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LETTER TO THE EDITOR

Study of magnetotransport in polycrystalline perovskite manganites

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Abstract

In this letter, a self-consistent effective-medium approximation is presented for the magnetotransport in the polycrystalline manganites. Both intrinsic properties which are achieved through strong-link grain boundaries and the extrinsic properties which are achieved through weak-link grain boundaries are taken into account. It is noted that the manganites are phase separated into a metallic phase and an insulating phase. The conduction of the system is determined by the metallic channels when the metallic phase has percolated. In the polycrystalline cases, the weak-link grain boundaries, spread along the percolating paths, are expected to inhibit the formation of metallic channels on the one hand, and to favour the low-field magnetoresistance on the other hand. The relationship between phase separation and percolation is investigated for various grain boundary conditions. Our calculations agree with experiments well.

Doped manganites of the type $RE_{1-x}A_xMO_3$, where RE stands for a rare-earth ion such as La, Nd, Pr or Gd and A denotes a divalent ion, such as Ca, Sr or Ba, have been among the most intensively studied materials in recent years because of their remarkable magnetotransport properties. They are generally believed to be double-exchange (DE) ferromagnets and therefore have nearly 100% spin polarization below the Curie temperature T_C [1], near which an extraordinary magnetoresistance is observed accompanied by a transition from the high-temperature paramagnetic (PM) insulator to a low-temperature ferromagnetic (FM) metal [2, 3]. This so-called colossal magnetoresistance (CMR) is restricted to a narrow range of temperatures around T_C, so it is difficult to make use of the effect in electronic devices in spite of the large magnitude. Various theoretical approaches have been proposed to explain the

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magnetotransport in doped manganites [4–6]. Recently, a model which takes into account phase separation and percolation has been presented and the calculations agree with the experiments well [7, 8].

Besides this intrinsic CMR effect observed in single-crystal samples, also polycrystalline samples exhibit an extrinsic magnetoresistance related to the presence of grain boundaries. Hwang *et al* [9] first described this phenomenon in detail by comparing the magnetotransport property in polycrystalline samples with that in the single crystal. It was found that the polycrystalline ceramics exhibited high resistivity values, which are far above those of single crystal, and a sharp drop of resistance in the low field. According to the experimental results, the authors ascribed this negative MR to spin-polarized tunnelling through an insulating grain boundary. With the DE mechanism, electrons in these materials are able to move easily when the spins of the ions (Mn^{3+} and Mn^{4+}) are parallel, and cannot move if they are antiparallel. As a consequence, the magnetic disorder in the interface region will sharply increase the resistance of the grain boundaries and form an insulating barrier through which spin-polarized tunnelling happens. The tunnelling probability of electrons depends on the relative orientation of the magnetization directions of neighbouring grains, which can be substantially altered by the application of a magnetic field.

The combination of these factors (both intrinsic and extrinsic) makes the transport behaviour of doped manganites complicated; e.g., the shift of the metal-to-insulator transition temperature T_{MI} to low temperature, the presence of high-field magnetoresistance, and a shoulder observed in the temperature dependence of the magnetoresistance below T_C [9–14]. Several approaches [6–11] have been proposed to explain these complicated phenomena; however, as they neglected either the intrinsic property or the extrinsic one, a comprehensive understanding is still lacking. In this letter, a self-consistent effective-medium theory based on a random resistor network is presented to explain these complex behaviours of the polycrystalline system in which both the intrinsic CMR and the extrinsic intergrain magnetoresistance are present at the same time. Most of the experimental observations can be well explained within our model.

