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Thermally activated drift mobility and small polaron conduction in $La_{0.75}Sr_{0.11}Ca_{0.14}MnO_3$ thin films investigated by the traveling wave method

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We have clearly observed the thermal activation of the drift mobility in $La_{0.75}Sr_{0.11}Ca_{0.14}MnO_3$ thin films above the Curie temperature. The drift mobility rises from 2.2×10^{-2} cm^2/Vs at 300 K to about 9.2×10^{-2} cm^2/Vs at 410 K with activation energy of 171 meV. The measurements of the drift mobility were made using the traveling wave method. Our results are in agreement with small polaron theory, which indicates that the conduction in the paramagnetic-insulator state of manganite films is dominated by thermally assisted hopping of small polarons. [S0163-1829(99)50934-X]

The transport mechanism in the paramagnetic-insulator state of the manganites initially was considered to be dominated by spin-disorder scattering. Recently, it is generally realized that the presence of polarons in doped lanthanum-based transition-metal oxide perovskites plays an important role in the transport properties of these materials.[1–6] A stable polaron in an ionic solid may be either a large polaron or a small polaron. Lattice distortion is associated with a large polaron that moves itinerantly extending over a wide spatial range. In contrast, small polarons move only by tunneling or thermally activated hopping and the lattice distortion extends over only one or few atomic sites.[7] The formation and transport properties of small polarons in strong electron-phonon coupled system were first discussed in disordered materials[8] and later extended to crystals.[9] Recently, Hall and thermopower measurements[10–14] have been used to investigate the transport properties in lanthanum-based transition-metal oxide perovskites. Although the Hall-effect sign anomaly has been taken as evidence for small polaron conduction in the manganites,[11] the most distinctive character of small polaron hopping conduction is the thermal activation of the drift mobility as pointed out by Emin and Holstein.[15]

In order to gain insight into the nature of the transport mechanism, we adopt the traveling wave (TW) method to investigate the transport properties of $La_{0.75}Sr_{0.11}Ca_{0.14}MnO_3$ thin films. Since it was introduced by Adler *et al.*,[16] the TW method has been utilized to investigate transport processes in amorphous semiconductors for several years.[17–19] One of the characteristics of this method is the possibility to get information on the transport mechanism in materials that have high resistance and low mobility.

In this paper, we used the TW method to measure conductivity and drift mobility in the paramagnetic-insulator state of $La_{0.75}Sr_{0.11}Ca_{0.14}MnO_3$ thin films at different temperatures. Thermal activation of the drift mobility in lanthanum-based manganites is clearly observed, which is a powerful evidence for thermally assisted hopping conduction of small polarons.

The samples were fabricated by pulsed laser deposition method using $La_{0.75}Sr_{0.11}Ca_{0.14}MnO_3$ ceramic target. A 248 nm KrF excimer laser source with 5 Hz in repetition rate and 30 ns in pulse width was used. The average laser energy density was 2.5 J/cm^2. The target and the substrate holder were rotated during the deposition. The films were deposited on fused silica substrates, with a thickness of 500 nm, at 800 °C in 30 Pa of oxygen. Immediately after the deposition the films were *in situ* annealed at 850 °C in pure oxygen of 0.5 atm for 1 h. A more detailed description on sample preparation procedure has been published in our previous work.[20] The chemical composition of the films was analyzed by inductively coupled plasma quantemeter (ICP). The results of ICP measurement show that the films are stoichiometry. The samples are single phase, as checked by x-ray diffraction. The Curie temperature T_C of the target used in this paper is 280 K. To meet the need of the TW measurements, coplanar electrodes with a distance of 1 mm were deposited by evaporation. The measurements were carried out in vacuum.

