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Enhancement of "intrinsic" magnetoresistance ratio and activation energy of $La_{0.67}Ca_{0.33}MnO_3$ single crystals by Fe doping*

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In order to avoid the complicated influence of grain boundaries on the resistivity in the investigation of the "intrinsic" magnetoresistance (MR) effect, the magnetic and magnetotransport properties of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}Mn_{0.96}Fe_{0.04}O_3$ single crystals were investigated. Owing to the absence of grain boundaries in the single crystals, MR ratio under 40×10^5 A/m is about two orders of magnitude larger than that in polycrystalline counterparts. A further enhancement of MR ratio from 3400% to 17600% was achieved by a few percent of Fe doping. On the basis of the small polaron model, the activation energy derived from fitting the resistivity above T_c was found to increase upon introducing Fe. A connection between the strong localization of electrons arising from magnetic polarons and the enhancement of MR was observed in the single crystals.

Keywords: perovskite manganites, colossal magnetoresistance (CMR), magnetic polarons
PACC: 7530V, 6170N, 6320P, 7530C

1. Introduction

Recently colossal magnetoresistance (CMR) in various perovskite manganese oxides $R_{1-x}A_xMnO_3$ (where R is trivalent lanthanide and A is divalent alkali earth metal) has become a topic of considerable research interest.[1−6] The magnetic properties, magnetotransport, and CMR effect of these manganese oxides have been extensively investigated. Although a large number of papers have been published to investigate the effect of Fe doping on the magnetic and magnetotransport properties of $La_{1-x}Ca_xMnO_3$ polycrystalline samples,[7−12] no sufficient reports have been published concerning the significant contribution of grain boundaries in polycrystalline samples to the resistivity, which always results in an "extrinsic" magnetoresistance (MR) besides the "intrinsic" MR effect. The resistive behaviour has been reported as a function of the grain size, which can be tuned by modifying the synthesis conditions. High-quality single crystals can help us to better understand the fundamental origin of CMR effect. In this paper, high-quality single crystals of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}Mn_{0.96}Fe_{0.04}O_3$ are grown for investigating the effect of Fe doping on the "intrinsic MR" effect when isolating the contribution of grain boundary to the magnetotransport behaviour. Furthermore, $La_{0.67}Ca_{0.33}Mn_{0.96}Fe_{0.04}O_3$ sample is attractive for investigating the magnetic polarons in the paramagnetic insulating phase due to the identical ionic radii of Mn^{3+} and Fe^{3+} ions in six-fold octahedral coordination, which induces minimal distortion in the lattice. On the basis of the small polaron model, the activation energy can be derived from fitting resistivity above T_c. The relationship between the intrinsic MR and localization of electrons arising from magnetic polarons can be achieved.

2. Experimental procedures

Single crystals with nominal composition of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}Mn_{0.96}Fe_{0.04}O_3$

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were successfully grown by the floating zone method with four ellipsoidal mirrors (Crystal Systems Inc, FZ-T-10000-H-VI-VP). Back-reflection Laue x-ray diffraction (XRD) experiment was carried out to check the single crystallinity and determine the crystallographic direction. Magnetization and resistivity measurements were performed on a commercial physical property measurement system (Quantum Design, PPMS-14). Both AC and DC magnetic fields are parallel to the longitudinal axis of the sample. The compositions of $La_{0.69}Ca_{0.31}MnO_3$ and $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ for these two sample crystals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), which are consistent well with the nominal ones.

3. Results and discussion

AC magnetic susceptibility for $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ single crystal was measured under an AC field of 800A/m with various frequencies of 10, 100, 1000Hz without bias DC field (Fig.1(a)) and with bias DC fields of 2.4×10^5, 4×10^5 and 8×10^5A/m (Fig.1(b)). Both AC magnetic susceptibility without bias DC field and DC magnetization (inset of Fig.1(a)) measured under 0.16×10^5A/m exhibit the same temperature dependence. With decreasing temperature, the susceptibility and DC magnetization increase rapidly around T_c, becoming nearly temperature independent below T_c. The transition temperature for $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ is about 174K, which is lower than that of $La_{0.69}Ca_{0.31}MnO_3$ single crystal ($T_c \approx 218$K), as shown in the inset of Fig.1(a). AC magnetic susceptibility shows no obvious frequency dependence. The evolution of the temperature dependence of the AC susceptibility in real component χ' (at 10Hz frequency) under different bias DC magnetic fields demonstrates that only one distinct peak appears around the transition temperature when the magnetic field is larger than 4×10^5A/m. With increasing bias DC field, the peak of χ' shifts to the higher temperature, and decreases in amplitude, which is a characteristic of ferromagnetic systems.[13] Although the substitution of Fe weakens the double-exchange interaction between Mn^{3+} and Mn^{4+} ions and decreases the Curie temperature, in contrast with $La_{0.67}Ca_{0.33}Mn_{0.90}Fe_{0.10}O_3$,[8] such a low concentration of Fe as dopant is not enough to destroy the double-exchange significantly and result in the appearance of spin-glass state in $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ single crystal.