The perovskite manganites are insulators at high temperature and transform to bad metals at low temperature when cooled through a metal–insulator transition temperature (T_{MI}). At T_{MI}, a peak in the resistivity ρ appears and separates the insulator from the metallic region. The transition in the electrical property is accompanied by a simultaneous PM-to-FM transition at almost the same temperature (i.e., the Curie temperature T_C). The application of magnetic fields shifts the transition to the higher-temperature range, causing a substantial reduction in resistivity near T_C and hence the CMR. Although the theoretical understanding of the CMR phenomenon is still incomplete, DE, electron–phonon coupling, and orbital ordering effects are usually adopted as the main ingredients. The DE mechanism [15] links the electronic transport to the magnetic transition and describes the hopping of electrons in e_g orbitals between neighbouring Mn^{3+} and Mn^{4+} sites with strong on-site Hund's coupling through an O^{2-} ion. The charge transport is enhanced in the FM states when the local Mn d-shell spins are parallel. In turn, the hopping electrons promote FM order, for they tend to preserve their spin direction. However, the DE mechanism alone is insufficient for correctly describing the high-temperature transport properties and quantifying the large resistance drop.

The recently proposed theoretical model based on phase separation and percolation explains the experimental data well [7, 8]. It has been commonly believed that the perovskite-related manganites can accomplish a dynamic phase separation. Experimental evidence for short-range FM domains of nanometre scale existing in the PM background can be shown by experiments such as electron PM resonance [16] and small-angle neutron scattering measurements [17]. On the other hand, experiments such as scanning tunnelling spectroscopy

and magnetic force microscope and electron microscope measurements confirm the coexistence of FM domains and PM regions below T_C directly [18, 19]. According to the DE mechanism, the electrical conductivity is metallic in the FM state and is insulating in the PM state. So it is reasonable to assume that the sample is phase separated into a mixture of FM domains and PM insulating regions. Within the framework of the effective-medium approximation [20], the conductivity of the three-dimensional system can be represented by the effective conductivity σ_e as in equation (1):

$$f\left(\frac{\sigma_{FM}-\sigma_e}{\sigma_{FM}+2\sigma_e}\right)+(1-f)\left(\frac{\sigma_{PM}-\sigma_e}{\sigma_{PM}+2\sigma_e}\right)=0, \tag{1}$$

where σ_{FM} (σ_{PM}) and f $(1-f)$ are the electrical conductivity and phase fraction of the ferromagnetic(paramagnetic) phase, respectively. Equation (1) can be rewritten in terms of the resistivity:

$$f\left(\frac{\rho_{FM}-\rho_e}{2\rho_{FM}+\rho_e}\right)+(1-f)\left(\frac{\rho_{PM}-\rho_e}{2\rho_{PM}+\rho_e}\right)=0. \tag{2}$$

For the PM insulator, the resistivity is written as

$$\rho_{PM}=\rho_0\exp(E_0/k_BT), \tag{3}$$

and for the FM metal, the resistivity is written as

$$\rho_{FM}=\rho_r+bT^2+cT^{4.5}, \tag{4}$$

where ρ_r is the residual temperature-independent resistivity due to scattering by impurities and defects, the second term with the coefficient b is due to electron–electron scattering, and the third term describes the second-order electron–magnon scattering. The parameters ρ_0, E_0, ρ_r, b, and c are determined by fitting the equations (3) and (4) with the resistivity in the low-temperature range and the high-temperature range, respectively.

Since f represents the fraction of FM phase, it should be proportional to the reduced magnetization m which can be determined by mean-field theory. According to this, m can be expressed in terms of solutions of the mean-field self-consistency equation

$$m(h,t)=B_J\left(\frac{3J}{J+1}\frac{m+h}{t}\right), \tag{5}$$

where B_J is the Brillouin function defined by

$$B_J(x)=\frac{2J+1}{2J}\operatorname{cotanh}\left(\frac{(2J+1)x}{2J}\right)-\frac{1}{2J}\operatorname{cotanh}\left(\frac{x}{2J}\right). \tag{6}$$

