Tunneling of Spin-Polarized Electrons and Magnetoresistance in Granular Ni Films*

J. S. Helman
Centro de Investigacion del Instituto Politécnico Nacional, México 14, Distrito Federal, México

and

B. Abeles†
RCA Laboratories, Princeton, New Jersey 08540
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Films consisting of fine Ni grains (~ 50 Å) dispersed in SiO_2 exhibit a large negative magnetoresistance. The effect is accounted for by the field dependence of the magnetic exchange energy, associated with tunneling of electrons between neighboring grains whose magnetic moments are not parallel.

Recent developments in the theory of the tunneling conductivity[1] of granular metal films[2] and in the physics of the tunneling of spin-polarized electrons from spin-oriented materials[3,4] find an interesting application in the explanation of the magnetoresistance of granular magnetic metal films[5] (GMMF). These films consist of fine nickel grains dispersed in amorphous SiO_2 and the conductivity is due to tunneling of electrons between the grains.

The fundamental quantity which determines the temperature dependence of the tunneling conductivity in granular metals is the electrostatic charging energy E_c^0 required to generate a pair of positively and negatively charged grains.[1] In this Letter, we generalize the conductivity theory to granular metals in which the metal grains are ferromagnetic. It is shown that in this case a small additional energy E_M (in addition to E_c^0) is required to generate a pair of charged grains. The energy E_M can be thought of as a magnetic exchange energy which arises when the magnetic moments of the grains are not parallel and electron spin is conserved in tunneling.[3] It is shown that the large negative magnetoresistance that has been observed in GMMF can be accounted for by the magnetic-field dependence of this exchange energy. The theory permits one to extract, from the temperature dependence of the observed magnetoresistance, details of the magnetic structure of the granular metal and to derive a value for the product PJ, where P is the polarization of the tunneling electrons, and J their exchange coupling constant within the ferromagnetic metal grains.

For the purpose of calculating the magnetoresistance, we shall use the conductivity model of Sheng and co-workers.[1] The granular metal is represented by a conductance network in which the metal grains are interconnected by conductances, σ_s, of the form

$$\sigma_s \propto \exp(-2\chi s - E_c^0/2kT), \tag{1}$$

where s is the tunnel-barrier thickness, $\chi = (2m\varphi/\hbar^2)^{1/2}$, m is the effective electron mass, φ is the barrier height, $\hbar$ is Planck's constant divided by 2π, T is the absolute temperature, and k is Boltzmann's constant. The following simplifying assumptions are made[1]: (I) The grains are assumed to be spherical in shape with a distribution in diameter d and charging energy E_c^0 ($\sim 1/d$) such that the product sE_c^0 is constant for a film of a given composition. We write

$$sE_c^0\chi = C, \tag{2}$$

where C and χ are constants that depend only on the volume fraction of the metal. (II) Only tunneling between nearest-neighbor grains which are equal or nearly equal in size is included. As a consequence of this condition (II) and Eqs. (1) and (2), at each temperature there is a tunnel-barrier thickness s_m

$$s_m = \frac{(C/kT)^{1/2}}{2\chi} \tag{3}$$

for which σ_s has a maximum, σ_m, given by $\sigma_m \propto \exp[-2(C/kT)^{1/2}]$. (III) It is assumed that the temperature dependence of the network conductivity $\sigma(T)$ is given by that of σ_m, i.e.,

$$\sigma(T) \propto \exp[-2(C/kT)^{1/2}]. \tag{4}$$

From Eqs. (2) and (3) it follows that the dominant contribution to the conductivity at high temperatures is due to tunneling between small grains (large E_c^0) separated by thin tunnel barriers (small s), while at low temperatures the dominant contribution is due to large grains (small E_c^0) separated by thick tunnel barriers (large s). It should be noted that the above model represents

a gross simplification of the actual conductivity network. In particular, the model does not take into account tunneling between grains of unequal size, and the contribution to the conductivity due to conductances other than σ_m.[5a] Notwithstanding these objections, the model does predict remarkably well the observed temperature dependence of the conductivity of granular metals, and hence is expected to contain the essential physics of the problem.

When the metal grains are magnetic, Eq. (1) becomes

$$\sigma_s(H,T) \propto \exp(-2\chi s)\{\tfrac{1}{2}(1+P)\exp[-(E_c^0+E_M)/2kT]+\tfrac{1}{2}(1-P)\exp[-(E_c^0-E_M)/2kT]\}, \quad (5)$$

or

$$\sigma_s(H,T) = \sigma_s(0,T)[\cosh(E_M/2kT) - P\sinh(E_M/2kT)]. \quad (6)$$

The coefficients $\frac{1}{2}(1+P)$ and $\frac{1}{2}(1-P)$ in Eq. (5) are the probabilities that an electron tunneling from grain 1 to grain 2 has its spin parallel and antiparallel, respectively, to that of grain 1; E_M is the difference between the exchange energies of an electron situated in grains 2 and 1; and H is the external magnetic field. Equation (5) expresses the fact that if the moments of grain 2 and grain 1 are not parallel, an additional energy E_M is required to transfer an electron if its spin is parallel to that of grain 1, while less energy (by an amount $-E_M$) is required if its spin is antiparallel to that of grain 1.

