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Spin Glass Behaviour and Spin-Dependent Scattering in $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ Perovskites

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The magnetic, electrical and thermal transport properties of the perovskite $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ have been investigated by measuring dc magnetization, ac susceptibility, the magnetoresistance and thermal conductivity in the temperature range of 5-300 K. The spin glass behaviour with a spin freezing temperature of 70 K has been well confirmed for this compound, which demonstrates the coexistence and competition between ferromagnetic and antiferromagnetic clusters by the introduction of Cr. Colossal magnetoresistance has been observed over the temperature range investigated. The introduction of Cr causes the "double-bump" feature in electrical resistivity $\rho(T)$. Anomalies on the susceptibility and the thermal conductivity associated with the double-bumps in $\rho(T)$ are observed simultaneously. The imaginary part of ac susceptibility shows a sharp peak at the temperature of insulating-metallic transition where the first resistivity bump was observed, but it is a deep-set valley near the temperature where the second bump in $\rho(T)$ emerges. The thermal conductivity shows an increase below the temperature of the insulating-metallic transition, but the phonon scattering is enhanced accompanying the appearance of the second peak of double-bumps in $\rho(T)$. We relate those observed in magnetic and transport properties of $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ to the spin-dependent scattering. The results reveal that the spin-phonon interaction may be of more significance than the electron (charge)-phonon interaction in the mixed perovskite system.

The perovskite manganese oxides with colossal magnetoresistance (CMR) effect have attracted a surge of interest.[1-3] In $R_{1-x}A_xMnO_3$ (R = rare earth, A = Ca, Sr, Ba, Pb) systems, for most cases, there is a common feature that a metal-insulator (MI) transition and CMR occur near the ferromagnetic ordering temperature T_C, in a certain doping range. The traditional explanation ascribed this to the "double exchange" (DE) of the Mn^{3+}-O^{2-}-Mn^{4+} mechanism. [4] In addition, in the DE theory the electron-phonon coupling via Jahn-Teller (JT) effect should be included.[5-9] Recently, it has been generally recognized that the system involves complex interplays between charge, lattice and spin. The phenomena on magnetic and transport properties arose from various complex interactions. It is worth noting that Cr^{3+} (d^3) ion is iso-electronic with Mn^{4+} ion. The authors of Refs.[10-16] tried to investigate the structural, transport and magnetic properties of $La_{1-x}Ca_xMn_{1-y}Cr_yO_3$ and they showed some very meaningful results, especially around y = 0.1. In this Letter, we investigate the magnetic, electrical and thermal transport properties of perovskite $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ by measuring dc magnetization, ac susceptibility, the magnetoresistance and thermal conductivity in the temperature range of 5-300 K. The spin glass behaviour has been well confirmed for this compound. Meanwhile, the *spin-dependent* scattering has been suggested for the anomalous magnetic properties and phonon scattering corresponding to double-bumps in electrical resistivity.

The bulk $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ was prepared by the conventional solid-state reaction method.[16] The structure and phase purity of samples were checked by powder x-ray diffraction (XRD) proving that the sample is of single phase in the orthorhombic perovskite structure. Magnetic and transport measurements were performed from 5 K to 300 K by a physical property measurement system (PPMS) of quantum design. In the zero-field-cooling (ZFC) measurements the sample was cooled down from room temperature to 5 K before a measured field was applied. In the field-cooling (FC) measurements the sample was cooled in an applied field from room temperature to 5 K. All the magnetization data, $M_{ZFC}(T)$ and $M_{FC}(T)$, were collected in warming the sample up to 300 K. The ac susceptibility measurements were carried out in an applied field H_{AC} = 10 G at different frequencies from 10 to 1003 Hz as well as at different applied dc fields from 0 to 500 G. The resistivity in magnetic field up to 7.0 T was performed by the standard four-probe method. The thermal conductivity was measured by means of the method of longitudinal steady thermal flow.

The $M_{ZFC}(T)$ and $M_{FC}(T)$ curves in the field of 50 G, 100 G and 500 G for $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ are presented in Fig. 1. The paramagnetic-ferromagnetic (PM-FM) transition occurs around T_C = 243 K.

M_{ZFC} (T) and M_{FC}(T) show a monotonic increase below T_C and are substantially identical in the region $T_R \leq T \leq T_C$. Here T_R is a temperature below which M_{ZFC} (T) deviates from M_{FC}(T) and shows a hump implying a reversibility of magnetization. This large difference between M_{ZFC} (T) and M_{FC}(T) below T_R indicates no simple ferromagnetic long-range order in this sample. At 70K, named T_F, the M_{ZFC} (T) curve appears as a bend. Below T_F M_{ZFC} (T) curve begins to deviate from the trace again and reduces fast.

