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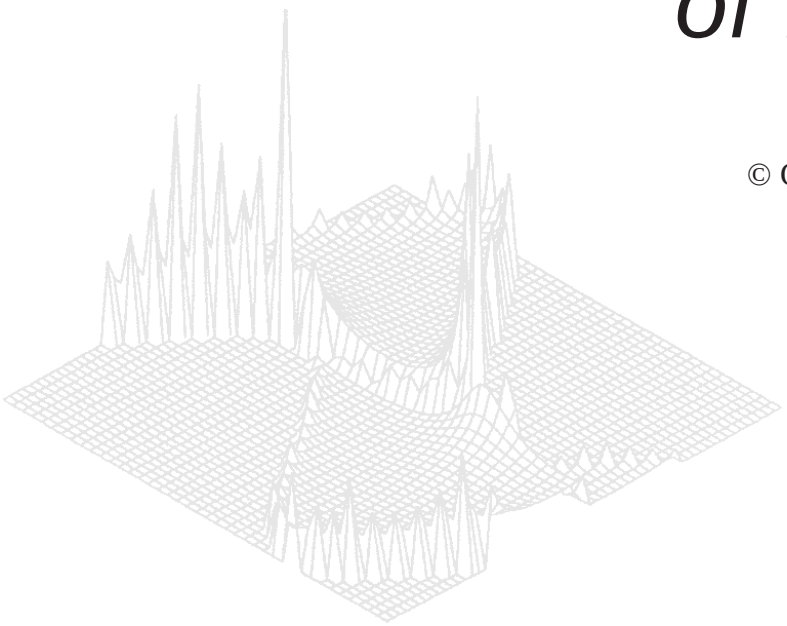

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Small Polaron Hopping Conduction in Samples of Ceramic $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$*

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Abstract

The ceramic sample of $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ exhibits the metal–insulator transition and a negative magnetoresistance in the vicinity of the Curie temperature ($T_C \simeq 100$ K). The dc magnetic susceptibility between 100 K and 280 K is nearly constant and decreases gradually with increasing temperature above 280 K. The measurements of dc resistivity and the thermoelectric power indicate that small polaron hopping conduction takes place at $T > 280$ K. The spin ordering due to the two-dimensional $d_{x^2-y^2}$ state occurring at $T > 280$ K is directly related to the hopping conduction above 280 K, although the spin ordering due to the one-dimensional $d_{3z^2-r^2}$ state takes place at $T > T_C$. The two-dimensional $d_{x^2-y^2}$ state extending within the MnO_2 sheets starts to narrow and leads to the carrier localisation at 280 K. The effective number of holes in this sample estimated from the thermoelectric power is considerably smaller than the nominal value. This indicates that the small polaron hopping conduction takes place predominantly within the in-plane MnO_2 sheets. A discussion is given of the experimental results of the ceramic sample of $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$.

1. Introduction

Hole-doped perovskite manganese oxides have attracted considerable attention because of the intrinsic colossal magnetoresistance (CMR) and the metal–insulator (MI) transition. The generic behaviour of the ferromagnetic metal (FM) to paramagnetic insulator (PI) transition with the negative magnetoresistance (MR) near the Curie temperature T_C is discussed within the framework of the double-exchange (DE) interaction due to the strong Hund's rule coupling between itinerant e_g electrons and localised t_{2g} spins ($S = \frac{3}{2}$) (Zener 1951; Anderson and Hasegawa 1955; de Gennes 1960). The MR behaviour, especially for $La_{1-x}Sr_xMnO_3$ (Tokura *et al.* 1994; Urushibara *et al.* 1995) having a large one-electron bandwidth W of e_g electrons, is well accounted for by the simple DE model. To explain a colossal value of MR for a system having a small W, e.g. $La_{1-x}Ca_xMnO_3$ (Schiffer *et al.* 1995), however, an additional mechanism for carrier localisation above T_C is required as well as magnetic-field release of localisation. The most

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intensive mechanism to supplement the DE model is polaron formation originating from the Jahn–Teller (JT) instability of MnO_6 octahedra (Millis *et al.* 1994, 1996). Most pseudocubic perovskite-type manganites which have been studied extensively have distorted perovskite structures with three-dimensional networks of MnO_6 octahedra, because a decrease in the averaged ionic radius at A site reduces W via a variation of Mn–O–Mn bond angle (Hwang *et al.* 1995).

