a strong energy redistribution during the diffusion time $\tau_D = 56$ ns. At $B = 2.1$ T, the broad dip found in the implanted sample has split into two dips for $U = 0.1$ and 0.2 mV, indicating that the energy exchange rate due to the Mn impurities is now smaller than $1/\tau_D$.

The coupling between electrons and magnetic impurities can be described by an exchange Hamiltonian, characterized by a coupling constant J. At zero magnetic field, this description leads to energy exchange in second order perturbation theory, as described in Ref. [6]. At finite magnetic field, the spin states of the impurities are split by the Zeeman energy $E_Z = g\mu_B B$. The energy E_Z can then be exchanged at the lowest order in perturbation theory between electrons and impurities. This approach is sufficient to understand qualitatively the magnetic field behavior: the rate of interaction decays rapidly when $E_Z > eU$, because very few electrons can excite the impurities. The magnetic fields $eU/g\mu_B$ (using $g = 2$ for Mn) are 0.86, 1.7, and 2.6 T for $U = 0.1$, 0.2, and 0.3 mV, which correspond in the implanted wire to the fields at which the curvature of $dI/dV(V)$ near $V = U/2$ changes sign.

In the bare sample, the double dip also gets sharper when B is increased. This is an indication that, as inferred from $\tau_\varphi(T)$ measurements, this sample also contained some magnetic impurities. However, the corresponding energy exchange rate is always smaller than $1/\tau_D$, and $dI/dV(V)$ displays a double dip.

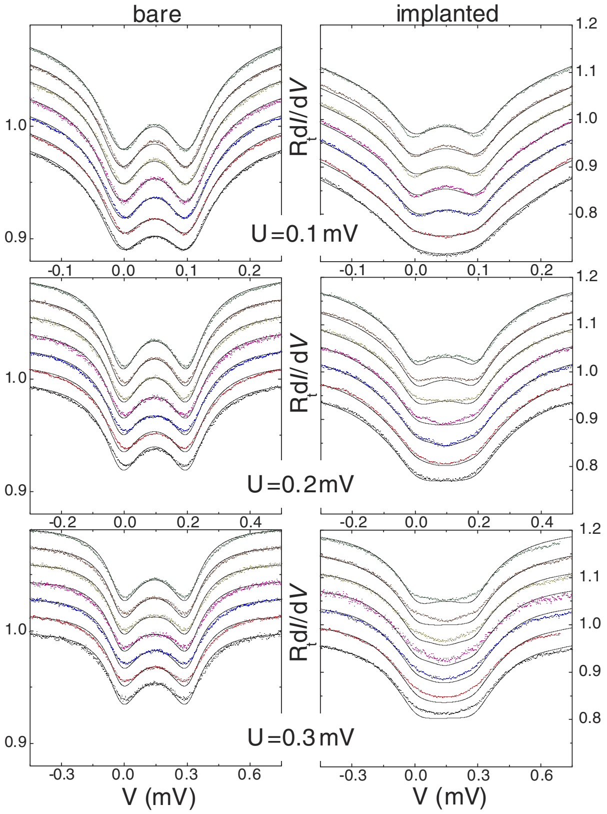

FIG. 2 (color online). Normalized differential conductance $R_t dI/dV(V)$ of the tunnel junction (see inset of Fig. 1) for the bare (left) and implanted (right) wires, for $U = 0.1$, 0.2, and 0.3 mV (top to bottom panels), and for $B = 0.3$ to 2.1 T by steps of 0.3 T (bottom to top in each panel). The curves were shifted vertically for clarity. Symbols: experiment. Solid lines: calculations using $c_b = 0.1$ ppm, $c_i = 0.95$ ppm, and $\kappa_{ee} = 0.05$ ns^{-1} meV$^{-1/2}$.

In order to compare quantitatively the measurements with theory, the renormalization of the coupling constant J by the Kondo effect needs to be considered. Very roughly, this renormalization amounts to [6] $J_{\rm eff}/J \approx [\nu_F J \ln(eU/k_B T_K)]^{-1} \approx 3$. More precisely, $J_{\rm eff}$ depends on the distribution function $f(E)$, and only the full theory of Ref. [11] is able to quantify this effect and to treat the exchange Hamiltonian at all orders on the same footing. We have therefore solved the Boltzmann equation for $f(E)$ self consistently, taking into account Coulomb interaction, electron-phonon interaction [28], and the effect of magnetic impurities in a magnetic field following the full theory of Ref. [11]. The concentration of magnetic impurities and the electron-phonon coupling were fixed at the values determined from the fit of $\tau_\varphi(T)$ [28]. We used $T_K = 40$ mK [24] and $g = 2.0$ [29]. Note that this theory assumes $S = 1/2$ whereas $S = 5/2$ for Mn atoms, but it is not expected that this difference has a large influence on the energy exchange [13]. The intensity of the Coulomb interaction alone could not be determined accurately from $\tau_\varphi(T)$, and since it was found that theory underestimates the intensity κ_{ee} of the Coulomb interaction [30], κ_{ee} was used as a free parameter, common to both samples. A slight increase in temperature of the contact pads of the wire with U (0.76 K/mV) was taken into account [28]. We also included in the calculation a slight heating of the electrons in the probe electrode at the junction interface, due to the fact that R_p is not negligible compared to R_t. The corresponding temperature $T_p(U, V)$ of the electrons in the probe electrode is $T_p \approx 0.34$ K in the bare and 0.16 K in the implanted sample at the dips ($V = 0$ or U), at $U = 0.3$ mV where T_p is expected to be the largest. The differential conductance $dI/dV(V)$ was then computed using Eq. (3). The resulting curves are displayed as solid lines in Fig. 2. The best agreement between theory and all the data was found for $\kappa_{ee} = 0.05\ \mathrm{ns}^{-1}\,\mathrm{meV}^{-1/2}$. This value is larger than the Altshuler-Aronov-Khmelnitsky prediction $\kappa_{ee}^{\mathrm{AAK}} = 0.016\ \mathrm{ns}^{-1}\,\mathrm{meV}^{-1/2}$ [1], as was repeatedly found in previous experiments [30]. A good overall agreement is found for both data sets, but some discrepancy appears for the implanted sample at $U = 0.3$ mV. We evaluated the sensitivity of the fits of the data on the implanted wire to the concentration c_i of the impurities, and found that the best agreement is obtained at $c_i = 0.9 \pm 0.3$ ppm, in good agreement with the value 0.95 ppm deduced from the data of Fig. 1.