Using assumption (III) and Eq. (6), the conductivity, $\sigma(H,T)$, is given by

$$\sigma(H,T) = \sigma(0,T)[\cosh(E_m/2kT) - P\sinh(E_M/2kT)]. \quad (7)$$

The magnetoresistance is defined by $\Delta\rho/\rho = -[\sigma(H,T)-\sigma(0,T)]/\sigma(H,T)$. By keeping only linear terms in the magnetic energy, the magnetoresistance is given by

$$\Delta\rho/\rho = [E_M(H) - E_M(0)]P/2kT. \quad (8)$$

The magnetic exchange energy E_M can be expressed in terms of the spin correlation function of two neighboring grains

$$E_M = \tfrac{1}{2}J[1 - \langle\vec{S}_1\cdot\vec{S}_2\rangle/S^2], \quad (9)$$

where spins $\vec{S}_1$ and $\vec{S}_2$ have the same magnitude, equal to S.

Because the energy $E_M(H)$ depends on the magnetic state of the grains, it is necessary to discuss in some detail the magnetic structure of GMMF. These materials, in general, possess two magnetic transitions: (1) A paramagnetic-superparamagnetic transition[2,5,6] at T_c, where magnetic ordering takes place in each grain, but there need be no magnetic ordering between the grains; and (2) a superparamagnetic-ferromagnetic transition[2,5] at $T_M \leq T_c$, where intergrain magnetic ordering takes place. From the fact that the observed intergrain magnetic ordering temperatures T_M in the films of Gittleman, Goldstein, and Bozowski[5] are large ($T_M > 100$ K), we conclude that an exchange interaction is responsible for the ordering of the grains. This interaction results from the overlapping of the wave functions of the magnetic electrons in neighboring grains. Since the grains are separated by an insulating barrier, we expect the exchange energy to decrease exponentially with intergrain separation. When there is a distribution in barrier thickness we expect the films to consist, in general, of a mixture of a superparamagnetic phase (corresponding to widely separated grains) and a ferromagnetic phase (corresponding to grains close to one another). Because the conductivity probes grains of different size (and hence of different magnetic state) as the temperature is changed, we expect this to be reflected in the character of the temperature dependence of the magnetoresistance.

We use molecular-field theory in Eq. (8) to approximate the spin correlation function. In the case where the grains are coupled ferromagnetically, we have

$$\langle\vec{S}_1\cdot\vec{S}_2\rangle/S^2 = m^2(H,T) = \mathrm{L}^2(\alpha), \quad (10)$$

$$\mathrm{L}(\alpha) = \coth\alpha - 1/\alpha, \quad (11)$$

$$\alpha = \mu H/kT + 3(T_M/T)\mathrm{L}(\alpha), \quad (12)$$

$$\mu = n\Omega\mu_0, \quad (13)$$

where $\mathrm{L}(\alpha)$ is the Langevin function, α is the root of Eq. (12), μ is the magnetic moment of the grain, n is the density of magnetic atoms, μ_0 is the magnetic moment per atom, and Ω is the volume of the grain. When the grains are superparamagnetic we have,

$$\langle\vec{S}_1\cdot\vec{S}_2\rangle/S^2 = \mathrm{L}^2(\mu H/kT). \quad (14)$$

Substituting results from Eqs. (10) or (14) into Eq. (9), we obtain from Eq. (8), for the ferromag-

netically coupled grains,[7]

$$\Delta\rho/\rho = -(JP/4kT)[m^2(H,T) - m^2(0,T)], \quad (15)$$

and for the superparamagnetic grains,

$$\Delta\rho/\rho = -(JP/4kT)L^2(\mu H/kT). \quad (16)$$

We have assumed that T is sufficiently high so that the superparamagnetic grains do not become blocked. This assumption is valid when $T > 70$ K.[8]

Gittleman, Goldstein, and Bozowski[5] measured the magnetoresistance of granular Ni-SiO_2 films which consisted of crystalline Ni grains, with an average diameter of 50 Å, dispersed in amorphous SiO_2. The transverse magnetoresistance of the film containing 48-vol% Ni, measured at 270 and 4000 G, is given in Fig. 1. The characteristic features of the low-field magnetoresistance [Fig. 1(a)] are a pronounced peak and a steep rise at low temperatures. The magnetoresistance peak shifts to lower temperatures as the Ni volume fraction decreases.[5] The structure in $-\Delta\rho/\rho$ becomes washed out at high fields [Fig. 1(b)].

