Spin-Dependent Electronic Transport in Granular Ferromagnets

A. Milner, A. Gerber, B. Groisman, M. Karpovsky, and A. Gladkikh

School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, 69978 Tel Aviv, Israel

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We report a comparative study of the spin-dependent electronic transport in two types of granular ferromagnetic systems: ferromagnet metal (Ni-Ag, Co-Ag) and ferromagnet insulator (Ni-SiO_2, Co-SiO_2). Both systems demonstrate remarkably similar magnetoresistive behavior of comparable magnitude: negative isotropic magnetoresistance below the ferromagnet percolation threshold and the anisotropic magnetoresistance above.

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Extensive studies of spin-dependent transport properties of heterogeneous magnetic solids were triggered a few years ago by a discovery of the so-called giant magnetoresistance (GMR) effect. It was found that the resistance can exhibit large changes of the same order of magnitude as the resistance itself upon the application of an external magnetic field. The effect was first discovered in magnetic multilayers like Fe-Cr or Co-Cu [1–4] and later in heterogeneous magnetic alloys with ferromagnetic grains embedded in nonmagnetic metallic matrix [5,6]. Although the exact mechanism of GMR remains elusive, it is believed to be a manifestation of the conduction electrons spin-dependent scattering dependence on the local magnetic configuration [7–9]. In the case of granular ferromagnets with antiferromagnetic or random distribution of magnetic moments at zero field, the applied field aligns the magnetic moments and, therefore, affects the spin-dependent scattering.

As a next step in the research of the spin-dependent transport phenomena in heterogeneous magnets it seems attractive to expand the studies to granular magnetic systems where small ferromagnetic grains are embedded in an immiscible *insulating* matrix. Macroscopic properties of metal-insulator mixtures depend on the metallic volume fraction x which can be controllably varied. At low x values metallic grains are isolated from each other and an electric transport is realized by intergranular tunneling or temperature activated hopping. When metal concentration is increased above a certain threshold, individual grains form an infinite cluster [10] with a continuous metallic conductance path.

Magnetic properties of granular ferromagnets are thoroughly studied [11,12] and known to depend on the magnetic material concentration, mean grain size, and intergranular distance. The isolated nanometer size ferromagnetic grains are single domains. At low concentrations the system behaves as the superparamagnet. At larger x and shorter intergranular distances the magnetic phase percolates throughout the material and a system like Ni-SiO_2 starts exhibiting superferromagnetism [13].

Spin-dependent tunneling between two ferromagnets has been predicted and observed [14] in single junctions with two ferromagnetic electrodes. Assuming that spin is conserved in the tunneling process one can expect [15–17] the tunneling conductance dependence on the conduction band spin polarization of the electrodes and, therefore, on their relative magnetization. Antiparallel relative magnetization corresponding to a minimum conductance of a junction can be aligned parallel by an applied magnetic field giving rise to a significant increase in the tunnel conductance. Indeed, large room temperature magnetoresistance up to the order of 10% has been recently reported [18,19] in ferromagnetic thin film tunnel junctions. Spin-dependent magnetoresistance was also observed by Gittleman, Goldstein, and Bozowski [13] more than 20 years ago in discontinuous nickel films and discussed by Helman and Abeles [20]. However, since these early works no systematic study of the spin-dependent transport in disordered ferromagnet-insulator systems has been performed.

In this Letter we report the results of a first comparative study of the magnetotransport phenomena in two types of granular ferromagnetic systems: ferromagnet metal and ferromagnet insulator. Both systems demonstrate a remarkably similar isotropic negative magnetoresistance below the ferromagnet percolation threshold and the anisotropic magnetoresistance above. In contrast to metallic ferromagnet-metal mixtures, where the magnetoresistance is attributed to the spin-dependent scattering on the boundaries of nonaligned magnetic grains, similar effect in discontinuous metal-insulator films is a manifestation of a spin-dependent tunneling process.