A schematic diagram of the traveling wave experiment is shown in Fig. 1. The sample is placed above the surface of $LiNbO_3$ single crystal plate with a gap of 12 μm. The transducers on the $LiNbO_3$ generate a surface acoustic wave (SAW) that propagates along the surface of the $LiNbO_3$ plate in $+z$ direction. Due to the piezoelectric properties of $LiNbO_3$, an electric field associated with the SAW couples into the sample to bunch the carriers into charge packets and drifts these carriers through the material, consequently an acoustic electronic direct current is produced and can be measured from two electrodes. Fritzsche and Chen and co-workers[17–19] have derived the relationship between drift mobility and the acoustic-electric current or the acoustic-electric voltage, as the following:[19]

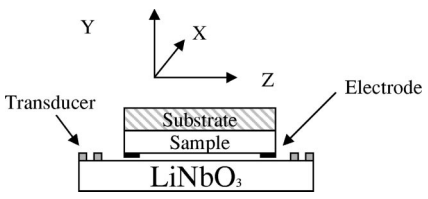

FIG. 1. A schematic diagram of the traveling wave experiment.

$$\mu=\frac{2I_{ae}v_s}{w\Phi_0 k\sigma\sinh(kd)[(|A|^2+|B|^2)\cosh(kd)-2(A\cdot B)\sinh(kd)]}, \tag{1}$$

$$\sigma=\frac{I_{ae}L}{V_{ae}dw}, \tag{2}$$

where I_{ae} is the short-circuit acoustic electronic current, V_{ae} the open-circuit acoustic-electronic voltage, k the wave vector of the SAW, v_s the velocity of the SAW, d the thickness of the sample, L the distance between the electrodes, w the width in the x direction of the sample. The symbol Φ_0 is the potential at the surface of the piezoelectric plate and is calculated from the power of the SAW.[21]

The coefficients A and B depend on the conductivity and the dielectric constant of the sample and the substrate. They can be described as

$$A=[\cosh(kh)+\epsilon^*(B/A)\sinh(kh)]^{-1}, \tag{3}$$

$$B/A=(\epsilon_s+\epsilon^* kd)/(\epsilon^*+\epsilon_s kd), \tag{4}$$

$$\epsilon^*=\epsilon-i4\pi\sigma/\omega, \tag{5}$$

where h is the gap between the sample and the piezoelectric plate, ϵ_s the dielectric constant of the substrate, ϵ the dielectric constant of the sample, ω the frequency of the SAW.

TW method can be used to investigate the transport process in the materials with high resistivity and low mobility, for which Hall measurement meets some difficulties. The transport process in doped La-based manganites in the paramagnetic state is semiconductorlike, and these materials have high resistivity and the mobility is rather low. At this case, TW method is suitable and advantageous to be used to investigate these materials. Therefore we can obtain conductivity and drift mobility with I_{ae} and V_{ae} from Eqs. (1) and (2), as all the other quantities are either known or measurable. The sign of I_{ae} depends on the type of majority carriers and the direction of the SAW. Since the direction of the SAW is controlled by the experiments, the type of majority carriers can be directly determined from the sign of I_{ae}.

The conductivity of the films was measured by TW method over the temperature range from 300 to 400 K. The conductivity obtained by TW method is in good agreement with that derived from normal I-V measurements. The value from TW method is 1.6×10^{-2} S/cm and the value from I-V measurement is 1.8×10^{-2} S/cm at room temperature. The temperature dependence of the conductivity is shown in Fig. 2(a). The conductivity increases with increasing temperature and extends from $1.6\times10^{-}2$ S/cm at 300 K to 9.6×10^{-2} S/cm at 400 K, which shows that the conduction property of the samples above T_c is semiconductorlike. This conduction behavior is consistent with that previously reported. We plot $\ln(\sigma T)$ vs $1000/T$ in Fig. 2(b). It is obvious that there is a well linear relationship between $\ln(\sigma T)$ and $1/T$, which means that $\sigma\propto(1/T)\exp(E/T)$.