J is the angular momentum quantum number, $t\,(T/T_c)$ is the normalized temperature, $h\,(H/H_e)$ is the normalized magnetic field, and H_e is the saturation exchange field. For the optimal perovskite manganites of the form $Re_{2/3}A_{1/3}MnO_3$, J is assumed to be 1.83. So the fraction of FM phase can be written as

$$f_{FM}=B_J\left(\frac{3J}{J+1}\frac{m+h}{t}\right), \tag{7}$$

and the fraction of the PM phase is written as

$$f_{PM}=1-B_J\left(\frac{3J}{J+1}\frac{m+h}{t}\right). \tag{8}$$

From the above consideration, we find that the conduction of the system is determined by the metallic channels when the metallic phase has percolated, i.e. $f_{FM}>\frac{1}{3}$. The effect of

external magnetic field is to increase the fraction of metallic phase near T_C and thus enhance the conduction.

For polycrystalline samples, the grains in the micrometre range and ceramics of high density are expected to form a percolating network of metallic conductance below T_C unless the grain boundary has an insulating character. Experiments have shown that the magnetotransport properties of polycrystalline manganites are strongly affected by grain size [21–23]. Yuan *et al* ascribed their results to the additional insulating phase, i.e. grain boundaries, as well as the part determined by equation (8). Within their model, the shift of the metal-to-insulator transition temperature and the broadening of the transition at zero magnetic field are well explained [22]. In fact, the insulating grain boundary acts as an energy barrier through which the process of spin-polarized tunnelling would happen if its thickness was comparable with the spin diffusion length. On the other hand, these weak links, spread along the percolation paths, are expected to inhibit the formation of metallic channels. Furthermore, experiments have shown that the weak-link grain boundaries should be distinguished from the strong-link boundaries [14]. The weak-link grain boundaries act as energy barriers, while the strong-link ones show metallic conductance below T_C [10, 11]. The ratio between strong links and weak links determines the overall measured resistance, insulator-to-metal transition temperature, and magnetoresistance.

With the above consideration, we present a random resistor network model to explain the magnetotransport properties in the polycrystalline manganites. Since the average grain size in the polycrystalline manganites is much larger than the size of metallic domains or insulating regions, the effective resistance for the strong-link grain boundaries is given as the intrinsic resistance [24]

$$R_{in} = \frac{\rho_e}{d}, \tag{9}$$

where d is the diameter of the grain and it is in the micrometre range. However, for the weak-link grain boundaries through which the spin-polarized tunnelling dominates, we apply the conventional model [25] of insulating granular system. This model treats a couple of grains separated by an insulating boundary as a small FM junction. The tunnelling process is determined by the combination of spin-dependent tunnelling and the charging energy E_c of the grains, which is the energy required to generate the positively and negatively charged grains. So the conductance can be expressed as

$$G_{ex} = G_0(1 + P^2 \cos\theta) \exp(-2\kappa s - E_c/k_B T), \tag{10}$$

where

$$P = \frac{D_\uparrow - D_\downarrow}{D_\uparrow + D_\downarrow} \tag{11}$$

and

$$\kappa = \sqrt{\frac{2m\phi}{\hbar^2}}. \tag{12}$$

Here, Θ is the relative orientation angle between the magnetizations of two adjacent FM grains. $D_\uparrow$ and $D_\downarrow$ are the density of states at the Fermi level E_F for spin-up electrons and spin-down ones, and s, m, ϕ represent the thickness of the barrier, the effective mass of electrons, and the barrier height, respectively.

So the resistance can be written as

$$R_{ex} = \frac{R_0}{1 + P^2 \cos\theta} \exp(2\kappa s + E_c/k_B T). \tag{13}$$

R_0 is the quantum limit $R_Q = h/2e^2 = 12.9\,\mathrm{k}\Omega$.

