Extra-Large Magnetoresistance in Fe/In_2O_3 Granular Films*

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Nanogranular $Fe_{0.35}/(In_2O_3)_{0.65}$ films with complex magnetic structure were prepared by the rf sputtering method. An extra-large magnetoresistance up to 506% was obtained at 2.2 K, which is two orders of magnitude larger than that obtained at room temperature. This is related to the interaction with the impurities influencing the local magnetization, which is quite different from the spin-dependent tunnelling effect at room temperature. The interspacing Fe atoms dispersed in the In_2O_3 matrix play an important role in the transportation properties of carriers at low temperature.

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Since the discovery of giant magnetoresistance (GMR) in heterogeneous granular films,[1,2] interest in their transport properties and applications in MR devices has been growing.[3,4] It is still believed that GMR arises from spin-dependent scattering or spin-dependent tunnelling. In this Letter, we present an extra-large MR observed in Fe/In_2O_3 films that could not be explained in the light of the mechanism mentioned above.

Samples were prepared by the rf sputtering system as described previously.[5] The composite target was a sintered In_2O_3 disc on which some small Fe discs were placed uniformly. The substrates were 0.2 mm thick glass slides. A very interesting sample, $Fe_{0.35}/(In_2O_3)_{0.65}$, was obtained by this system, where the subscripts indicate the volume concentrations. We focus our attention on this sample in this Letter. Transmission electron microscopy (TEM) observations confirm the granular structure of this sample.[5] The average diameter of Fe particles dispersed in the In_2O_3 matrix is about 5 nm which was estimated from the TEM pattern. The x-ray diffraction showed that the as-sputtered film was in the amorphous state. The composition of the samples was determined by the energy dispersive x-ray analysis (EDXA), and the volume concentration can be estimated from the composition results. The magnetic properties and MR of the samples were measured by a commercial superconducting quantum interference device (SQUID) magnetometer with the magnetic field up to 2 T in the temperature range from 1.5 K to 300 K. The MR was measured by using the standard four-point technique.

Figure 1 shows the magnetization curves obtained at three different typical temperatures. Curve *a* shown in Fig. 1 was obtained at room temperature. This is a typical curve for the sample in the superparamagnetic state, and it follows the Langevin function well, confirming the superparamagnetic feature of the film.[5] The average diameter of particles calculated from the fitting results can be estimated to be 4.8 nm, which fits well with that observed by TEM. According to the fitting value, the saturation magnetization of Fe particles, $M_{Fe} = 162\ Am^2/kg$, can be obtained, which is much smaller than that of bulk Fe, $221.7\ Am^2/kg$. A similar result was obtained by Wang *et al*[6] in an Fe–Ag granular system, and it was explained that the spin waves in small particles are softened substantially due to the magnetic surface effect and the finite-size effect.[3] At the interfaces of Fe particles, some Fe atoms lose their magnetic moments because their Fe neighbours are too few, i.e. there is a magnetic dead layer on the Fe particle surface.[7]

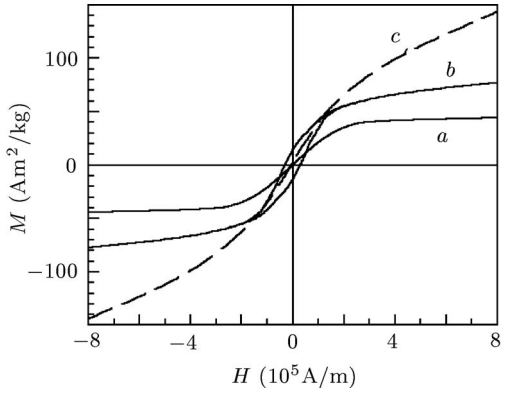


Fig. 1. Magnetization M of $Fe_{0.35}/(In_2O_3)_{0.65}$ versus magnetic field H at (*a*) room temperatures, (*b*) 20 k, and (*c*) 5 K.