Fig. 1. *Temperature dependence of magnetization M(T) in ZFC and FC processes in the fields of 50 G, 100 G and 500 G for* $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$.

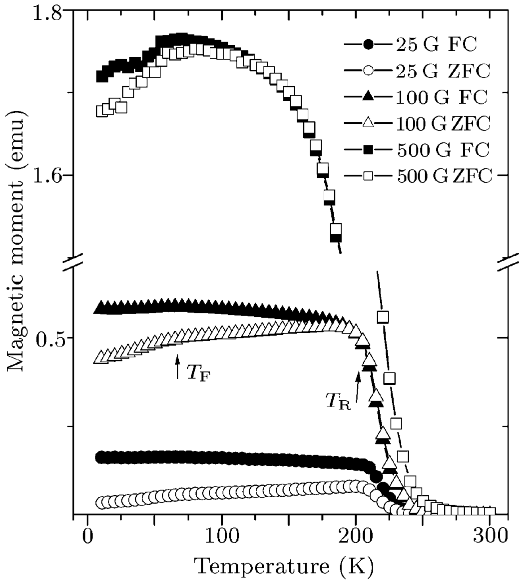
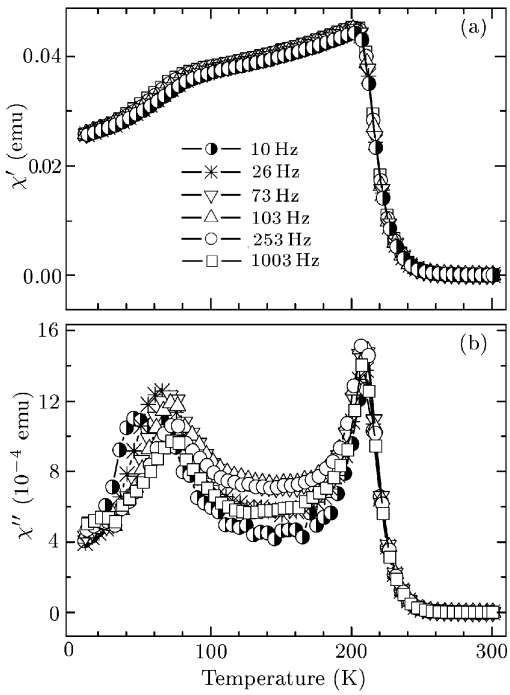
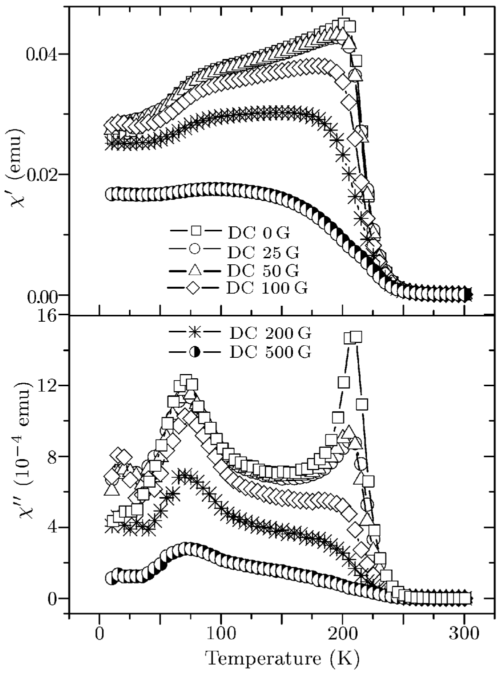


Fig. 2. *The ac susceptibility (a) χ' and (b) χ" measured in ac field of 10 G at different frequencies for* $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$.