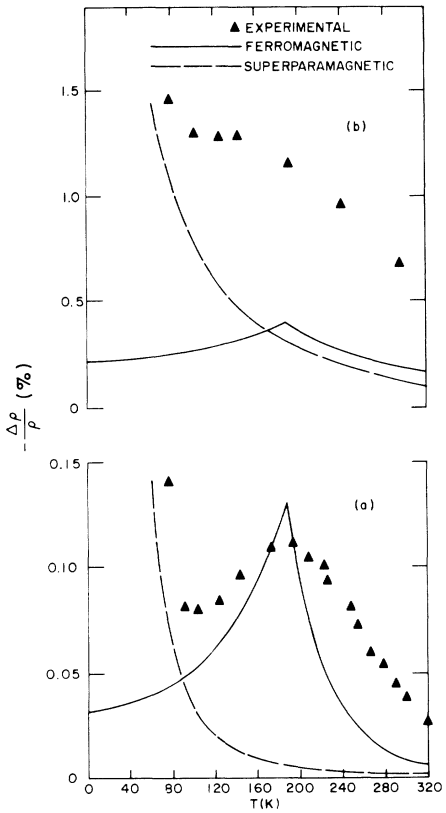

FIG. 1. Transverse magnetoresistance versus temperature of a granular Ni-SiO_2 film containing 48-vol% Ni; applied magnetic fields (a) 270 G and (b) 4000 G Theoretical curves were calculated from Eqs. (15) and (16).

The fact that there are two distinct contributions to the magnetoresistance with characteristically different temperature dependences—a contribution due to tunneling between ferromagnetically coupled grains at high temperatures, and a contribution due to the superparamagnetic grains at lower temperatures—is shown in Fig. 1 by the curves computed from Eqs. (15) and (16), respectively. The curves were calculated by fitting Eq. (15) to the high-temperature data and Eq. (16) to the low-temperature data with JP as an adjustable parameter. The other parameters were determined as follows: $\mu_0 = 0.6\mu_B$ per atom of Ni, where μ_B is the Bohr magneton; Eq. (13) yields $\mu = 2.83\times10^{-17}$ erg/G, by assuming Ni spheres to have a diameter of 48 Å[2] and that $n = 8.8\times10^{22}$ atoms/cm^3[9]; and $T_M = 188$ K was determined from magnetization measurments.[5] The best fit to the experimental data was obtained for $JP = 0.35$ meV. Comparably good agreement between theory and experiment was obtained for films of other compositions using the same value of the parameter JP and the corresponding ordering temperatures T_M.

Within the framework of the present theory, it is not possible to predict the temperature dependence of the magnetoresistance in the transition region from conduction due to ferromagnetically coupled grains, to conduction due to superparamagnetic grains. The temperature where this transition takes place is given roughly by the minimum in the negative low-field magnetoresistance. In Fig. 1, this minimum occurs at 100 K. From Eq. (3) this corresponds to a value of $\chi s_m = 0.7$,[10] where for C we have used the value 0.015 eV determined from the temperature dependence of the zero-field conductivity.

The fact that the transition from conduction due to the ferromagnetically coupled grains to that due to the superparamagnetic grains takes place near $\chi s_m = 0.7$ is entirely reasonable, since the strength of the intergrain magnetic interaction is proportional to $\exp(-2\chi s)$, the value of the overlap of the electron wave functions of neighboring grains. Furthermore, it is found that with increasing volume fraction of nickel, the ordering temperature T_M increases while the parameter χs_m decreases; this is consistent with the fact that smaller χs_m is associated with larger intergrain interaction energy and hence greater T_M. It should be pointed out, however, that this argument is only qualitative since for the d electrons, which are the ones responsible for the magnetic

interactions, the effective value of χs_m is likely to be different from that derived from the electrical conductivity.

From the value obtained for the parameter JP (=0.35 meV), it is possible to infer the relative contributions of the s and d electrons to the magnetoresistance effect. The s-d exchange interaction J_{s-d} has been estimated to be $\lesssim 0.02$ eV[11]; and the polarization of the s electrons, P_s, has been estimated to be less than 1%.[4] Thus, $J_{s-d}P_s \lesssim 0.2$ meV, which is smaller than the observed value of JP, indicating that either P_s is larger than 1% or that the d electrons also contribute to the tunneling conductivity. The latter conclusion is supported by the fact that the ratio of the tunneling probability of d and s electrons in Ni is thought to be in the range 10^{-1} to 10^{-2}.[12]

In conclusion, we note that our model reproduces, with a single adjustable parameter, the main features and the magnitude of the magnetoresistance over a wide range of magnetic fields (270 to 4000 G) involving variations of two orders of magnitude in $-\Delta\rho/\rho$. The fit achieved is remarkably good, considering the rough approximations in the conductivity model and the use of molecular-field theory to approximate the correlation function, which exaggerates the sharpness of the peak of $-\Delta\rho/\rho$ at T_M.

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