Kondo-like behavior near the metal-to-insulator transition of nanoscale granular aluminum

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We show that the normal state transport properties of nanoscale granular aluminum films, near the metal to insulator transition, present striking similarities with those of Kondo systems. Those include a negative magnetoresistance, a minimum of resistance R at a temperature T_m in metallic films, a logarithmic rise at low temperatures, and a negative curvature of $R(T)$ at high temperatures. These normal state properties are interpreted in terms of spin-flip scattering of conduction electrons by local magnetic moments, possibly located at the metal/oxide interfaces.

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We present new transport measurements on aluminum films consisting of nanoscale Al grains, about 2 nm in size, weakly coupled through thin Al oxide barriers.[1] We find that near the metal-to-insulator transition (MIT) their magnetoresistance is increasingly negative and scales with (H/T), with an exponent close to 2, up to about 100 K. Additionally, samples having a positive resistance temperature coefficient (metallic behavior) present a minimum of resistance R at a temperature T_m of several 10 K depending on the film's resistivity and a temperature dependence of the resistance compatible with a logarithmic increase below T_m. All metallic films near the MIT display a negative curvature of the $R(T)$ curves. These transport properties point to spin scattering of conducting electrons, as occurs in Kondo systems.[2,3] We discuss possible origins of localized magnetic moments in these films.

Samples were prepared by thermal evaporation of 99.999% pure Al pellets from ceramic crucibles under a reduced pressure of oxygen in the range of $1\text{–}3.5 \times 10^{-5}$ Torr. Substrates of Si-Si_2O were cooled by liquid nitrogen during evaporation. The room temperature resistivity, ρ_{RT}, of the films was controlled by the oxygen pressure used during evaporation and by the evaporation rate. Fine tuning of this pressure allowed a detailed study of the immediate vicinity of the MIT. Samples whose Kondo-like properties are as mentioned above have normal state resistivities ranging from about 100 $\mu\Omega$ cm up to several 1000 $\mu\Omega$ cm. In that range the grain size does not vary much and is about 2 nm.[1] The films, about 100 nm thick, are three-dimensional in the sense that their thickness is more than 1 order of magnitude larger than the grain size. They are superconducting with a critical temperature of about 3.2 K with a sharp transition (width of about 0.01 K) indicating a high degree of homogeneity.

Figure 1 shows the temperature dependence of the resistance of a number of films having a small resistance coefficient of temperature. Table I summarizes some of their properties. While from earlier measurements[4] films were simply classified as metallic ($dR/dT > 0$) or insulating ($dR/dT < 0$), a close examination of Fig. 1 shows that $R(T)$ curves have a nontrivial structure. For resistivities less than ≈300 $\mu\Omega$ cm, the behavior is indeed metallic-like, but with a minimum of resistance at a temperature T_m that increases with the normal state resistivity. Below T_m the resistance reaches a maximum at a temperature T_M, below which it starts to decrease towards the superconducting transition. We show in Fig. 2 a more detailed view of the behavior of one of these metallic films. As can be seen in the inset, below T_m the temperature dependence of resistance is compatible with a logarithmic increase. Samples having resistivities smaller than ≈100 $\mu\Omega$ cm do not show this low temperature rise (Fig. 3).

For resistivities larger than ≈300 $\mu\Omega$ cm, the films resistance rises monotonically as the temperature is reduced. A logarithmic increase of resistance of high resistivity films at low temperatures is observed in these films over a broader temperature range than in metallic films, consistent with earlier findings in similar films.[5]

Above T_m and close to the MIT, $R(T)$ displays a negative curvature from T_m up to about 200 K.

All the films listed in Table I have a negative magnetoresistance (MR) above T_M, up to a temperature of the order of 100 K. This negative MR does not saturate up to the highest field reached (14 T in most cases). Below T_M the behavior of the MR is more complex, being clearly influenced by superconducting fluctuations that give rise to the ghost critical field effect.[6]

Figure 4(a) shows a set of MR data obtained on a high resistivity sample (no. 2425) above T_M. We have examined whether the MR data scales as a function of (H/T), as it does and is theoretically predicted in Kondo systems consisting of a metallic matrix and magnetic impurities.[2,3] Figure 4(b) shows that this scaling is well obeyed at temperatures ranging from

TABLE I. Characteristics of selected samples. $\Delta\rho = \rho(14\ \text{T}) - \rho(0\ \text{T})$ was obtained at 20 K. An asterisk denotes not measured for this sample.