The ac susceptibility measurements are a compatible technique usually adopted to research the magnetic glass behaviour in a material. The temperature dependences of real and imaginary components of ac susceptibilities χ'(T) and χ''(T) were measured in an ac field of 10 G at different frequencies from 10 to 1003 Hz and are displayed in Fig. 2. In addition, $\chi'(T)$ and $\chi''(T)$ were measured in different applied dc fields from 25 to 200 G and are displayed in Fig. 3, while $\chi'(T)$ in Fig. 2 includes a maximum at high temperature and a bend at low temperature, The maximum should be the PM-FM transition observed in dc $M_{ZFC}(T)$ curves, and the bend may be qualitatively explained in the same way as the bend in M_{ZFC} (T). There are two peaks emerging in the $\chi''(T)$ curve. One at high temperature appears at the same temperature related to the PM-FM transition and its position in temperature coordinate is independent of frequency. The other sharp peak is located near the temperature of the bend in $\chi'(T)$, but the position of this peak is dependent on frequency and shifts to higher temperature when the frequency of the ac field increases from 10 to 1003 Hz. Furthermore, the peak is depressed when a dc field is applied in Fig. 3 from 0 to 500 G. These phenomena are typical features of a spin glass. [17] Thus the spin freezing temperature T_{SG} can be determined to be about 70 K, which is related to T_F in M_{ZFC} (T).

Fig. 3. *The ac susceptibility (a) χ' and (b) χ'' measured at a frequency of 73 Hz in different applied dc fields for $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$.*



The spin (cluster) glass behaviour is usually observed in doped manganite with Fe [18] and Ni [19] on Mn sites. It is a most important prerequisite for a spin glass that the randomness of spins of the neighbouring coupling, ferromagnetic or antiferromagnetic, exists in the system. For undoped $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$, except for the DE of Mn^{3+}-O-Mn^{4+}, which mediates ferromagnetism and metallic conduction, there is a generic antiferromagnetic superexchange interaction of Mn^{4+}-O-Mn^{4+}, but the former is overwhelming in the dual ratio of Mn^{4+}/Mn^{3+} ions, so they show ferromagnetic and metallic behaviour. Cr partly replaces the Mn sites a double exchange-like and/or superexchange (SE) ferromagnetic interaction could take place through Mn^{3+}-O-Cr^{3+} due to the identical electronic configuration between Cr^{3+} and Mn^{4+}. [10-12] 0n the other hand, the substitution of Cr for Mn sites induces antiferromagnetic interaction between Cr^{3+}-O-Cr^{3+} and promotes the proportion of Mn^{4+}-O-Mn^{4+}. Therefore, mixed magnetic interactions exist in $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$. Their ferromagnetic coupling is due to the double-exchange interaction between the bond key of Mn^{3+}-O-Mn^{4+} and DE and/or SE interactions of Cr^{3+}-O-Mn^{3+}, respectively. The antiferromagnetic coupling originates from the bond key of Cr^3+-O-Cr^3+ and Mn^{4+}-O-Mn^{4+}. The competition between both the kinds of magnetic interactions determines the magnetism of the material. With decreasing temperature, the ferromagnetic and antiferromagnetic competing interactions finally make the magnetic coupling frozen up in the system, which goes into a spin glass state. Actually, the spin glass state is a metastable state of the co-existence of spatial random frozen ferromagnetic and antiferromagnetic clusters.[17]

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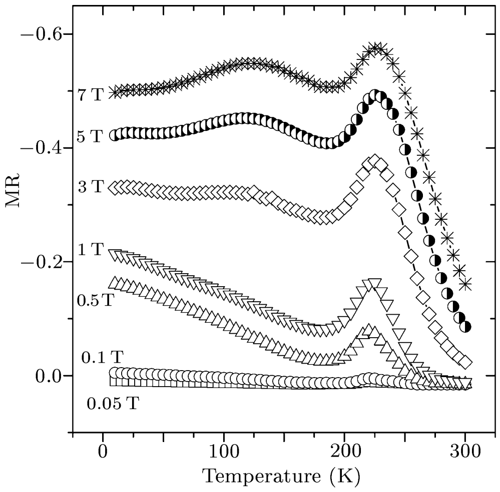
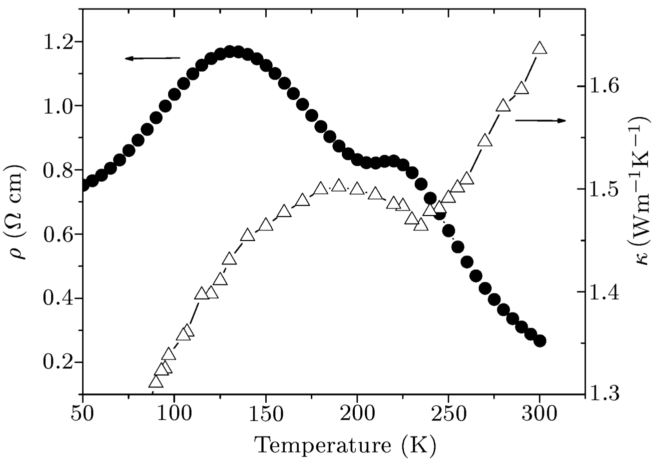
Fig. 4. *Temperature dependence of magnetoresistance in applied fields from 0.05 T to 7.0 T for* $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$*.*