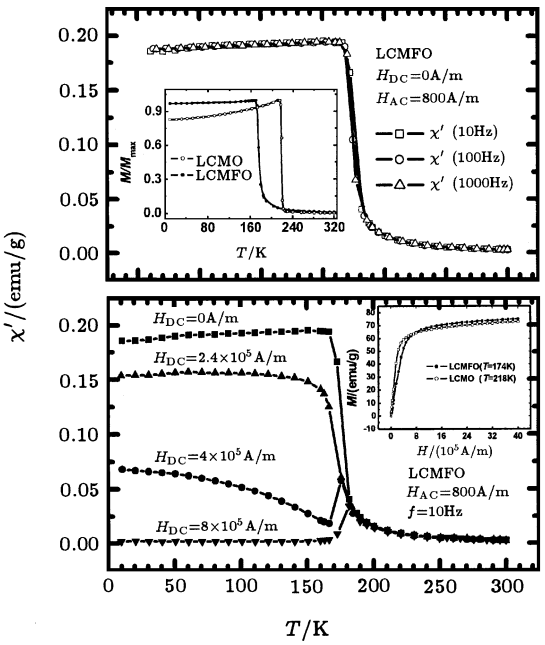


Fig.1. Temperature dependence of AC susceptibility for 800A/m and 10, 100, 1000Hz applied AC magnetic field without bias DC magnetic field (a), and with various DC magnetic fields (b). Thermomagnetization curves and magnetization curves are plotted in the insets.

Temperature dependences of the resistivity of the two samples are shown in Figs.2(a) and 2(b). The current runs parallel to the longitudinal axis of sample. The data display a transition from a low-temperature metallic state to a high-temperature insulating state around T_c. Unlike polycrystalline samples, which exhibit a broad resistivity peak around T_c, the zero-field resistivity transition of the single crystals of $La_{0.69}Ca_{0.31}MnO_3$ and $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ is observed to be very sharp, without any intermediate step around metal-insulator transition temperature T_p. It was proven that the presence of a shoulder below T_p in the resistivity curve is the signature of the effect of grain boundary in the double-grain sample,[14] the sharp transition in resistivity without any inflexion point or shoulder (foot-like structure) confirms that no grain boundary exists in the present single crystal samples. Without scattering introduced by grain boundaries, the resistivity in the low-temperature regime ($T < T_c$) in single crystals is at least two orders of magnitude smaller than that in polycrystalline counterparts. A few percent of Fe dopant results in that the resistivity in $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ single crystal is an order of magnitude larger than that in Fe-free crystal. In the Fe-free single crystal, the con-

duction mechanism can be explained by the e_g electrons hopping between Mn^{3+} and Mn^{4+} sites on the basis of the double-exchange model.[15] The electron hopping between Mn^{3+} and Fe^{3+} sites is forbidden because of the lack of available electronic states in the Fe e_g orbital. As Fe^{3+} replaces Mn^{3+}, the ratio Mn^{3+}/Mn^{4+}, as well as the number of hopping electrons, decreases, thus increasing the resistivity.

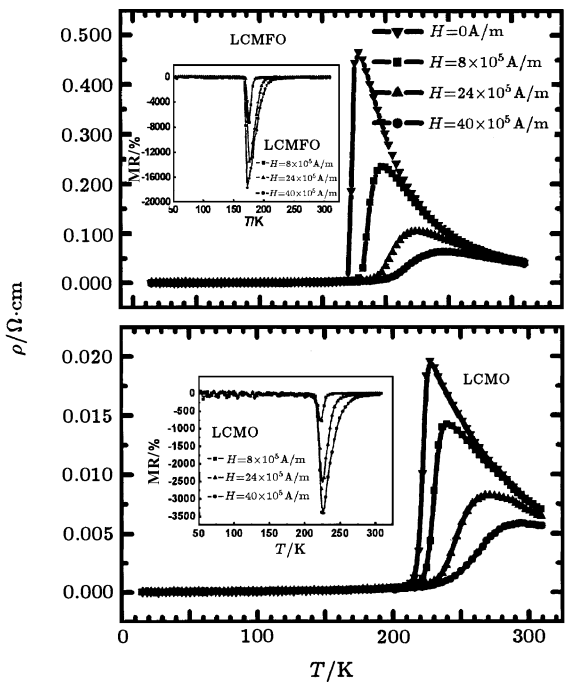


Fig.2. ρ-T curves under various applied magnetic fields for $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ (a) and $La_{0.69}Ca_{0.31}MnO_3$ (b). Insets: MR ratios under various applied field as a function of temperature.