Unlike the conventional dielectric granular systems in which the distribution of E_c depends on that of the grain diameter D, the polycrystalline manganites show a homogeneous distribution of grain size. But for the different kinds of connectivity between grains (weak-link grain boundaries and strong-link grain boundaries), there are some grains which are well connected, forming large clusters, as well as grains which are well separated. So we propose that there still exists a distribution of grain size D and s. On this basis, the application of the conventional model is reasonable. As Sheng proposed, the ratio D/s should have the same values for different regions in the systems although D and s may each have a wide distribution [26]. It follows that the product sE_c is invariant; this can written as

$$\kappa s E_c = c, \tag{14}$$

where κ is a constant. For the polycrystalline sample with large grain size, the term $\kappa s E_c$ is very small [12].

Using the method of steepest descent, the resistance of the insulating grain boundary is given as

$$R_{ex} = \frac{R_0}{1 + P^2\langle\cos\theta\rangle} \exp\bigl(\sqrt{8c/k_BT}\bigr). \tag{15}$$

The difference between $\langle\cos\theta\rangle$ in various external magnetic fields causes the low-field magnetoresistance. The temperature dependence of the spin polarization P is written as [27]

$$P = \frac{\sqrt[3]{1+m(T)} - \sqrt[3]{1-m(T)}}{\sqrt[3]{1+m(T)} + \sqrt[3]{1-m(T)}}, \tag{16}$$

where m is determined by equation (5).

The effective resistance of the whole system (three dimensions) can be calculated in the scheme of the effective-medium approximation from

$$(1 - f_{in})\frac{R_{ex} - R_m}{2R_{ex} + R_m} + (f_{in})\frac{R_{in} - R_m}{2R_{in} + R_m} = 0, \tag{17}$$

where $1 - f_{in}$ and f_{in} are the fractions of extrinsic and intrinsic resistors. It is noted that the high external field aligns the spin disorders at the grain boundaries, thus improving the connectivity between grains. Within the two-channel model, the assumption of linear increase of the metallic channels with external magnetic field agrees with experimental data well [10, 11]. So we propose that the fraction of intrinsic resistor f_{in} increases in a linear way with the external magnetic field (h). Then f_{in} can be written as

$$f_{in} = f_0 + \chi h. \tag{18}$$

As the coefficient χ is very small in the latter calculation, the increase of the fraction of intrinsic resistor in the low-field range can be neglected. The coefficient χ is related to the high-field behaviour.

We find that in our model, which applies the concept of phase separation and percolation with weak links, there exist two kinds of percolation threshold. One is related to the intrinsic properties and is associated with the CMR. The other is associated with grain boundaries and might be responsible for the enhancement of magnetoresistance found in mixtures of manganites and insulators at the percolation threshold of manganites [28, 29] and it is an extrinsic effect. When the fraction of intrinsic resistor f_{in} is above the percolation threshold ($p_c = \frac{1}{3}$), the whole system can accomplish a dynamic phase separation. The metallic channels are formed, and CMR which is associated with the intrinsic properties is observed. In contrast, when f_{in} is below the percolation threshold ($p_c = \frac{1}{3}$), the CMR disappears and the low-field magnetoresistance is observed. The competition between the intrinsic factor and the extrinsic

factor determines the behaviour of the magnetotransport in the polycrystalline manganites, and this can be tuned via changing the grain size [23] or changing the connectivity between grains [10, 11].

In order to test the validity of our model, here we compare it with two experiments. In our calculation, the MR is defined as