The resistivity $R_H(T)$ was measured in applied fields from 0 to 7.0 T, then the magnetoresistance (MR) defined as MR = $\{R(H)R(0)\}/R(0)$ is shown in Fig. 4. The resistance of the compound is suppressed drastically in the whole investigation temperature range. The magnitude of MR at 40 K, 130 K and 225 K is about 50%, 55% and 58%, respectively, in a field of 7.0 T.

The temperature dependence of thermal conductivity $\kappa(T)$ has been compared with the electrical resistivity $\rho(T)$ in zero field for $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$, as shown in Fig. 5. The double bumps in the ρ-T curve are obvious. The one at the higher temperature is the common feature related to DE, which zooms out when a magnetic field is applied. The other peak located around 130 K is very large and broad. We can see that the thermal conductivity $\kappa(T)$ first decreases with the decreasing temperature and a sharp increase appears at the temperature of the MI transition. This observation is consistent with the result previously published on the Mn^{3+}/Mn^{4+} pervovskites and can be attributed to unusually static and/or dynamic lattice distortions accompanied by charge transportation. The localization of carriers causes disorder of lattice polarons in the high temperature region. In the metallic state, the carriers are delocalized, and any distortion will be uniformly averaged over Mn-O sites. Such a transition from the dynamic Jahn-Teller state to the static Jahn-Teller state leads to a sharp increase of $\kappa(T)$ by increasing the mean-free path of phonon. However, the thermal conductivity is suppressed in a wide temperature range below T_C where the second bump in $\rho(T)$ commences. The electron (charge) contribution to heat transport has been estimated from the resistivity data by using the Wiedemann-Franz law to be less than 1% of the total thermal conductivity and can be negligible. Thus $\kappa(T)$ is almost entirely due to phonons in the present sample.

Fig. 5. *Temperature dependence of resistivity and thermal conductivity for* $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$*.*



It is a common phenomenon that the temperature dependence of electrical resistance shows double peaks in manganese oxides when the ratio of Mn^{4+} is in a certain ranged[20,21] Rao *et al.* related this to the magnetic double phase elicited from the magnetic phase diagram for the $LaCaMnO_3$ system by the neutron diffraction method. In undoped $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$, the CMR effect appears at the metallic-insulating (MI) transition near the Curie temperature of about 265 K. With the Cr doping, the MI transition shifts to lower temperature, and an additional broad peak around 130 K grows up in the ρ-T curve for $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$. It should be noticed that in our experiments, anomalies on the susceptibility and the thermal conductivity associated with the double-bumps in ρ $\rho(T)$ are observed simultaneously. Here $\chi''(T)$ in the ac susceptibility shows a sharp peak at the temperature of the MI transition, T_{IM}, where the first resistivity bump is observed, but it is a deep-set valley near the temperature at which the second bump in $\rho(T)$ emerges, indicating where conduction electrons are scattered strongly by turning freely located magnetic moments. When $T>T_{SG}$ spins begin to run freely. The relaxation time of located magnetic moments decreases with the increasing temperature, and then the scattering for conduction electrons increases. On the other hand, the appearance of spin clusters disturbs the spin lattice in the ferromagnetic transition section, which brings on the state of location and magnetic polarization partially and results in the increasing resistivity with the decreasing temperature though the magnetic order favours the motion of carrier below T_C. Thus we relate the second peak of the double bumps observed in electrical resistance of $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ to a *spin-dependent* scattering. An applied magnetic field tends to align the spin direction, promotes the conductivity, and leads to CMR. Then magnetic sensitive resistivity occurs in a wide temperature range.

