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Thermal conductivity and infrared spectra study of polycrystalline $La_{0.67}Ca_{0.33}MnO_3$

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Abstract

The thermal conductivity and infrared transmission spectra of $La_{0.67}Ca_{0.33}MnO_3$ are investigated systematically. The thermal conductivity increases abruptly as the temperature is decreased through the Curie temperature. The effective charge carriers number and the frequency of transverse optic phonon corresponding to the stretching mode also increase dramatically along with decreasing temperature near Curie temperature. Combining our observation with previous reported results, we ascribe the abrupt change of thermal conductivity to the itinerating of the charge carriers due to the remarkable reduction of Jahn–Teller distortion below the Curie temperature.

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The discovery of "colossal" magnetoresistance (CMR) [1] and its potential application have stimulated considerable interest on structural, magnetic and transport properties of these materials. In particular, a large fraction of investigations in manganites focuse on $La_{1-x}Ca_xMnO_3$ series since these are the ones that present the largest CMR effects [2–4], which are associated with the presence of charge ordering tendencies. The complete phase diagram of the intermediate-bandwidth manganites had already been obtained [5]. Among the $La_{1-x}Ca_xMnO_3$ series, the $x = 0.33$ compound has relative higher Curie temperature and thus attracts considerable attention. The ground state of this hole-doped manganese oxide is ferromagnetic, exhibits a paramagnetic insulator (PI) to ferromagnetic metal (FM) transition near the Curie temperature (T_C) excepting the CMR effect. The magnetic and electronic properties have traditionally been examined within the framework of "double exchange (DE)", which considers the magnetic coupling between Mn^{+3} and Mn^{+4} that results from the motion of an electron between the two partially filled d shells with strong on-site Hund's coupling [6–8]. But now it is shown that DE alone is insufficient to explain all magnetotransport properties and that the Jahn–Teller effect and strong electron–phonon interaction must be taken into account [9,10].

Since the thermal conductivity cannot only reflect the phonon–phonon interaction but also represent the electron–phonon coupling, we investigate the temperature dependence of the thermal conductivity for $La_{0.67}Ca_{0.33}MnO_3$ sample at different magnetic fields in the present Letter. We also present a systematic measurement of the infrared transmission spectra of the sample between 10 and 290 K to reveal more information related to electron–phonon coupling on this compound.

$La_{0.67}Ca_{0.33}MnO_3$ powder sample was synthesized via sol–gel route (Pechini process) [11] in order to obtain well mixed reagents. The powders were pressed into discs and sintered at 1623 K for 24 h and then furnace cooled to room temperature. Finally, the discs were annealed in O_2 at 1173 K for 48 h to

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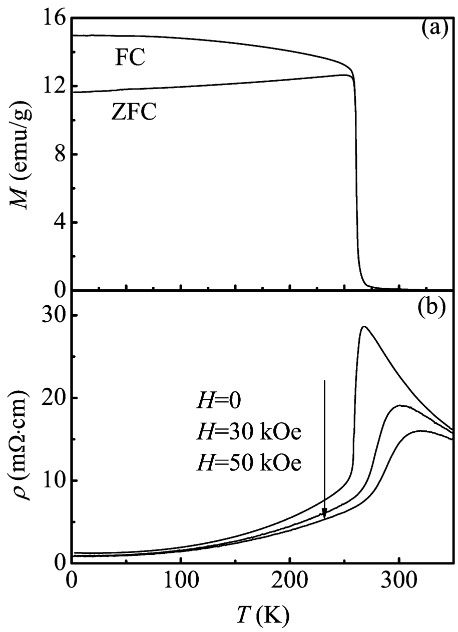

Fig. 1. (a) Magnetization versus temperature under 100 Oe for $La_{0.67}Ca_{0.33}MnO_3$ measured at zero-field cooling and field cooling mode. (b) Temperature dependence of the resistivity of the $La_{0.67}Ca_{0.33}MnO_3$ under different applied fields.