Recent attention in this field has focused on the layered perovskite series of Ruddlesden–Popper compounds such as $La_{2-2x}Sr_{1+2x}Mn_2O_7$, which is constructed by inserting a rock-salt-type block layer of $(La,Sr)_2O_2$ every MnO_2 sheet (Moritomo *et al.* 1996; Kimura *et al.* 1996). The separation of MnO_6 octahedra along the c axis inhibits both the interlayer magnetic coupling and the electrical conduction (Louca *et al.* 1998). Furthermore, the static JT distortion of MnO_6 octahedra due to the tetragonal crystal field ($I4/mmm$) *a priori* lifts the degeneracy of e_g orbitals, and hence the system is free from the dynamical JT effect (Moritomo *et al.* 1997, 1998). Transport measurements in $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ single crystals ($x = 0\cdot4$) show that the resistivity along the c axis is about two orders of magnitude greater than across the ab plane (Moritomo *et al.* 1996). The resistivity profile in the ab plane of the $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ single crystal ($x = 0\cdot3$) is also quite different from the profile along the c axis. In fact, the MI transition in the ab plane of this compound takes place around 280 K ($>T_C$) but at 100 K ($\simeq T_C$) along the c axis (Kimura *et al.* 1996, 1997).

Specific features due to the two-dimensionality are also observed in the magnetic properties. The recent magnetic neutron scattering measurement on $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ single crystals ($x = 0\cdot4$) provided the evidence for the existence of short-range antiferromagnetic (AF) spin ordering coexisting with the two-dimensional FM fluctuations above $T_C \simeq 120$ K, which could be the origin of carrier localisation in this material (Perring *et al.* 1997). The neutron-diffraction measurements on $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ single crystals ($x = 0\cdot4$) reveal that MnO_6 octahedra are more severely distorted when the carrier is itinerant below T_C than when it is localised above T_C (Mitchell *et al.* 1997; Argyriou *et al.* 1997). These experimental results strongly suggest that the carrier localisation mechanism in layered manganites is very different from that in pseudocubic perovskite manganites in which the enhanced JT effect above T_C narrows the bandwidth W and consequently causes the localisation. The pair density function analysis of pulsed neutron diffraction data for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ single crystals ($x = 0\cdot3$) indicates the presence of large local JT distortion which is comparable to JT distortion in the pseudocubic perovskite manganites, while the crystallographic structure shows a very small JT effect (Louca *et al.* 1998). Heffner *et al.* (1998) reported zero-field muon spin rotation data in single crystals of $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ (i.e. $x = 0\cdot3$) which provided no evidence for two-dimensional spin ordering or predominant ab plane spin correlations above $T_C \simeq 100$ K.

$La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ ($x = 0\cdot4$) exhibits magnetic properties and structural response to carrier delocalisation which are dramatically different from $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ ($x = 0\cdot3$). In the $x = 0\cdot4$ material, carrier delocalisation is accompanied by ferromagnetic interlayer coupling below $T_C \simeq 120$ K as suggested by the DE mechanism, while antiferromagnetic interlayer coupling below $T_C \simeq 100$ K strongly correlates with carrier delocalisation in the $x = 0\cdot3$ oxide (Argyriou 1998). The charge-lattice couplings in these compounds ($x = 0\cdot3$ and $0\cdot4$) are then very

different from each other because this coupling is very sensitive to the e_g orbital character of Mn^{3+} which depends on the amount of doped holes. Moritomo *et al.* (1997, 1998) have investigated lattice effects on the magnetic and transport properties in $(La_{1-z}Nd_z)_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ single crystals ($x = 0\cdot4$) by changing z, where the ionic radius of the Nd^{3+} ion is smaller than that of the La^{3+} ion (Shannon and Prewitt 1970). Reduction of the in-plane Mn–Mn distance with increasing z, which is expected to enhance both the transfer integral t and T_C value, suppresses the FM state, and eventually the FM state disappears at $z \geq 0\cdot4$. Such a contradiction indicates that the suppression of the FM state is ascribed to a variation of the e_g electron character from the two-dimensional $d_{x^2-y^2}$ state having large t to the one-dimensional $d_{3z^2-r^2}$ state having small t. This implies that the resultant reduction of t governs the suppression of the FM state in this system (Moritomo *et al.* 1997, 1998).