Sample	ρ_{RT} ($\mu\Omega$ cm)	$\rho_{4.2K}/\rho_{RT}$	T_c (K)	T_M (K)	T_m (K)	$\Delta\rho$ ($\mu\Omega$ cm)
65	65.3	0.91	2.32			−0.018
130	130	0.978	3.12	9.1	25	−0.04
145	145.7	0.98	3.18	8.9	25.1	−0.08
202	202.3	0.981	3.05	9	28	−0.12
237	237.3	0.992	3.11	8.9	44	*
310	309.5	0.998	3.16	8.3	58	−0.2
323	323.1	1.004	3.15	8.2		−0.25
408	408.5	1.01	3.1	7.5		−0.25
529	529	1.013	3.06	9.2		−0.63
2425	2425	1.21	2.76	5		−2.71
3470	3470	1.3	2.2	5.5		−12.46

about 15 K (outside the range of superconducting fluctuations) up to a temperature of about 90 K, somewhat below that where the negative MR cannot be detected anymore. The dependence on (H/T) is nearly parabolic with a power-law best fit of 1.9. The MR of lower resistivity films also scales as a function of (H/T) but the range of fields where it does so with an exponent close to 2 is limited.

We have also checked the anisotropy of the MR, between magnetic field orientations parallel and perpendicular to the sample surface, while maintaining it perpendicular to the current in the sample. Both field configurations showed a negative MR being larger by about 30% to 40% in the parallel configuration. This anisotropy was found to be almost temperature independent.

We show in Fig. 5(a) how the MR amplitude varies as a function of temperature for a set field of 14 T, for a series of samples having different resistivities. The MR amplitude is seen to rise considerably with resistivity. But, as shown in Fig. 5(b), all the data scale in the same way with temperature.

A resistance minimum and logarithmic rise at low temperatures, and a negative MR, might also be due to weak electron localization.[5] However the observed T^{-2} dependence of the negative MR rules out this interpretation. In weak localization (WL) theory the temperature dependence of the MR is given by that of the inelastic scattering time τ_{in}. It is proportional to $\tau_{in}^{3/2}$ in three dimensions,[7] with $\tau_{in} \propto T^{-p}$ where the value of p depends on the scattering mechanism. For our range of temperatures, $T \geqslant 14$ K, electron-phonon scattering is the dominant mechanism[8] and $p = 3$. This gives a temperature dependence of $T^{-9/2}$, which is inconsistent with our experimental result.

Another important aspect of WL is the anisotropy of the MR. In three-dimensional WL there should be no anisotropy. However, if one considers two-dimensional WL,[5] an anisotropy should be observed. It depends on the relative strength of the spin-orbit and inelastic scattering times.[9] But there is no case where a negative MR is predicted for both magnetic field orientations, contrary to our results. Earlier MR measurements on granular Al, mostly performed at lower temperatures, also pointed out difficulties with a WL interpretation.[10] The negative curvature of $R(T)$ at $T > T_m$ is another feature than cannot be explained by WL. Rather it reminds one of a similar effect seen in Kondo lattices[11–13] and in underdoped cuprates.[14]

We thus turn our attention back to spin-flip scattering as a more likely origin of the observed negative MR and Kondo-like behavior. It requires the interaction of conduction electrons with localized moments, as happens when certain impurities are in solution in a metallic matrix, for instance Fe in Cu. However, due to the high electronic density of states in Al, even Fe does not bare a magnetic moment in an Al matrix. We thus rule out the presence of magnetic impurity in Al as the origin of the magnetic moments interacting with conduction electrons.