Granular films of Ni-SiO_2 and Co-SiO_2 were studied in comparison with similarly prepared films of Ni-Ag and Co-Ag. Thin films of both types have been prepared by coevaporation of starting materials on a room temperature glass substrate. The deposition rate and the relative volume concentration of two components were monitored and controlled by two quartz thickness monitors. Usually, a set of up to 24 samples has been deposited simultaneously with the relative concentration of the components varying smoothly due to a shift in geometrical location relative to the materials' evaporation sources. Samples with Ni (Co) volume concentration from 30% up to 100% were prepared. The absolute concentration accuracy de-

fined by the deposition rate control is about $\pm 5\%$. The relative concentration accuracy of the samples of the same deposition series, as defined by their geometrical location, is better than $\pm 0.3\%$. The films had a strip form with linear dimensions about 8×2 mm and 100 nm thickness. The samples were studied by transmission electron microscopy (TEM). Ni, Co, and Ag in Ni-Ag and Co-Ag films were found to be crystalline with a typical grain size of the order of 30–40 Å. SiO_2 matrix in Ni(Co)-SiO_2 was found to be amorphous.

Magnetoresistance was measured at room temperature in fields up to 10 kOe at different orientations of an applied field in respect to the samples' plane and the current flow direction. The results for four selected Ni-based samples are shown in Fig. 1. Two essentially distinct phenomena can be pointed out. Negative isotropic magnetoresistance only is pronounced in both Ni-Ag and Ni-SiO_2 samples at nickel concentrations below (45–48)% [Figs. 1(a) and 1(b)]. In contrast, magnetoresistance of nickel-rich samples depends strongly on the relative field orientation [Figs. 1(c) and 1(d)]. The positive magnetoresistance stroke developed at low fields (below few kOe) is largest when the field is applied parallel to the current flow and changes to negative when the field is perpendicular to the film plane. Both Ni-SiO_2 and Ni-Ag systems demonstrate almost identical sensitivity for the applied field orientation. Similar behavior was found in Co-based series as well.

Ferromagnet-*metal* granular alloys were extensively studied [21,22]. The positive longitudinal magnetoresistance and negative transverse magnetoresistance as observed in ferromagnet-rich Ni-Ag and Co-Ag films is attributed to the anisotropic magnetoresistance phenomena (AMR) [22]. The negative isotropic magnetoresistance is identified as the GMR, although the value of the effect in certain compounds is not "giant" as in the case of Ni-Ag. Qualitatively, magnetoresistance of ferromagnets-metal [Ni(Co)-Ag] and ferromagnets-insulator [Ni(Co)-SiO_2] systems is very similar. The same two phenomena AMR and GMR can, therefore, be identified in ferromagnet-insulator Ni-SiO_2 and Co-SiO_2 granular system.

Similarity of both systems in the Ni-rich samples is not surprising. Resistivity of Ni_x-Ag_{100-x} and Ni_x-$(SiO_2)_{100-x}$ with $x = 88\%$ is about 2×10^{-5} and 5×10^{-5} Ω cm, respectively. Field dependent electrical conductivity is determined here by a massive bulk of metallic ferromagnet and an influence of small inclusions of either metal (Ag) or insulator (SiO_2) is limited. The difference in resistivity of the two systems increases gradually at lower Ni concentrations reaching a ratio of $1{:}10^5$ for the concentration of 45%. (The resistivity of two samples presented in Figs. 1(a) and 1(b) with nickel concentration about 45% are 3×10^{-5} Ω cm in Ni-Ag and 2 Ω cm in Ni-SiO_2.) Changes of resistivity caused by the AMR effect in the bulk of Ni are clearly observed in low resistance Ni-Ag in a complete range from 45% to 100%, but are negligible and, therefore, obscure in Ni-SiO_2 with Ni concentration below 80% and the resistivity exceeding 100 $\mu\Omega$ cm.