These previous reports indicate that the nature of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ depends sensitively upon the competition between the two-dimensional $d_{x^2-y^2}$ state and the one-dimensional $d_{3z^2-r^2}$ state of the e_g orbitals. In particular, the carrier localisation in this system is subject to the type of spin ordering. It is then of great importance to investigate which spin ordering, the spin ordering due to the two-dimensional $d_{x^2-y^2}$ state or the one-dimensional $d_{3z^2-r^2}$ state, governs the carrier localisation. Since the carrier localisation leads to polaronic conduction, electric transport properties could provide significant information on the real feature of spin ordering. From this point of view, the present study has carried out measurements of thermoelectric power, dc conductivity, and dc magnetic susceptibility for the layered manganite $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ ($x = 0\cdot3$) together with the pseudocubic perovskite $La_{2/3}Ca_{1/3}MnO_3$ ($x = 0\cdot33$).

2. Experimental Details

Polycrystalline samples of $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ and $La_{2/3}Ca_{1/3}MnO_3$ were synthesised by reacting La_2O_3, $SrCO_3$, $CaCO_3$ and MnO_2 (Johnson Matthey, 5N Grade) at 1273 K for 48 h on an Al_2O_3 crucible in air. The powders were then reground and further reacted at 1473 K for 24 h. This heating process was repeated a total of three times. The powders were pressed into pellets which were heated in air at 1673 K for 120 h for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ and at 1573 K for 48 h for $La_{2/3}Ca_{1/3}MnO_3$. The densities of the samples were about 70% of the theoretical values. The X-ray diffraction pattern of $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ could be indexed in the body-centred tetragonal unit cell ($I4/mmm$) (Mitchell *et al.* 1997) with $a = b = 3\cdot885$ Å and $c = 20\cdot277$ Å, while the sample of $La_{2/3}Ca_{1/3}MnO_3$ showed the single-phase pattern of pseudocubic perovskite with $a = 3\cdot866$ Å. The oxygen contents were determined by chemical analyses which yielded $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$.

As shown in Fig. 1, X-ray photoelectron spectra (XPS) were measured at room temperature with a commercial X-ray photoelectron spectrometer (PHI ESCA-5600). The base pressure in the chamber was about $3\sim5\times10^{-9}$ Torr. The X-ray source is the monochromatised Al $K\alpha$ line (1486·6 eV) with a combined energy resolution of about 0·75 eV. The Mn $2p_{2/3}$ core level binding energies in both $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ appear at the same level, i.e. 641·8 eV. The XPS results imply that the Mn electronic state is nearly equal in both samples.

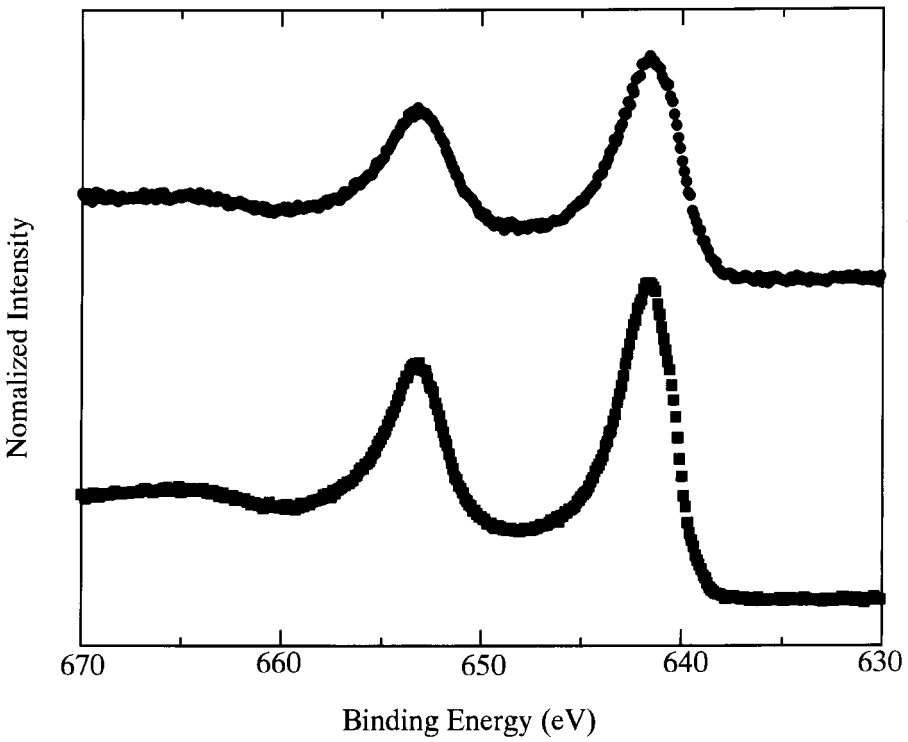

Fig. 1. X-ray photoelectron spectra (XPS) measured at room temperature for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ (circles) and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ (squares).