We see two other possible origins for magnetic moments interacting with conduction electrons in granular Al. Maybe the most obvious one is the presence of free spins at the Al/Al oxide interface, invoked by Sendelbach *et al.*[15] to explain the observed $1/f$ flux noise in superconducting quantum

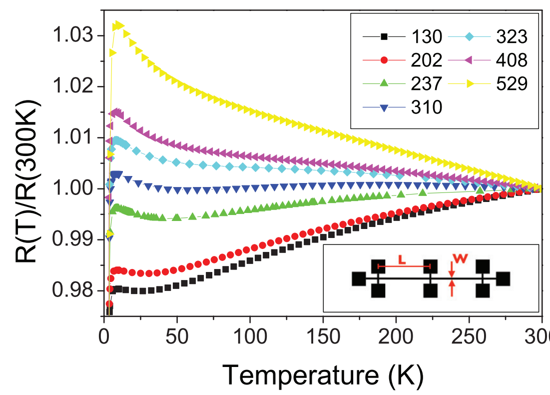

FIG. 1. (Color online) Temperature dependence of the normalized resistivity of selected samples near the MIT. A negative curvature and resistivity minimum are observed in films with $\rho \lesssim 300\ \mu\Omega$ cm. The inset shows a typical hall bar geometry of our samples with a distance between voltage pads of $L = 400\ \mu$m and a bar width of $W = 10\ \mu$m.

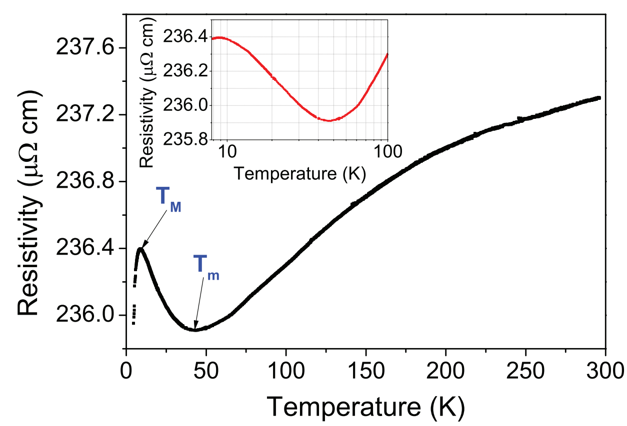

FIG. 2. (Color online) Resistivity as a function of temperature of a metal-like sample (no. 237) close to the MIT which shows a negative curvature at high temperature, a resistivity minimum, and a $\log(T)$ dependence at low temperature.

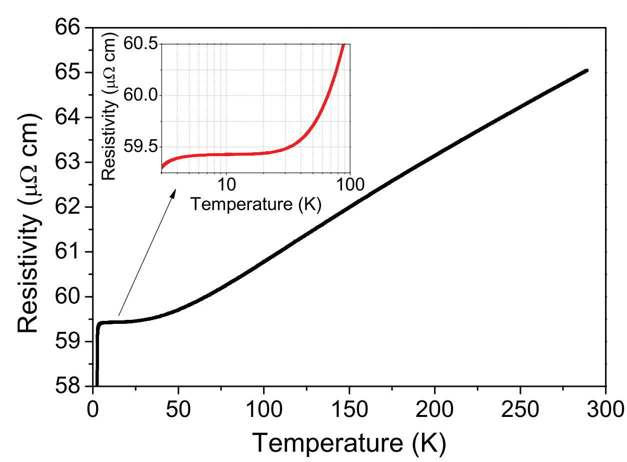

FIG. 3. (Color online) Resistivity as a function of temperature of a low resistivity sample (no. 65) far from the MIT. Inset shows the resistivity as a function of $\log(T)$. There is no upturn in the resistivity below 20 K.