The influence of the applied field ranging from 0 to 40×10^5A/m on the electrical resistivity was investigated as well. With the increase of the applied field, the resistivity peaks decrease in magnitude and shift towards higher temperatures. The insets of Figs.2(a) and 2(b) show the MR ratio (defined as $(R_H - R_0)/R_H$) as a function of temperature for $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ and $La_{0.69}Ca_{0.31}MnO_3$, respectively. At low temperatures, negligible MR is related to the high order of spin arrangement. With increasing temperature around T_c, a significant enhancement of negative MR ratio is concentrated within a narrow temperature range owing to the suppression of spin fluctuation.[16] In contrast to the polycrystalline sample, which exhibits a large MR at low fields, the MR of single crystal is not easily saturated at low magnetic field. Decreasing the grain boundary is in favour of enhancing MR, but a high magnetic field is required. Up to 3400% of MR is achieved under 40×10^5A/m for $La_{0.69}Ca_{0.31}MnO_3$ single crystal, which is two orders of magnitude larger than that of polycrystalline sample.[7−12] The sizeable negative MR of the single crystal is mainly due to the suppression of spin fluctuation in magnetic fields, as expected in a double-exchange ferromagnet. With a few percent of Fe dopant, a further enhancement of MR from 3400% to 17600% is achieved under 40×10^5A/m. Since the relative variation in the magnetization between $La_{0.69}Ca_{0.31}MnO_3$ and $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ is the same once the magnetic domain rotation is completed, further enhancement of MR by the substitution of 4% Fe cannot be explained only by the suppression of spin fluctuation. Therefore, the localization mechanism should also be taken into account for the mechanism of enhancement of MR of the single crystal.

It is proven that the conducting mechanism of perovskite manganite compounds in a paramagnetic state can be well described by the thermally activated hopping of the small polaron model.[17−20] The resistivity in the paramagnetic state can be fitted by the expression $\rho(T) \propto T\exp(E_A/k_BT)$ (inset of Fig.3), where k_B is the Boltzmann constant and E_A is the activation energy. The value of E_A (∼100.7meV) for $La_{0.69}Ca_{0.31}MnO_3$ single crystal under a zero magnetic field is in good agreement with the typical values of 100.0meV for polycrystalline sample reported by other authors.[19] Although the presence of grain boundaries in polycrystalline materials increases significantly the resistivity and influences the electronic transport in low-temperature regime, the same values of the activation energy of magnetic polarons have

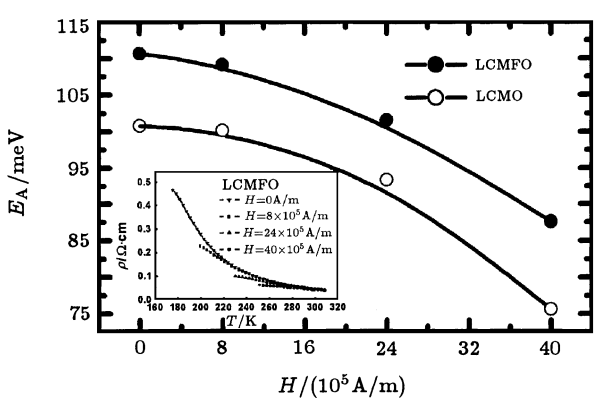


Fig.3. The magnetic field dependence of the activation energy $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ and $La_{0.69}Ca_{0.31}MnO_3$ single crystal samples, respectively. The inset shows the small polaron model fitting of the resistivity of $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ above T_c.

been obtained in the paramagnetic state between single crystal and polycrystalline materials, suggesting that the activation energy reflects an intrinsic property. The fitting results of the experimental curves (inset of Fig.3) reveal that the doping of Fe increases the activation energy, implying a stronger localization of electrons. This is consistent with the results of MR. The carrier localization may be another important factor for the sizeable negative MR of the single crystal sample.

An applied magnetic field aligns the spins of Mn^{3+} and Mn^{4+} ions, which increases the kinetic energy, and hence decreases the effective electron-phonon coupling. Therefore, the activation energy decreases significantly with increasing magnetic field (as shown in Fig.3). In the case of magnetic polarons, there is a magnetic exchange contribution to the activation energy. In the presence of a magnetic field, the activation energy is replaced by $E_A = E_A^0 \left[1 - \left(\frac{M}{M_s}\right)^2\right]$, where M and M_s are magnetization and saturation magnetization, respectively.[20] This is the origin of the decrease of the resistivity as well as the shift of the resistivity peaks to higher temperatures with increasing magnetic field.

4. Conclusion

In summary, the effect of Fe doping on magnetic properties and the "intrinsic MR" for single crystal $La_{0.67}Ca_{0.33}MnO_3$ has been investigated. Absence of grain boundary increases the MR ratio up to 3400% and 17600% for the Fe-free and the Fe-doping single crystal samples, respectively. Further enhancement of MR by a few percent of Fe dopant results from the increase in the activation energy in $La_{0.68}Ca_{0.32}Mn_{0.96}Fe_{0.04}O_3$ single crystal sample, besides the suppression of spin fluctuations.

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