A Keithley 619 Resistance Bridge, an Advantest TR 6871 digital multimeter and an Advantest R 6161 power supply were used for the conductivity–measurement by the four-probe method. The thermopower was measured with a precision digital multimeter in the temperature range of about 80 to 330 K using a home-made device. The magnetoresistance was measured in a magnetic field of 0·85 T using the magneto of the Hall effect apparatus. The dc magnetic susceptibility was measured as a function of temperature in the warming run with a field of 1 mT, after cooling down to 10 K in the zero field using a SQUID (Quantum Design, MPMS) magnetometer.

3. Results and Discussion

Fig. 2*a* shows the temperature dependence of the dc resistivity for the layered and pseudocubic compounds, i.e. polycrystalline samples of $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ respectively. Sharp drops in the resistivities by more than one order of magnitude are observed around $T_C \simeq 100$ K in $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $T_C \simeq 250$ K in $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$. In each sample, a negative MR has also been observed even in weak magnetic fields like 0·85 T in the vicinity of T_C. The shift of the MI transition point to a higher temperature under the action of the magnetic field suggests a field-induced MI transition in each compound.

As shown in Fig. 2*b*, the steep rise in the magnetisation with decreasing temperature around T_C indicates a phase transition from the PI to FM state.

Although $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ is in the FM state below $T_C \simeq 100$ K, the magnetic susceptibility of this sample is nearly constant between 100 K and 280 K and then decreases gradually with increasing temperature, i.e. a gradual transition to the PI from FM state. Kimura *et al.* (1996) reported the anisotropic carrier motion in a single crystal of $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$. In their result, the metallic behaviour associated with the three-dimensional spin ordering is predominant below T_C. At $T > T_C$, the resistivity along the c axis (ρ_c) exhibits an insulating behaviour, while the resistivity perpendicular to the c axis (ρ_{ab}) involves the MI transition point around 280 K ($>T_C$). Such a markedly anisotropic conduction indicates that the two-dimensional ferromagnetic fluctuations survive up to 280 K (Kimura *et al.* 1996). Potter *et al.* (1998) observed a similar magnetic behaviour