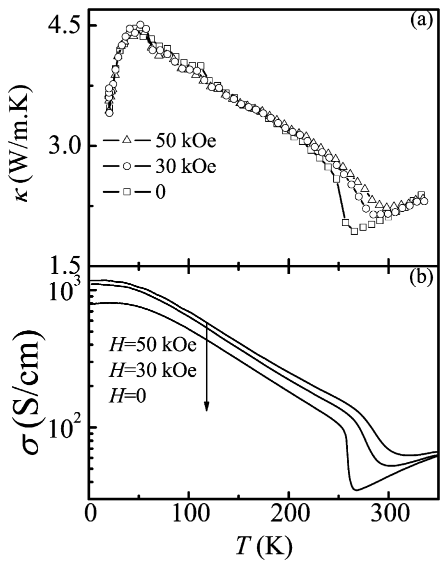

Fig. 2. (a) Thermal conductivity, and (b) electrical conductivity vary as functions of temperature for $La_{0.67}Ca_{0.33}MnO_3$ under different magnetic fields.

avoid oxygen inhomogeneity. The phase analysis and the structure of the sample were identified by X-ray diffraction (XRD) analysis using Rigaku X-ray diffractometer ($D/\max{-}2500\times$) at room temperature. Infrared transmission spectra were collected on a WQF-410 Fourier Transform Infrared Spectrometer (FTIS), and the wave number varied from 400 to 4000 cm^{-1}. In the measurement, the polycrystalline compound was finely milled, diluted in KBr (1 : 100 in weight), and pressed into pellets with 0.5 mm in thickness. Magnetic measurements were made using a vibrating sample magnetometer (VSM) which is equipped in a physical properties measurement system (PPMS-6000, Quantum Design). The resistivity measurements were carried out by a standard four-probe method. The thermal conductivity was measured by a four-probe leads configuration method, in which two calibrated Cernox 1050 thermometers are used to measure the temperature of hot and cold probes, respectively. The pressure in the sample chamber is less than 1×10^{-4} Torr during the measurements.

The X-ray patterns indicate that the sample is single phase, and the diffractograms can be indexed in the *Pnma* space group. The corresponding lattice constants at room temperature are $a = 5.3229$ Å, $b = 7.6821$ Å and $c = 5.6072$ Å, respectively, which is quite identical to that in previous reports [12]. Fig. 1(a) shows the temperature dependence of the magnetization recorded at zero field cooling (ZFC) and field cooling (FC) mode under 100 Oe. Both the ZFC and FC curves show a sharp paramagnetism to ferromagnetism transition and the transition temperature, defined as the temperature of the maximum slopes in $|dM/dT|$, is 261.2 K [4,13,14]. The temperature dependence of the resistivity under different magnetic fields is shown in Fig. 1(b). In zero field, a sharp metal–insulator (M–I) transition peak appears around 267 K, which is close to the magnetic ordering temperature. When a magnetic filed is applied, the M–I transition temperature is increased and the resistivity at a given temperature is decreased, which is the CMR characteristics of the manganites. The magnetic and electrical transport properties of the $La_{0.67}Ca_{0.33}MnO_3$ are consistent with that reported by other group [15–17], which indicates the high quality of our sample.

Fig. 2 shows the temperature dependence of the thermal conductivity $\kappa(T)$ and the electrical conductivity $\sigma(T)$ of the $La_{0.67}Ca_{0.33}MnO_3$ sample under different magnetic fields. From Fig. 2(a) one can see that the magnitude of $\kappa(T)$ lies in the range of 2–4.5 W/(m K) typical for amorphous materials [18]. The value of $\kappa(T)$ decreases with decreasing temperature down to T_C, which has been attributed to local anharmonic lattice distortions associated with small polarons [18]. The increase of thermal conductivity with decreasing of temperature well below T_C is due to a reduction in umklapp scattering, and the peak of $\kappa(T)$ at 50 K can be attributed to a crossover from umklapp-limited to defect-limited scattering [18]. In the ferromagnetic–paramagnetic phase transition range a sharp increase of thermal conductivity is found. In magnetism, the sample experiences a spin disordered to spin ordered states transition through the Curie temperature. However, it is reported that even maximal spin disorder does not scatter electrons very much [19]. Hence, the suppression of spin scattering increases the thermal conductivity somewhat, but its contribution is negligible [20]. Visser et al. [18] attribute the abrupt increase of thermal conductivity near Curie temperature to two reasons: the first originate from the reduction in phonon–phonon scattering due to local Jahn–Teller disorder, and the second is an enhanced electronic contribution due to the reduction in electron–phonon scattering. However, which is the dominant reason is still enigmatic.

Recently, we investigated the thermal conductivity of the charge ordered $Nd_{0.75}Na_{0.25}MnO_3$ manganite [21]. The resistivity of $Nd_{0.75}Na_{0.25}MnO_3$ increases with decreasing temperature at zero field, i.e., it reveals insulator behavior and the