On the other hand, the similarity between two systems in a low concentration regime is remarkable. As shown in Figs. 2 and 3 the value of GMR defined as $(\rho_0 - \rho)/\rho_0$, where ρ_0 and ρ are resistivities measured at 0 and 10 kOe field, respectively, reaches its maximum of about 0.6%

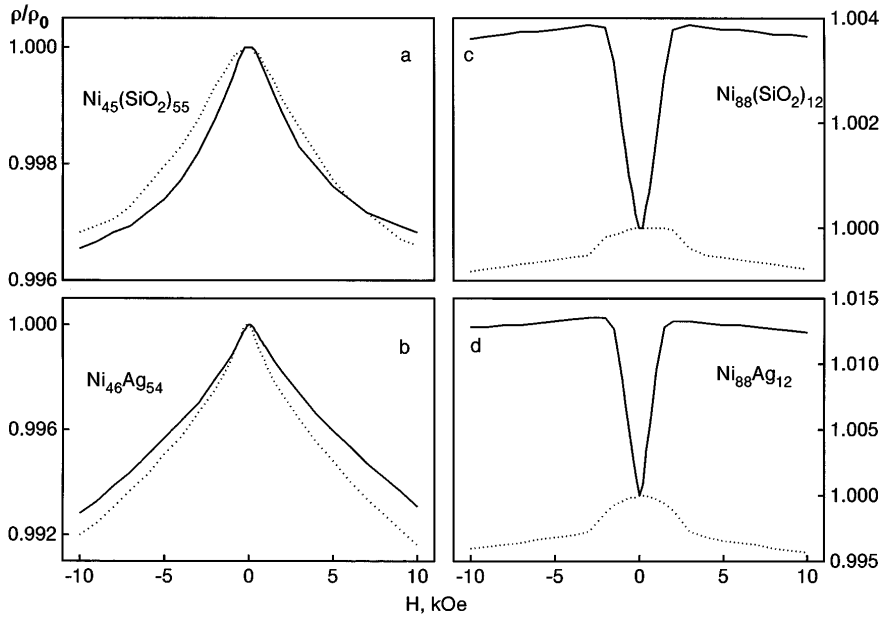

FIG. 1. Room temperature magnetoresistance of two $Ni_x(SiO_2)_{100-x}$ (a),(c) and two Ni_xAg_{100-x} (b),(d) films at different orientations of the applied magnetic field: solid curves: field parallel to the sample plane along the measuring current; dotted curves: field is normal to the sample plane (a) $Ni_x(SiO_2)_{100-x}$, $x = 44.7\%$, $\rho = 2$ Ω cm; (b) Ni_xAg_{100-x}, $x = 46.4\%$, $\rho = 3 \times 10^{-5}$ Ω cm; (c) $Ni_x(SiO_2)_{100-x}$, $x = 88\%$, $\rho = 5 \times 10^{-5}$ Ω cm; (d) Ni_xAg_{100-x}, $x = 88\%$, $\rho = 2 \times 10^{-5}$ Ω cm.

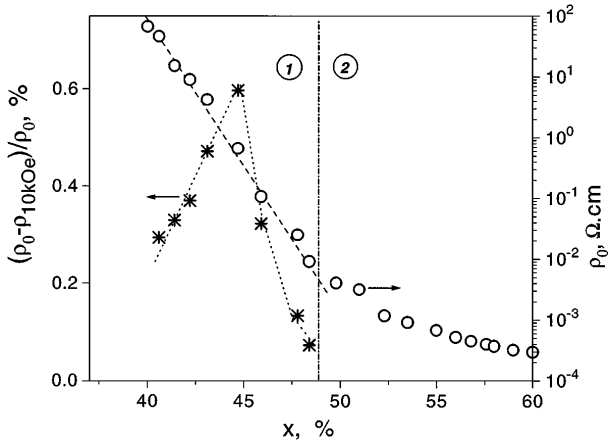

FIG. 2. Normalized GMR magnetoresistance (∗) and the room temperature zero field resistivity (∘) of $Ni_x(SiO_2)_{100-x}$ samples as a function of Ni volume concentration x. The dotted curve is a guide to the eye. The dashed line is the fit curve $\rho = 65\exp[-(x - 40)]$. Resistivity-temperature coefficient of $Ni_x(SiO_2)_{100-x}$ samples is negative in region (1) for $x < 49\%$, and positive in region (2) for $x > 49\%$.

in both Ni-SiO_2 and Ni-Ag systems at nickel volume concentration of the order of 45%–47%. It can be shown for both compounds that the maximum is located in the vicinity of the same (±5%) Ni percolation threshold.