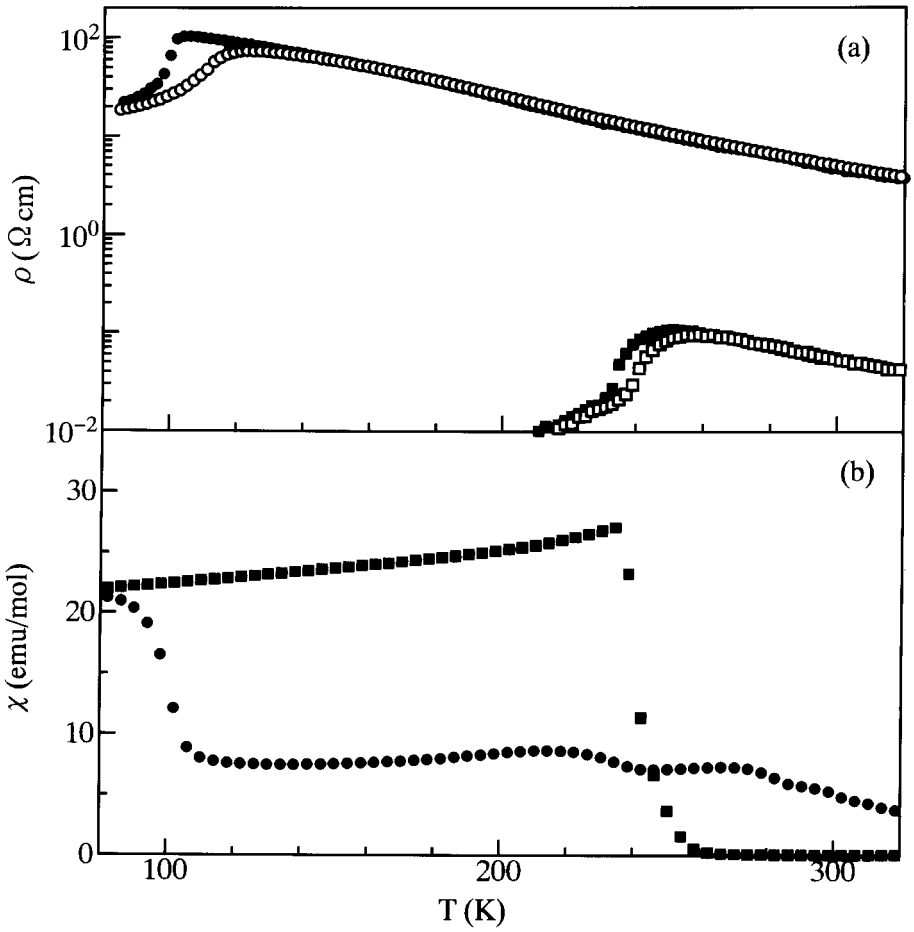

Fig. 2. (*a*) Temperature dependence of the dc resistivity ρ obtained by the four-probe method; solid circles are the experimental plots for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and solid squares for $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ in a zero field. Open circles and squares are for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ in a magnetic field of 0·85 T. (*b*) Temperature dependence of the dc magnetic susceptibility χ in the warming run in a magnetic field of 1 mT after cooling down to 10 K in a zero field; circles are for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and squares for $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$.

on the $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ single crystal to the result of Kimura *et al.* (1996) for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$, but argued that such magnetic signatures in $La_{1\cdot2}Sr_{1\cdot8}Mn_2O_7$ may be due to perovskite intergrowths in the layered manganites. They also suggested that the hump around 300 K is most likely due to impurities or perovskite inclusions.

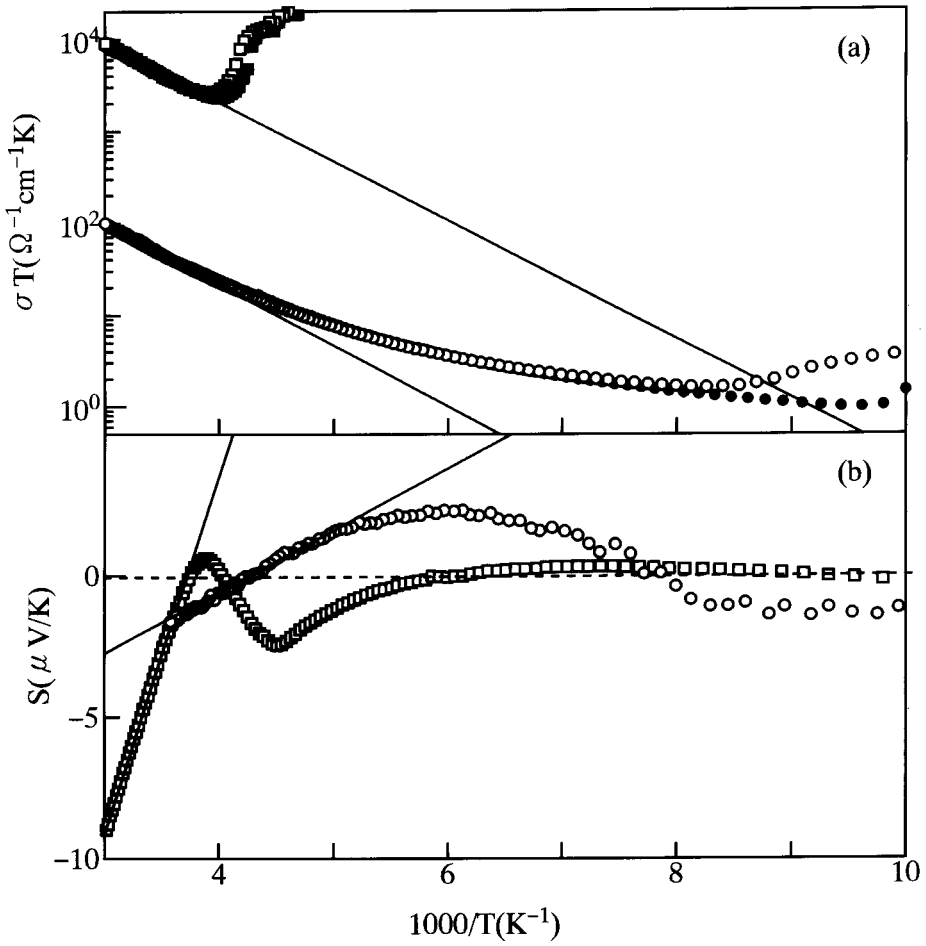

Fig. 3. (*a*) Arrhenius relations σT and $1/T$; solid circles and squares are for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ in a zero field respectively. Open circles and squares are for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ in a field of 0·85 T. (*b*) Relation of S and $1/T$; circles and squares are the experimental plots for $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ and $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ respectively.