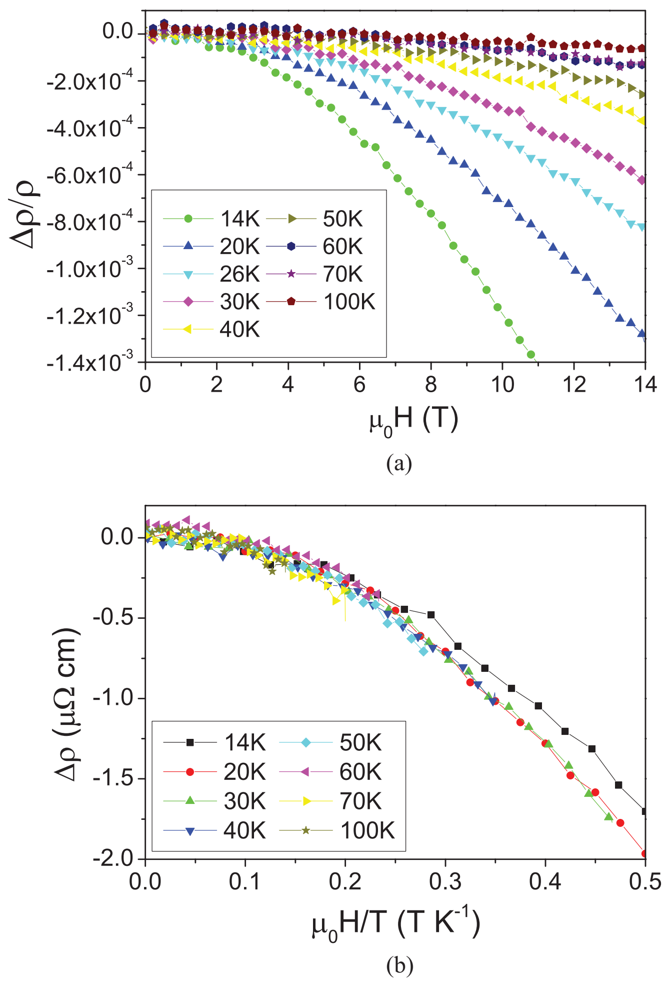

FIG. 4. (Color online) (a) MR of a high resistivity sample (no. 2425), showing a (nearly) quadratic dependence. (b) The MR scales with H/T as expected for a spin-flip scattering mechanism.[3]

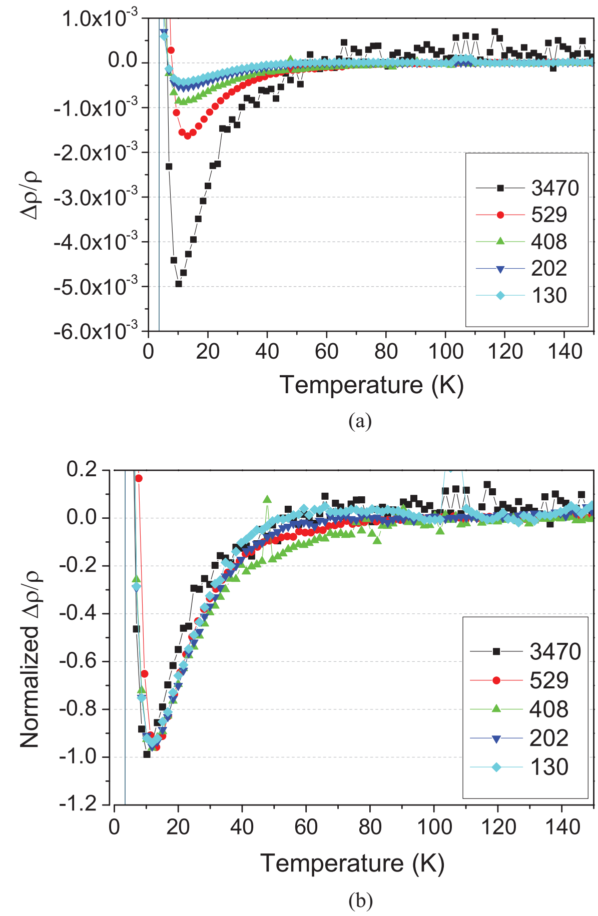

FIG. 5. (Color online) $\Delta\rho/\rho$ as a function of temperature for selected samples at a set field of 14 T. Panel (a) shows the negative MR enhancement with room temperature resistivity. Panel (b) shows that the temperature dependence is similar in all of our samples after scaling the raw data to the same maximum amplitude.

interference devices (SQUIDs). Interaction of these spins with conduction electrons has been postulated to explain the experimental results.[16] A spin density σ_s of 5×10^{17} m^{-2} has been calculated by Sendelbach *et al.*,[15] while Faoro and Ioffe[16] suggest a value of 1×10^{16} m^{-2}. The model of Faoro and Ioffe[16] assumes that Al conduction electrons interact with interface magnetic moments. Therefore, a negative MR in a medium consisting of small Al grains and oxide interfaces is in agreement with their model.