Considering the phonon thermal conductivity, we can find that $\kappa(T)$ shows an increase below T_{IM}, while the phonon scattering is enhanced, accompanied by the appearance of the second peak of the double bumps in $\rho(T)$. The scattering to phonons via electron (charge)-lattice coupling has been regarded as dominant, although the electron (charge) contribution to thermal transportation as heat carriers is beyond our consideration.[16] Another additional scattering for phonons may be expected to be observed at low temperatures due to *spin-dependent* scattering via the interaction between spin and lattice excitations.[22] The magnetic polarization on spin lattice or localized spin fluctuation will add scattering to the phonon, which leads to decrease of $\kappa(T)$ accompanied by the appearance of the second peak of the double bumps in $\rho(T)$. Therefore, both the local fluctuation of the lattice structure related to the state of charge carriers and the *spin-dependent* scattering related to the state of spin coupling act on the phonon transportation. Actually, the electron-phonon interaction is very complex. If we give an expression of the electron (charge)-phonon interaction for the former, the latter would be marked as a spin-phonon interaction in order to attend to the effect of magnetic polarization or spin fluctuation on thermal transportation. The analysis is based on a simple idea: although the electrical current probes the charge response only, the heat current is sensitive to charge and spin excitation.[22,23] Thus our results indicating the spin-phonon interaction may be of more significance than the electron (charge)-phonon interaction in $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$. The present study on the heat transportation may open an available route for the investigation of CMR materials.

In summary, we have studied magnetic, electrical and thermal transport properties for perovskite $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$. The spin glass behaviour with a freezing temperature of 70 K and the CMR effect appearing in a wide temperature range have been found in this compound. The results can be ascribed to the coexistence of ferromagnetic and antiferromag-netic clusters and competition between them by the introduction of Cr^{3+} ions. The double bumps in the *p-T* curve is obvious. At present, $\chi''(T)$ shows a sharp peak at T_{IM}, but it is a deep-set valley near the temperature at which the second bump in $\rho(T)$ emerges. The thermal conductivity shows an increase below T_{IM}, but the phonon scattering is enhanced, accompanied by the appearance of the second peak in $\rho(T)$. We relate those observed magnetic and transport properties of $La_{0.7}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ to the *spin-dependent* scattering. The results exhibit the importance of spin-phonon interaction other than the electron (charge)-phonon interaction in a mixed perovskite system.

References

[1] Jin S, Tiefel T H, Meconnack M, Fastnacht R A, Ramesh R and Chen L H 1994 *Science* **264** 413

[2] Helmolt R V, Wecker J, Holzapfel B, Schultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331

[3] Chahara K, Ohno T, Kasai M and Kosono Y 1993 *Appl. Phys. Lett.* **63** 1990

[4] Zener C 1951 *Phys. Rev.* **82** 403

[5] Zhou J S and Goodenough J B 1998 *Phys. Rev. Lett.* **80** 2665

[6] Millis A J 1998 *Nature* **392** 147

[7] Hwang H Y, Cheong S W, Radaelli P G, Marezio M and Batlogg B 1995 *Phys. Rev. Lett.* **75** 914

[8] Roder H, Zang J and Bishop A R 1996 *Phys. Rev. Lett.* **76** 1356

[9] Zheng W H, Wu B M, Yang D S, Li J Y, Liu X R and Li B 2001 *Chin. J. Temp. Phys.* **23** 216

[10] Sun Y, Xu X J and Zhang Y H 2001 *Phys. Rev.* B **63** 054404

[11] Ganguly R, Gopalakrishnan I K and Yakhmi J V 2000 *Physica* B **275** 308

[12] Rivadulla F, LÓpez-Quintela M A, Hueso L E, Sande P, Rivas J and Sanchez R D 2000 *Phys. Rev.* B **62** 5678

[13] Cabeza O, Barca O, Francesconi G, Bari M A, Severack C, Muirhead C M and Miguelez F 1999 *J. Magn. Magn. Mater.* **196-197** 504

[14] Moritomo Y, Machida A, Mori S, Yamanoto N and Naka- mura A 1999 *Phys. Rev.* B **60** 9220

[15] Cabeza O, Long M, Severac C, Bari M A, Muirhead C M, Francesconi M G and Greaves C 1999 *J. Phys.: Condens. Matter.* **11** 2569

[16] Zheng W H et al 2002 *Chin. J. Temp. Phys.* **24** 230

[17] Mydosh J A 1993 *Spin Glass: An Experimental Introduction* (London: Taylor and Francis)

[18] Cai J et al 1997 *J. Appl. Phys. Lett.* **71** 1727

[19] Wang Z H et al 1999 *J. Appl. Phys.* **85** 5399

[20] Rao G H et al 1996 *J. Phys.: Condens. Matter* **8** 5393

[21] Li G, Ze X et al 2002 *J. Magn. Magn. Mater.* **239** 51

[22] Sologubenko A V et al 2001 *Phys. Rev.* B **64** 054412

[23] Lorenz T et al 2002 *Nature* **418** 614