In conclusion, in this comparative experiment, the observed effect of well-identified magnetic impurities on the energy exchange is found to be in good quantitative agreement with the theory of Ref. [11], the concentration of impurities being fixed to the value deduced from the temperature dependence of the phase coherence time, which is also compatible with the expected value from implantation. This well-controlled experiment shows that the interaction mediated by dilute, low Kondo temperature magnetic impurities is well understood. However, it remains that, in this experiment as in all previous ones, the Coulomb interaction seems to be more efficient for energy exchange than predicted [30]. Open questions remain also on the contribution of the Kondo effect to dephasing and energy exchange at energies below T_K [14], on the effect of the interactions between impurities at larger concentrations [18,19], and on finite size effects [12].

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[1] B. L. Altshuler, A. G. Aronov, and D. E. Khmelnitsky, J. Phys. C **15**, 7367 (1982).

[2] For a review, see E. Akkermans and G. Montambaux, *Physique Mésoscopique des Électrons et des Photons* (CNRS-Editions, Paris, 2004).

[3] F. Pierre *et al.*, Phys. Rev. B **68**, 085413 (2003).

[4] P. Mohanty, E. M. Q. Jariwala, and R. A. Webb, Phys. Rev. Lett. **78**, 3366 (1997).

[5] For a review, see J. J. Lin and J. P. Bird, J. Phys. Condens. Matter **14**, R501 (2002).

[6] A. Kaminski and L. Glazman, Phys. Rev. Lett. **86**, 2400 (2001).

[7] H. Pothier *et al.*, Phys. Rev. Lett. **79**, 3490 (1997).

[8] F. Pierre *et al.*, J. Low Temp. Phys. **118**, 437 (2000).

[9] A. Anthore *et al.*, Phys. Rev. Lett. **90**, 076806 (2003).

[10] A. Anthore, Ph.D. thesis, Université Paris 6, 2003, available on the website tel.ccsd.cnrs.fr

[11] G. Göppert *et al.*, Phys. Rev. B **66**, 195328 (2002).

[12] O. Ùjsághy, A. Jakovác, and A. Zawadowski, Phys. Rev. Lett. **93**, 256805 (2004).

[13] Georg Göppert and Hermann Grabert, Phys. Rev. B **68**, 193301 (2003).

[14] G. Zaránd *et al.*, Phys. Rev. Lett. **93**, 107204 (2004).

[15] Georg Göppert and Hermann Grabert, Phys. Rev. B **64**, 033301 (2001).

[16] J. Kroha and A. Zawadowski, Phys. Rev. Lett. **88**, 176803 (2002).

[17] O. Ùjsághy and A. Zawadowski, Phys. Rev. B **57**, 11 598 (1998).

[18] M. Vavilov, L. Glazman, and A. Larkin, Phys. Rev. B **68**, 075119 (2003).

[19] F. Schopfer *et al.*, Adv. Solid State Phys. **43**, 181 (2003).

[20] James F. Ziegler *et al.*, computer code SRIM-2003.26, www.srim.org, 2003. Because of the finite thickness and width of the wire, out of four Mn ions impinging on the wire, only three stop inside it.

[21] I. L. Aleiner, B. L. Altshuler, and M. E. Gershenson, Waves Random Media **9**, 201 (1999).

[22] P. Santhanam, Phys. Rev. B **35**, 8737 (1987).

[23] The width of the weak localization dip in the magnetoresistance, ≈10 mT, was small enough to neglect the variation of the spin-flip rate with magnetic field.

[24] M. Maple, in *Magnetism*, edited by H. Suhl (Academic, New York, 1973), Vol. 5; C. Van Haesendonck, J. Vranken, and Y. Bruynseraede, Phys. Rev. Lett. **58**, 1968 (1987).

[25] The difference between the $\mathcal{B}$ parameters is not understood, but it only affects the dependence of $\tau_\varphi(T)$ above 2 K, whereas the impurity concentrations c_i and c_b are determined by low-T behavior.

[26] For a review, see G.-L. Ingold and Yu. Nazarov, in *Single Charge Tunneling*, edited by H. Grabert and M. H. Devoret (Plenum, New York, 1992).

[27] P. Joyez and D. Esteve, Phys. Rev. B **56**, 1848 (1997); Phys. Rev. B **58**, 15 912 (1998).

[28] F. Pierre, Ann. Phys. (Paris) **26**, No. 4 (2001).

[29] G. E. Brodale *et al.*, J. Magn. Magn. Mater. **54**, 194 (1986).

[30] B. Huard *et al.*, Solid State Commun. **131**, 599 (2004).