$$\mathrm{MR} = \frac{R(H=0) - R(H)}{R(H=0)}. \tag{19}$$

First, let us take a look at the experiment on the polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ by Wang [14]. In this experiment, it is found that weak-link samples show large low-field magnetoresistance over a wide temperature range, while the partially melted samples exhibited the same magnetoresistance behaviour as single crystals, with a maximum peak MR of 15% in a narrow temperature around the FM transition. It is noted that the sample prepared by sintering is porous with a small grain size of 1–3 μm. This clearly shows that such a sample contains a large number of weak-link grain boundaries. By contrast, the sample prepared by partial melting looks relatively dense and no clear boundaries can been seen. The measurements on the temperature dependence of resistance show similar results. For both samples, the resistance at zero field increased with decrease of temperature until a major transition occurred at T_C. Below the transition temperature, the resistance decreases with further cooling. However, these two samples were quite different in their transition width. Most significantly, low-field magnetoresistance has been found in the weak-link samples. To explain the observed results, we calculate the magnetoresistance within our model; see figure 1(a). For the case of the partially melted sample, we choose $f_0 = 1$, which indicates that there exist no weak links; while for the sintered sample, we choose $f_0 = 0.34$. Since there exist a large number of weak-link grain boundaries whose connectivity will be improved in the high magnetic field, we propose an increase of f_{in} in the high magnetic field which is due to the alignment of spin disorder at grain boundaries for the porous sample, and χ is assumed as 0.1. Good agreement can be seen in figures 1(a) and (b).

Next let us take a look at another experiment [30] in which magnetotransport properties are investigated for polycrystalline $La_{0.7}Ca_{0.3}MnO_3$. Unlike the sintered sample which is very porous and contains a large number of weak-link grain boundaries or the partially melted sample which is like a single-crystal sample, the sample used in this experiment is composed of two or three grain types. The magnetotransport properties are studied both inside the grains and across the grain boundaries. As compared with that inside a grain, the resistance across a grain boundary is at least two orders of magnitude higher. More interestingly, a shoulder is observed in the temperature below the main peak. As shown in [30], the attempt to get the contribution from the grain boundary by extracting the 'inside' resistance from the 'across' resistance did not give a satisfactory result. It is noted that the system is expected to be more complicated than resistances placed in series, i.e., the current may flow across the boundary through some percolation paths corresponding to the best-coupled neighbouring regions. In our model, these factors are considered. The weak-link grain boundary and the strong-link one are distinguished. In figure 2(a), the temperature dependence of the magnetoresistance is calculated for three external magnetic fields. The fraction of intrinsic resistor f_0 is chosen as 0.37 and χ is chosen as 0.1. We find that there exists a shoulder in the intermediate temperature range in addition to the main peak near the transition temperature. In figure 2(b), we also show the temperature dependence of the magnetoresistance across the grain boundary reproduced form [30]. Although our calculation near the transition temperature T_C does not present the steep change shown in the experiment, the resemblance between our calculation and the experiment can be easily seen. The main feature of the temperature dependence of the magnetoresistance has been reproduced.