Figure 2 shows the temperature dependence of the low-field susceptibility $\chi(T)$ of the $Fe_{0.35}/(In_2O_3)_{0.65}$ film in zero-field-cooled (ZFC) and field-cooled (FC) modes. One can see from Fig. 2 that the block temperature transited from superparamagnetic to ferromagnetic state is about 50 K. The magnetization

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hysteresis loop, as shown by the curve b in Fig. 1, confirms the ferromagnetic state of the sample at 20 K, which is below the blocking temperature. There is a minimum value in the ZFC curve and an upturn knee in the FC curve at 10 K suggesting another magnetic transition. In order to ascertain the property of this magnetic transition, we measured the magnetization curve at 5 K and the result is shown by curve c in Fig. 1. There are two evident characteristics for this curve. Firstly, no hysteresis appears in the magnetization curve. Secondly, the magnetization process is a signature of magnetic moment rotation and it is difficult to reach saturation until $H = 1$ T. This phenomenon can be explained in the following. During the process of preparation, there are inevitably some Fe atoms dispersed into the In_2O_3 matrix as interspacing atoms. The spacings between these isolated Fe atoms are too large to couple with each other by the exchange interaction at higher temperature. When the temperature decreases to a critical value T_f (freezing temperature), the exchange interaction becomes strong enough to couple them into composite clusters. In this case, the Fe particles can be coupled into a local particle group (called the particle-spin-cluster) by means of exchange coupling between the interspacing Fe atoms and the interface Fe atoms in the Fe particles. Because of the random arrangement of Fe atoms and particles in the In_2O_3 matrix, the magnetic moment of each particle-spin-cluster is in disorder. For such a particle-spin-cluster system, the magnetization process has to overcome the anisotropy and rotate the moment of each cluster to the direction of applied magnetic field. The freezing temperature T_f is about 10 K, which is obtained from the minimum value in the ZFC curve of Fig. 2. Below T_f, the magnetization of the film is related to three contributions: the first comes from the core of Fe particles, the second comes from the "revived" Fe atoms at the interfaces of Fe particles, and the third is from the individual Fe atoms dispersed in the In_2O_3 matrix. These contributions induce the magnetization of the film to

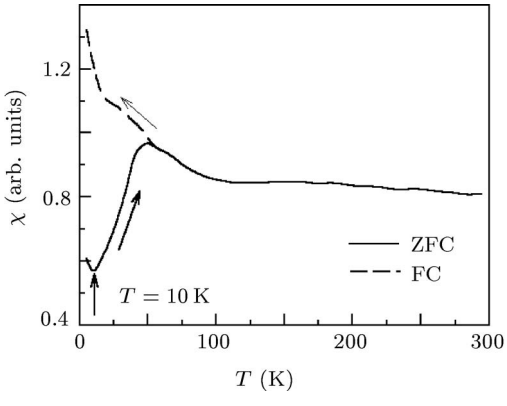


Fig. 2. Magnetic susceptibilities χ as a function of temperature T for $Fe_{0.35}/(In_2O_3)_{0.65}$ in ZFC and FC modes.

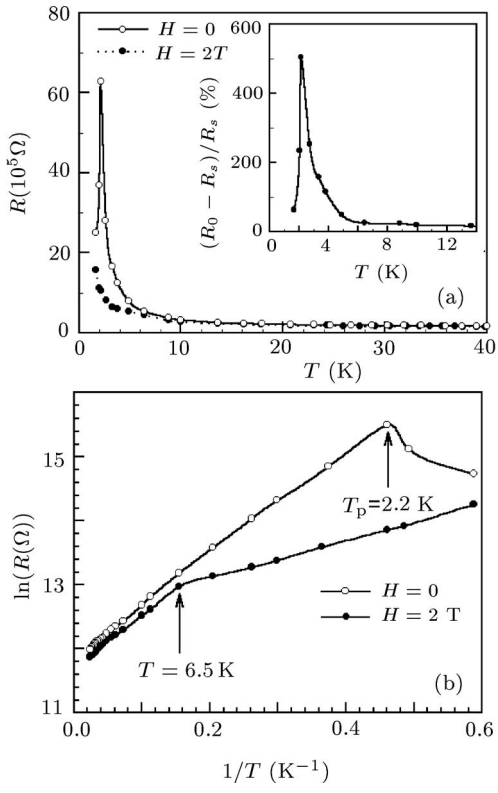


Fig. 3. Resistance R of the film versus temperature T in R–T coordinates (a) and in $\ln(R) - 1/T$ coordinates (b). The inset shows the GMR ratio versus temperature.

increase. Therefore, a rotating magnetization curve with an enhanced magnetization was obtained at 5 K.