In a small polaron model, the dominant transport mechanism at high temperatures is the thermally activated hopping of the carriers, with the conductivity and the mobility[10]

$$\sigma=\frac{c(1-c)e^2}{\hbar a}\left(\frac{T_0}{T}\right)^s\exp\left(-\frac{E_0+(W_H-J^{3-2s})}{k_BT}\right), \tag{6}$$

$$\mu=\frac{c(1-c)ea^2}{\hbar}\left(\frac{T_0}{T}\right)^s\exp\left(-\frac{W_H-J^{3-2s}}{k_BT}\right), \tag{7}$$

where a is the hopping distance, J the transfer integral, c the polaron concentration, E_0 the energy difference between identical lattice distortions with and without the hole or electron, and W_H is one half of the polaron formation energy E_p. When the adiabatic limit is kept, s is equal to 1 and k_BT_0

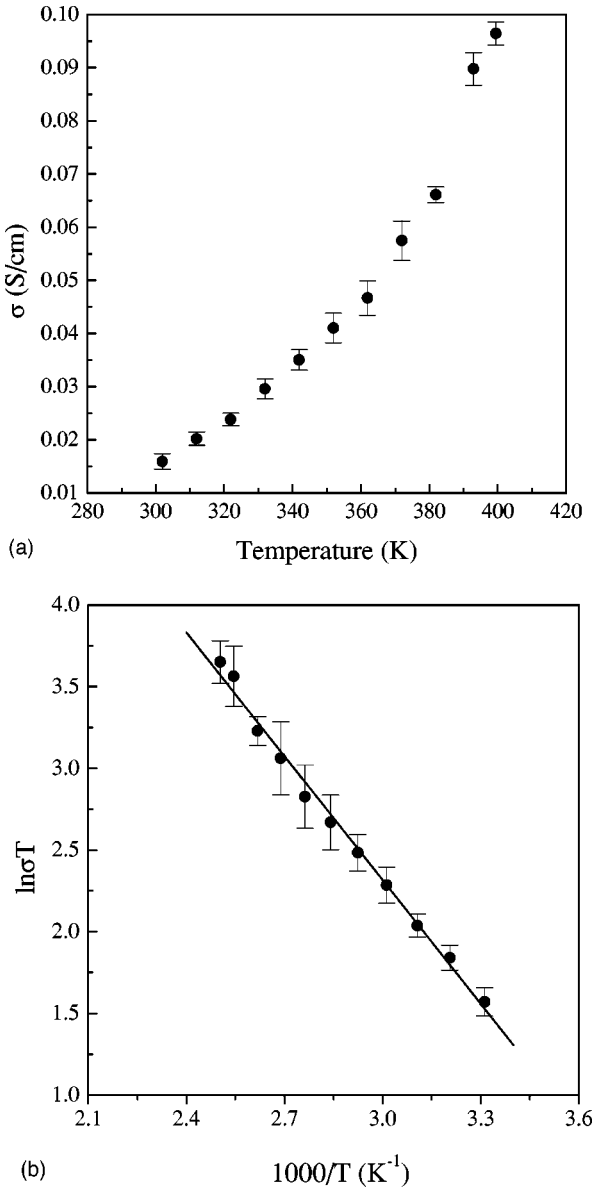

FIG. 2. (a) The resistivity vs temperature. (b) The resistivity plotted in the adiabatic limit. The fine line is a linear fit indicating an activation energy of 219 meV.

$=h\omega_0/2\pi$, where ω_0 is the optical phonon frequency.[22] In the nonadiabatic limit, $s=3/2$ and $k_BT_0=(\pi J^4/4W_H)^{1/3}$. As shown in Fig. 2(b), our finding is consistent with a small polaron hopping model in the adiabatic limit. The activated energy of the conductivity E_σ is obtained to be 219 meV.

The drift mobility of the films in the temperature range from 300 to 410 K was also measured by TW method, as shown in Fig. 3(a). The drift mobility at 300 K is about $2.2\times10^{-2}\,\mathrm{cm^2/Vs}$, which approaches to the mobility ($0.03\,\mathrm{cm^2/Vs}$) given in Refs. 11 and 23. The value obtained for the drift mobility in our samples is much smaller than 1 $\mathrm{cm^2/Vs}$, which is a distinct character of small polarons. The drift mobility increases with increasing temperature and extends to $9.2\times10^{-2}\,\mathrm{cm^2/Vs}$ at 410 K. We plot the $\ln(\mu T)$ vs $1000/T$ in Fig. 3(b). The thermal activation of the mobility is clearly observed and the activation energy E_d is 171 meV, which is also evidence for the thermally assisted hopping conduction of small polarons. The purely magnetic polarons also can be formed and may affect the transport processes in the manganites. The mobility of the purely magnetic polaron is diffusive in nature, it has a power law rather than thermally activated temperature dependence.[24] However, from Fig. 3, it is obvious that the temperature dependence of the mobility is thermally activated. This result shows that the polarons in manganites are not purely magnetic polarons but lattice polarons that are the carriers self-localized by the lattice distortions.