In pseudocubic perovskite manganites, the JT distortion enhanced above T_C reduces the Mn–O–Mn bond angles, narrows the bandwidth W, and then leads to the reduction of t (Hwang *et al.* 1995; Millis *et al.* 1994, 1996). Consequently, the carrier localisation is realised above T_C. In the $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ sample, the temperature dependence of the conductivity follows the polaronic relation above T_C as shown in Fig. 3*a*, i.e. $\sigma T \propto \exp(-E_\sigma/k_BT)$ with $E_\sigma = 133$ meV.

The thermoelectric power S would provide important knowledge on the electrical transport because the characteristic energy of the thermoelectric power E_S is much lower than the energy required for the conduction E_σ above T_C, i.e. $E_S \ll E_\sigma$, if a hopping process of small polarons dominates the conduction (Mott and Davis 1971; Mott 1984). The thermoelectric power varies in the PI state as $S = (k_B/e)(E_S/k_BT) + S_\infty$ (Jaime *et al.* 1997*a*, 1997*b*), where S_∞ is the $T \to \infty$ limit of the thermoelectric power which has a negative value (Heikes 1960; Chaikin and Bani 1976). As shown in Fig. 3*b*, the linear relation between S and $1/T$ at $T > T_C$ yields $E_S = 13$ meV and $S_\infty = -47\ \mu$V/K for $La_{2/3}Ca_{1/3}MnO_{2\cdot 98}$. The large difference in magnitudes between $E_\sigma = 133$ meV and $E_S = 13$ meV provides strong evidence in favour of small polaron hopping conduction, excluding the conventional band transport.

In layered manganites, the system is free from the dynamical JT effect as described in the Introduction (Moritomo *et al.* 1997, 1998). In the body-centred tetragonal unit cell ($I4/mmm$), the Mn–O–Mn bond angle along the c axis is set by symmetry to 180°, while the in-plane Mn–O–Mn bond angles are 179° (Mitchell *et al.* 1997; Argyriou *et al.* 1997*a*, 1997*b*). In the $La_{1\cdot 2}Sr_{1\cdot 8}Mn_2O_7$ single crystal, however, MnO_6 octahedra are more severely distorted when the carrier is itinerant than when it is localised (Mitchell *et al.* 1997; Argyriou *et al.* 1997*a*, 1997*b*). Therefore, the carrier localisation mechanism above T_C for layered manganites is very different from that for pseudocubic perovskite manganites in which JT distortion plays an important role in carrier localisation at $T > T_C$. Based upon the magnetic neutron scattering experiments on the $La_{1\cdot 2}Sr_{1\cdot 8}Mn_2O_7$ single crystal, Perring *et al.* (1997) argued that the origin for carrier localisation in this layered compound at $T > T_C$ is the existence of short-range AF spin ordering coexisting with the two-dimensional FM fluctuations. One should note however that the physical profile in the $La_{1\cdot 2}Sr_{1\cdot 8}Mn_2O_7$ single crystal is quite different from the profile in the $La_{1\cdot 4}Sr_{1\cdot 6}Mn_2O_7$ single crystal. In fact, Argyriou *et al.* (1999, present issue p. 279) argue that the carrier delocalisation in $La_{1\cdot 2}Sr_{1\cdot 8}Mn_2O_7$ is accompanied by ferromagnetic interlayer coupling due to the $d_{x^2-y^2}$ state, but by antiferromagnetic interlayer coupling due to the $d_{3z^2-r^2}$ state in $La_{1\cdot 4}Sr_{1\cdot 6}Mn_2O_7$. According to Moritomo *et al.* (1997, 1998), the suppression of the FM state in $(La_{1-z}Nd_z)_{1\cdot 2}Sr_{1\cdot 8}Mn_2O_7$ single crystals is induced by the variation of the e_g electron character from the two-dimensional $d_{x^2-y^2}$ state having large t to the one-dimensional $d_{3z^2-r^2}$ state having small t with increasing z. These facts indicate the competition between $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states in e_g orbitals dominates the characteristic properties in layered perovskite-type manganites.