In metal-insulator mixtures the metallic percolation threshold can be easily identified by (a) the divergence of the resistivity and (b) the change of the resistivity temperature coefficient from positive in the metallic regime above the threshold to negative in the dielectric regime below it. As demonstrated in Fig. 2, this recipe works well in the Ni-SiO_2 system, where the zero field resistivity starts to diverge exponentially and the resistivity-temperature coefficient changes its polarity in the vicinity of $x = 49\%$. The metallic continuity threshold can be pointed out at this concentration.

In Ni-Ag the resistivity of both components is very close and no singularity is found at the threshold. However,

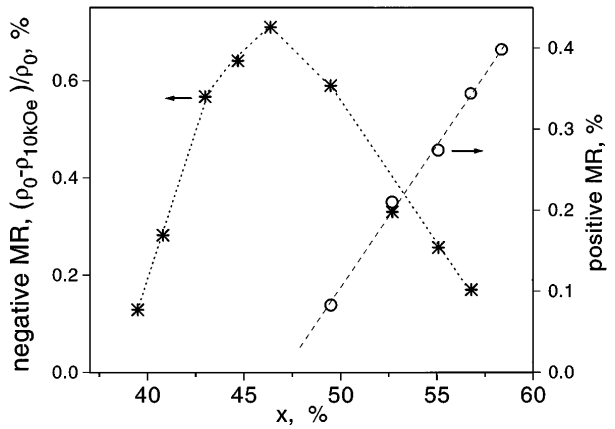

FIG. 3. Normalized GMR (∗) and AMR (∘) magnetoresistance of Ni_xAg_{100-x} films as a function of Ni volume concentration x. The dotted line is a guide to the eye. The dashed line represents a linear fit.

the magnetic properties of granular ferromagnets depend on the magnetic material concentration and, in particular, on the continuity of the magnetic phase. By crossing the ferromagnetic metal continuity threshold a system like Ni-SiO_2 starts exhibiting a bulk ferromagnetism [13] and associated with it an anisotropic magnetoresistance. Development of the latter indicates the ferromagnetic continuity threshold. We plot in Fig. 3 the value of the AMR (defined as a difference between the longitudal and transverse resistivity measured at 10 kOe) in Ni-Ag as a function of nickel concentration. The data extrapolate to $x = 47\%$ in an immediate vicinity of the GMR peak. We can, therefore, conclude that in both Ni-Ag and Ni-SiO_2 systems the GMR is largest slightly below the same (±5%) nickel continuity threshold.

The most intriguing result is the equality of the GMR effect in Ni-Ag and Ni-SiO_2 systems. As shown in Figs. 2–4 the magnitude of the GMR effect is almost identical for both systems. This is extraordinary since the resistivity of Ni-SiO_2 at $x = 45\%$ is 5 orders of magnitude higher than that of Ni-Ag.

Similar results were obtained in cobalt-based (Co-Ag and Co-SiO_2) films. The maximum value of the normalized magnetoresistance was found to be an order of magnitude higher than in Ni-based compounds and reached about 10% in Co-Ag and 4.5% in Co-SiO_2 at a Co concentration $x = 38\%$ (Fig. 4). The difference in magnitude of the effect between Co-SiO_2 and Co-Ag series is negligible comparing to the ratio of their absolute resistivities: 10^6 at $x = 38\%$ and 10^7 at $x = 32\%$.

Due to the basic difficulties in microscopic analysis of crystalline metallic mixtures we do not possess an accurate topological map of metallic Ni-Ag and Co-Ag films. We, nevertheless, can conclude that the ferromagnetic material topology in these samples is similar to that in ferromagnet-

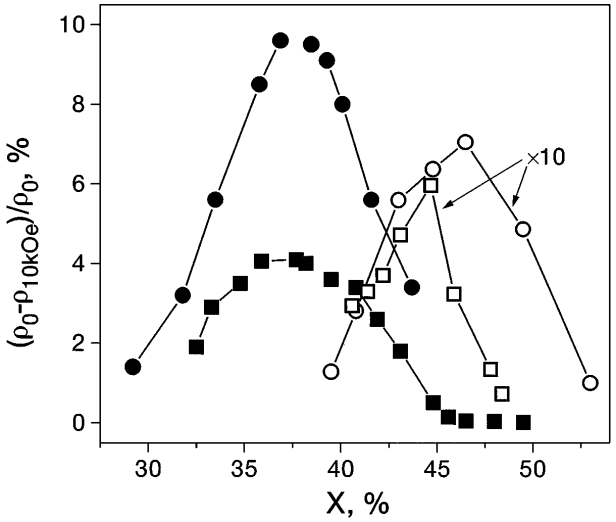

FIG. 4. Normalized GMR magnetoresistance as a function of the ferromagnet material component concentration: full circle: Co-Ag; full square: Co-SiO_2; open circle: Ni-Ag; open square: Ni-SiO_2. The results for Ni-based series are multiplied by 10.