The maximum MR ratio of the film at $H = 1$ T is about 5.2% at room temperature and is believed to be a spin-dependent tunnelling GMR. In order to investigate the temperature behaviour of MR, the dependence of resistance R on T were measured at temperatures ranging from 1.5 K to 300 K without and with a field of $H = 2$ T, respectively. Figure 3(a) gives the results in the most interesting temperature region. The inset of Fig. 3(a) shows the GMR ratio of the film versus temperature T, where $\Delta R/R = (R_0 - R_S)/R_S$ with R_0 and R_S being the resistances of film in zero-field and in $H = 2$ T field, respectively. One can see from Fig. 3(a) that a transition temperature, $T_P = 2.2$ K, from metal to semiconductor exists when $H = 0$, but this transition disappears when a magnetic field of 2 T is applied. A maximum GMR ratio up to 506% is obtained at T_P. This behaviour is very similar to the colossal magnetoresistance (CMR) obtained in doped rare-earth manganites. However, in CMR materials the magnetic field usually shifts the transition temperature (around the magnetic transition point T_C) to higher temperature. This phenomenon has never been observed in any other granular systems to date. This GMR cannot be induced by the spin-dependent scattering or spin-dependent tunnelling effect as that occurring at room temperature. We suppose that the resistance peak and significant change of

resistance in the field is related to a certain magnetic mechanism, perhaps related to the transition from ferromagnetic to particle-spin-cluster state. Nagaev indicated that CMR in doped rare-earth manganites is related to the interaction with the impurities influencing the local magnetization.[8] His theoretical analysis showed that the resistance peak is related to a joint action of the magnetization and of the impurity. Our results seem to agree with Nagaev's proposal. The dispersive Fe atoms in the In_2O_3 matrix act as the impurities. Below T_f, the charge carriers entering the clusters will be polarized and become the self-trapping state. The hopping mobility of charge carriers among clusters is lower than that occurring within one cluster because the carriers must change their spin direction when they hop from one cluster into another. A magnetic field aligns the moments of local clusters along the field direction and increases the inter-cluster hopping mobility of carriers. This causes the resistance of the sample to decrease. Therefore, this is another type of GMR observed in granular films.

Figure 3(b) shows R versus T curves on a new coordinate, where the ordinate is $\ln(R)$ and abscissa is T^{-1}. The straight line above T_P shows that the conductive mechanism in semiconductor state in zero field belongs to the thermal active type, i.e. the resistance of the film follows the Arrhenius law, $R = R_0 \exp[E_\sigma/(K_B T)]$, where E is the thermal activation energy and K_B is the Boltzmann constant. When $T > T_P$ and $H = 0$, $E_\sigma = E_\sigma^0 = 0.689\,\mathrm{meV}$. After a magnetic field of 2 T is applied, E_σ decreases to $E_\sigma^{\mathrm{H}} = 0.2485\,\mathrm{meV}$ below 6.5 K, and is almost the same as E_σ^0 above 6.5 K. Below 6.5 K, the magnetic field causes the activation energy to decrease remarkably. One can see from the inset of Fig. 3(a) that 6.5 K is about the point below which the MR ratio increases sharply. This indicates that the GMR mechanism above 6.5 K is as the same as that observed at room temperature, but it changes to the impurity mechanism below 6.5 K. The decrease in the hopping activation energy of carriers in a magnetic field is the reason for GMR at low temperature in this granular film. This coincides with the above analysis.

In summary, at room temperature, the $Fe_{0.35}/(In_2O_3)_{0.65}$ film shows a superparamagnetic behaviour and a 5.2% MR ratio is obtained. Blow a certain freezing temperature T_f of about 10 K, the film transits from ferromagnetic state to the particle-spin-cluster state. In this case, the MR ratio of the film increases dramatically with decreasing temperature. A maximum GMR ratio up to 506% is obtained at a metal–semiconductor transition temperature of about 2.2 K. The mechanism of this GMR is related to the interaction with the impurities influencing the local magnetization which is quite different to the spin-dependent tunnelling effect at room temperature.

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