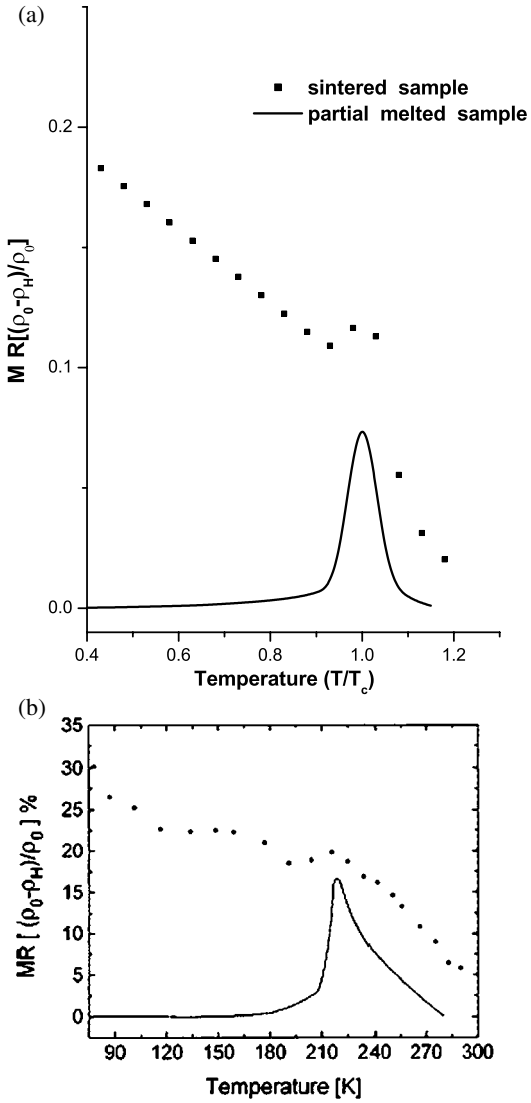

Figure 1. (a) The calculated temperature dependence of the magnetoresistance of the partially melted sample and the sintered sample with $f_0 = 1$ and 0.34, respectively. (b) The temperature dependence of the magnetoresistance of the partially melted sample and the sintered sample reproduced from [14]. The dotted curve represents the sintered sample and the solid line represents the partially melted sample.

From the above consideration, we find that, by taking the two kinds of links into account in our model, magnetotransport properties of polycrystalline samples can be well explained.

In summary, in this letter, we have studied the magnetotransport in the polycrystalline perovskite manganites by using the effective-medium approximation on the basis of a random resistor network model. Both intrinsic properties which are achieved through the strong-link grain boundaries and the extrinsic properties which are achieved through the weak-link grain boundaries are taken into account. It is noted that the manganites are phase separated into a metallic phase and an insulating phase. The conduction of the system is determined by the

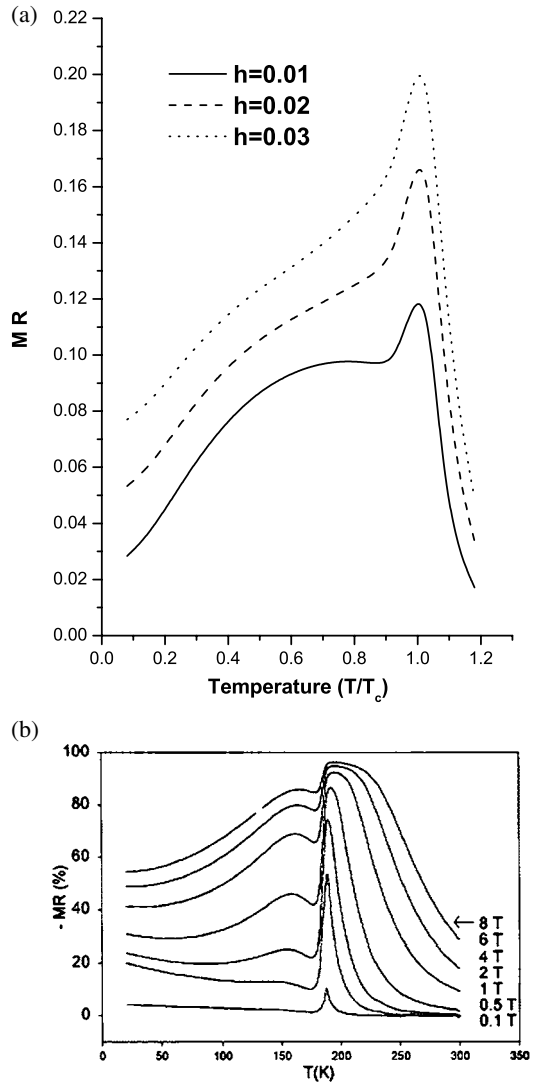

Figure 2. (a) The calculated temperature dependence of the magnetoresistance with $f_0 = 0.37$ and $\chi = 0.1$. (b) The temperature dependence of the magnetoresistance across the grain boundary reproduced from [30].

metallic channels when the metallic phase has percolated. In the polycrystalline cases, the weak-link grain boundaries, spread along the percolating paths, are expected to inhibit the formation of metallic channels on the one hand, and to favour the low-field magnetoresistance on the other hand. The relationship between phase separation and percolation is investigated for various grain boundary conditions. Most of the experimental observations can be explained within our model.

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