insulator mixtures Ni-SiO_2 and Co-SiO_2, respectively. We are supported in this conclusion by the fact that (1) the grains' dimensions, as found in TEM study, are comparable; and (2) the ferromagnet material percolation threshold is the same in ferromagnets metal and ferromagnets insulator: 48% in Ni-based systems and 44% in Co-based ones. We can, therefore, suggest that the normalized magnetoresistance of the system in which a granular ferromagnetic structure is immersed in a nonmagnetic matrix is nearly independent of the nature of the intergranular matrix.

The mechanisms of electronic transport in metallic and dielectric granular magnets are different and the magnetoresistance effects were so far treated separately. Following the early experiments of Gittleman, Goldstein, and Bozowski [13] on discontinuous Ni films, the magnetoresistance of ferromagnet-insulator mixtures was derived by Helman and Abeles [20] in the framework of the tunneling theory of spin-polarized electrons. Here, the probability of an electron tunneling across an intergranular barrier was calculated by taking into account an additional magnetic exchange energy arising when the magnetic moments of the neighboring grains are not parallel and electron spin is conserved in tunneling. In this model, the conductivity (σ) of the system is proportional to the product of the nonmagnetic and the spin-dependent terms. Magnetoresistance is defined as $\Delta\rho/\rho = -[\sigma(H,t) - \sigma(0,T)]/\sigma(H,T)$, and by keeping only linear terms in the magnetic energy E_m the normalized magnetoresistance can be approximated by

$$\Delta\rho/\rho = [E_m(H) - E_m(0)]P/2kT\,,$$

where P is polarization of the tunneling electrons. The magnetic exchange energy E_m can be expressed in terms of the spin correlation function of two neighboring grains. In the case of the ferromagnetically coupled grains the magnetoresistance is given by

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

where J is the exchange coupling constant and M is magnetization. Within this model the normalized magnetoresistance does not depend on the total resistivity of the sample.

In metallic magnetic systems the GMR is regarded as the *extra* electrical resistance due to scattering from nonaligned ferromagnetic entities. At finite temperatures, the fractional GMR is given [23] by

$$\Delta\rho/\rho = -\rho_m(T)/[\rho_0 + \rho_{\rm ph}(T) + \rho_m(T)]F(M/M_s)\,,$$

where ρ_0 is the temperature independent contribution from defects, $\rho_{\rm ph}(T)$ is the phonon contribution, and ρ_m is the magnetic resistivity responsible for GMR. $F(M/M_s)$ is usually well described by $F = \alpha(M/M_s)^2$. Although both magnetic and nonmagnetic resistivities depend on the density of charge carriers, it is not *a priori* obvious that the ratio $\Delta\rho/\rho$ is independent of the total resistivity value in the range from 10^{-5} to 10^3 Ω cm.

We can briefly summarize the main experimental findings as follows: (1) Granular ferromagnet-insulator mixtures demonstrate isotropic negative magnetoresistance similar to the GMR effect in heterogeneous ferromagnet-normal metal alloys; (2) in both ferromagnet-metal and ferromagnet-insulator mixtures the largest normalized magnetoresistance is found in samples in the vicinity of the ferromagnetic material percolation threshold; (3) despite the difference of many orders of magnitude in the absolute resistivities of ferromagnet-insulator and ferromagnet-metal mixtures, the values of the normalized negative magnetoresistance found in both types of the systems are close to each other. This can indicate that the normalized magnetoresistance of the system in which a granular ferromagnetic structure is immersed in a nonmagnetic matrix is nearly independent of the nature of the intergranular matrix.

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