As shown in Fig. 3*a*, the temperature dependence of the conductivity in the $La_{1\cdot 4}Sr_{1\cdot 6}Mn_2O_{7\cdot 06}$ sample follows the polaronic relation at $T > 280$ K, i.e. $\sigma T \propto \exp(-E_\sigma/k_BT)$ with $E_\sigma = 129$ meV. In Fig. 3*b*, moreover, the linear relation between S and $1/T$ at $T > 280$ K yields $E_S = 2$ meV and $S_\infty = -9\ \mu$V/K. The large difference in magnitude between $E_\sigma = 129$ meV and $E_S = 2$ meV indicates that small polaron hopping conduction takes place at $T > 280$ K. In $La_{1\cdot 4}Sr_{1\cdot 6}Mn_2O_7$, the spin ordering due to the one-dimensional $d_{3z^2-r^2}$ state emerges at T_C but the ordering due to the two-dimensional $d_{x^2-y^2}$ state emerges at 280 K (Kimura *et al.* 1996). This is one of the main reasons for the strong anisotropic transport properties in this material. In fact, there

is no evidence for the two-dimensional spin ordering or predominant *ab* plane spin correlations in the temperature range of T_C to 280 K (Heffner *et al.* 1998). The hopping conduction observed in the $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ sample at $T >$ 280 K in the present study indicates that the spin ordering due to the two-dimensional $d_{x^2-y^2}$ state is predominantly responsible for the carrier localisation. Though Potter *et al.* (1998) insist that perovskite intergrowths in the layered manganites contribute predominantly to such anisotropic conduction transport, the experimental behaviour of the $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ sample obtained in the present study is explained self-consistently by the interpretation of Kimura *et al.* (1996) for anisotropic conduction in this material.

Using the experimental values for S_∞, the theoretical formula in an insulator, i.e. $S_\infty = -(k_B/e)(\ln(\frac{5}{4}) + \ln[c(1-c)/(1–2c)^2])$, yields $c = 0\cdot30$ and $0\cdot23$ for $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ and $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$, respectively, where c is the hole concentration. As for $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$, a good agreement with the nominal value is obtained, but the hole concentration responsible for the hopping conduction in $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ is considerably smaller in comparison with the nominal value. This must be possibly because the small polaron hopping conduction takes place predominantly within the in-plane MnO_2 sheets, although polycrystalline ceramic samples are employed in the present study.

4. Conclusion

Measurements of thermoelectric power, dc conductivity and dc magnetic susceptibility have been carried out on $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$ and $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ ceramic samples. Each compound exhibits the MI transition and negative MR in the vicinity of T_C. In $La_{2/3}Ca_{1/3}MnO_{2\cdot98}$, the JT distortion is enhanced remarkably above $T_C \simeq 250$ K and the reduction of W leads to the formation of small polarons of holes.

$La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ is in the FM state at $T < T_C \simeq 100$ K and exhibits insulating behaviour at $T > T_C$. The dc magnetic susceptibility between 100 K and 280 K is nearly constant and decreases gradually with increasing temperature above 280 K. The dc resistivity and thermoelectric power measurements indicate polaronic conduction at $T > 280$ K. This is interpreted in terms of a carrier localisation mechanism quite different from the localisation in pseudocubic perovskite-type manganites. The emergence of spin ordering due to the one-dimensional $d_{3z^2-r^2}$ state and the two-dimensional $d_{x^2-y^2}$ state at different temperatures, i.e. $T_C \simeq 100$ K and 280 K, brings about the markedly anisotropic transport properties in the $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_7$ single crystal. The spin ordering due to the two-dimensional $d_{x^2-y^2}$ state taking place at $T > 280$ K is related directly to the hopping conduction above 280 K observed in the present study. This implies that the two-dimensional $d_{x^2-y^2}$ state extending within the MnO_2 sheets starts to narrow and leads to the carrier localisation around 280 K.

The effective number of holes in the $La_{1\cdot4}Sr_{1\cdot6}Mn_2O_{7\cdot06}$ sample estimated from the thermoelectric power at $T \to \infty$ is considerably smaller than the nominal value. This suggests that small polaron hopping conduction takes place predominantly within the in-plane MnO_2 sheets.

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