Another possible origin of localized magnetic moments would be the spins of unpaired electrons in small grains, on the condition that these grains have an electronic shell structure (otherwise the electronic wave functions of the single electrons are too similar to those of conduction electrons to produce a localized magnetic moment).[17]

The negative MR for the case of dilute magnetic impurities in the small field limit ($\alpha = \frac{g\mu_B H}{k_B T} \ll 1$) is given by

$$\Delta\rho = -\frac{3\pi}{2\epsilon_F}\frac{m}{e^2\hbar}c\upsilon_0 J^2\alpha^2 u, \qquad (1)$$

where ϵ_F is the Fermi energy, c the magnetic impurities concentration, υ_0 the atomic volume and J the interaction parameter. u is given as a function of the spin S of the magnetic impurity, the Coulomb interaction V, J and ϵ_F [Eq. (26) of Ref. 3]. As remarked by Béal-Monod and Weiner[3] the negative MR is driven primarily by the progressive freezing out of spin-flip scattering when α is increased. Although our granular films are quite different from a pure metallic matrix, we assume that this argument also applies to them. We retain the general idea that in the small field/high temperature limit the MR of a given sample should vary as α^2. This immediately explains our central observation that the negative MR scales nearly as T^{-2}.

We have used Eq. (1), in the form of $\Delta\rho = A\alpha^n$, in order to fit our MR data in the regime of $\alpha \lesssim 0.25 \ll 1$. Here A includes all the other parameters given in Eq. (1). In our case, the exponent of α varies from 1.75 ± 0.07 in the low resistivity regime to 1.9 ± 0.02 in the high resistivity regime for the given range of α. We have compared our results of sample no. 145 with the CuMn experimental MR data,[2] in order to estimate the magnetic impurity concentration, c. For the CuMn MR data $A \approx 4 \times 10^{-3}$ $\mu\Omega$cm while for sample no. 145 we get $A \approx 178 \times 10^{-3}$ $\mu\Omega$ cm. This result suggests that the concentration c in our sample is about 3400 ppm. Although ϵ_F and υ_0 of Al are different than those of Cu, and J and u are unknown for Al, we assume that they do not change this result by orders of magnitude. This concentration corresponds to about 1 spin per 2-nm grain. According to the surface spin densities given by Sendelbach *et al.*[15] and Faoro and Ioffe[16] we would get between 0.1 and 6 spins per 2-nm grain, respectively.

As seen from Fig. 5(a), the amplitude of the negative MR increases rapidly as the MIT is approached. We can qualitatively understand it if the MIT is of the Mott type. This is because, as a Mott transition is approached, the Fermi energy and the electron mass are not anymore those of the parent metal. Instead, the electronic structure is expected to be characterized by a narrow peak near the Fermi level, or in other terms by a decreasing Fermi energy and an increasing effective electron mass. Both would contribute to an increase of the MR amplitude.

In summary, the combined observations of a resistance minimum, a logarithmic resistance increase at low temperatures, a negative curvature of $\rho(T)$ at high temperatures, and the scaling of the negative MR with (H/T) strongly suggest the presence of spin-flip scattering in granular Al films in the vicinity of the MIT.

The presence of free spins can be attributed to surface effects at metal/oxide interfaces or to a volume effect. The concentration of magnetic moments estimated from the measured MR of films not too close to the MIT is of the order of one spin per grain. It is also compatible with values of the density of free spins at metal/oxide interfaces obtained from the $1/f$ flux noise seen in SQUIDs.[15] Regardless of the origin of these localized magnetic moments, their measurable interaction with conduction electrons is a unique feature of nanoscale granular Al. In large Al grains of the order of 10 nm (Ref. 18) these moments are negligible and contribute no paramagnetic signal in the magnetic susceptibility.

The interaction of conduction electrons with local magnetic moments should result in a decrease of the critical temperature, contrary to the increase seen in granular Al films.[1,4,19] Our new findings showing the coexistence of magnetic properties in the normal state along with enhanced superconducting properties thus raise the question of the mechanism for superconductivity in these films.

Further theoretical and experimental work is necessary to establish the exact origin of the spins interacting with conduction electrons in granular films, namely, whether they originate from electronic level splitting due to the small grain size or from the metal/oxide interfaces. In this respect a comparison between the behavior of granular films and that of nongranular thin films will be useful.

In conclusion, we have demonstrated the coexistence of spins interacting with conduction electrons and an enhanced T_c. This coexistence strongly suggests an unconventional mechanism for superconductivity in granular films.

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