From Eqs. (6) and (7), the energy E_0 and the polaron formation E_p are obtained to be 48 meV and 342 meV, respectively. The energy E_0 is significantly smaller than the activation energy of the conductivity E_σ (219 meV), which can be taken as evidence of the small polaron motion.[11] The energy E_d (171 meV) is much larger than the activation energy of the Hall coefficient (91 meV) from Hall measurements.[11] In the small polaron model, the activation energy of the drift mobility is always more than that of the Hall mobility E_H.[11] The sign of I_{ae} in our work shows that the behavior of the majority carriers in the films is electronlike, and the carrier concentration is about $4.5\times10^{18}/\mathrm{cm^3}$ at room temperature.

In conclusion, we have investigated the transport mechanism in the paramagnetic-insulator state of manganite films by the traveling wave method. The conductivity and the drift mobility of the manganite films were measured at different temperatures. The drift mobility at room temperature is much smaller than 1 $\mathrm{cm^2/Vs}$ as predicted by a small polaron model. Thermal activation of the drift mobility in manganites has been clearly observed. This means that lattice polarons are present in the manganites and the transport mechanism in the paramagnetic-insulator state of the manganites is dominated by thermally assisted hopping of small polarons.

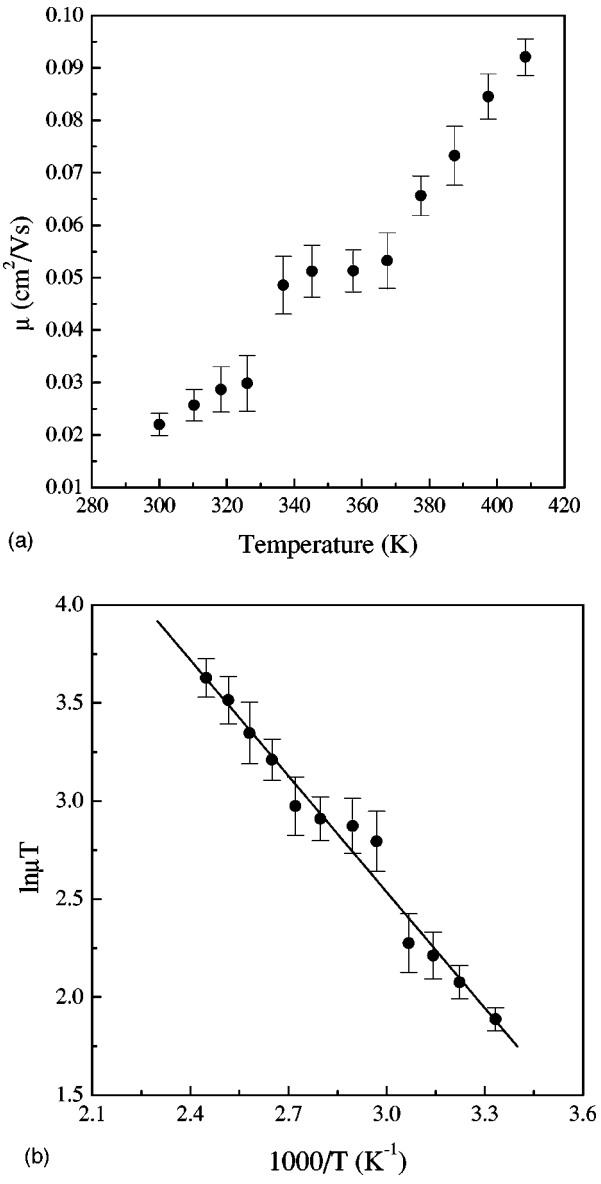

FIG. 3. (a) The drift mobility vs temperature. (b) The drift mobility plotted in the adiabatic limit. The fine line is a linear fit indicating an activation energy of 171 meV.

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