Ultrasonic Study of La$_{0.7}$Ca$_{0.3}$MnO$_3$

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We have measured the resistivity and the ultrasonic sound velocity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ as functions of temperature and magnetic field. As the temperature is lowered through $T_c$, where the magnetic phase transition occurs, the sound velocity increases rapidly in the narrow temperature region around $T_c$. The region where the velocity change occurs shifts up to higher temperatures, as a larger magnetic field is applied. The qualitative behavior of the sound velocity as a function of temperature may be explained in terms of phonon hardening which is due to the combined effect of the double-exchange and the strong electron-phonon interaction.

Key words: double exchange, magnetoresistance, ultrasound, phonon-hardening

1. Introduction

Perovskite manganites with mixed manganese valence, La$_{1-x}$D$_x$MnO$_3$, where D is divalent metal, has been paid much recent attention because of the colossal magnetoresistance (CMR) effect for 0.2<x<0.4. In this composition range, the system shows the simultaneous appearance of metallic conduction and ferromagnetism at low temperatures. This correlation between transport and magnetism has been traditionally explained by the double-exchange model (DEM) which was originally proposed by Zener. The DEM assumes a strong on-site Hund coupling $J_H$ between the localized $t_{2g}$ and itinerant $e_g$ electrons in Mn $d$ orbitals. The $e_g$ electrons can hop from a Mn site to another Mn site via the intermediate oxygen $2p$ orbital, and this itinerancy is represented by the hopping integral $t$. The DEM refers to the situation in which $t \ll J_H$ and the hopping integral $t$ is given by $t = t_0 \cos \theta / 2$ where $t_0$ denotes the bare value and $\theta$ is the angle between neighboring localized spins.

Despite the success of the DEM in accounting for some qualitative features of the CMR system, for example, the increase of the ferromagnetic transition temperature ($T_c$) and decrease of resistivity ($\rho$) in the presence of a magnetic field, it is becoming increasingly clear that the DEM may not be the solely relevant physics of the system. Millis et al. asserted that the polaron effect due to a strong electron-phonon coupling is needed as an additional physics in the system. Indeed, it is known that a Mn$^{3+}$ ion in an octahedral oxygen environment exhibits a static Jahn-Teller (JT) effect and the JT effect would induce a strong electron-phonon coupling. There are many experimental evidences indicating the importance of the electron-phonon (lattice) coupling in perovskite manganites. $T_c$ and magnetoresistance (MR) depend sensitively on Mn-O-Mn bond angles and/or bond lengths. The application of a hydrostatic pressure increases $T_c$ monotonically and strongly suppresses the magnitude of MR. An anomalous thermal expansion and a large magnetovolume effect are observed around $T_c$. In particular, the discovery by Zhao et al. of the oxygen isotope shift of $T_c$ in La$_{0.8}$Ca$_{0.2}$MnO$_3$ lends support to the JT polaron formation. In this paper, we report the results of ultrasonic study on La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO), which is a representative CMR system.

2. Experiments

LCMO samples were made by the conventional solid-state reaction processing from the powders of La$_2$O$_3$, CaCO$_3$, and MnO$_2$. The resistance and magnetoresistance were measured with the four-probe method. The longitudinal sound velocity was measured for a disk-shaped sample (diameter 10 mm, thickness 3.5 mm) with a phase sensitive detection system, adopting the standard pulse echo method at 13.3 MHz.

3. Results and Discussion

In Fig. 1, we show the resistivity and the sound velocity of LCMO as functions of temperature ($T$) and magnetic field ($B$). In the inset of Fig. 1(a) shown is $\rho$ at zero field, normalized to the value at 260 K, as a function of $T$ on a wide scale. $\rho$ increases as $T$ is lowered, and reaches a maximum at $T_c = 239.2$ K. Below $T_c$, $\rho$ decreases as $T$ is further reduced. Fig. 1(a) is the plot of resistivity at several field strengths in the region where the measurements of the sound velocity were carried out. In accordance with various previous reports, the resistivity peak shifts up to higher $T$ as $B$ is increased. Fig. 1(b) displays the sound velocity of LCMO as a function of $T$ and $B$. The velocity data are normalized to the value at $T = 260$ K and $B = 0$ T. It should be noted that as $T$ decreases, there occurs a sharp increase of a few percent in sound velocity (phonon-hardening) in the same temperature region as $\rho$ goes through a maximum. The figure also reveals that the phonon-hardening moves to higher $T$ in the same fashion as $\rho$ does, as larger fields are applied. This indicates that the phonon degrees of freedom are strongly coupled to the electronic ones, and that the phonon-hardening is related to the phase transition of
Fig. 1 (a) Resistivity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ as functions of temperature and magnetic field. The data are normalized to the value at 260 K and zero field, and the field strengths are indicated in the figure. The inset shows resistivity at zero field on a wide temperature scale. (b) The ultrasound velocity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ as a function of temperature at various magnetic fields. The data are normalized to the value at 260 K and zero field.

Electronic origin.

Recent theoretical works$^{15,16}$ stressed the importance of the electron-phonon coupling in the CMR system; however, the focus of these studies were on the transport properties. Lee and Min$^{17}$, on the other hand, studied the phonon property of the CMR system as well with a model combining the DEM and the lattice polaron. For the sake of completeness, we briefly summarize this model: consider a Hamiltonian,

$$\mathcal{H} = t_0 \cos \frac{\theta}{2} \sum_{\langle i,j \rangle} c_i^\dagger c_j + \sum_q \omega_q a_q^\dagger a_q$$

$$+ \sum_{iq} c_i^\dagger c_i e^{iq \cdot \vec{R}} M_q (a_q + a^\dagger_{-q}),$$

(1)

where $c$ and $a$ denote electron and phonon operators, respectively. The first term is the double exchange with nearest neighbor hopping, the second one represents the bare phonon energy, and the last one is the electron-phonon interaction with a coupling strength $M_q$. To calculate $\rho$, the double-exchange part is treated within the mean field theory$^{18}$, in which $\cos(\theta/2)$ is replaced by the thermal average $\langle \cos(\theta/2) \rangle \equiv \gamma(T)$. $\rho$ calculated with this model exhibits a peak as $T$ decreases through $T_c$, and this peak corresponds to the crossover from the self-trapped small polaron state to the quantum tunnelling band regime$^{19}$. The polaron bandwidth, proportional to $\gamma(T)$, increases with decreasing $T$ or external magnetic field. Thus this combined model of the double exchange and the small polaron physics provides a qualitative explanation of the magnetotransport phenomena in CMR.

Due to the electron-phonon interaction of Eq. (1), the phonon frequency is altered from the bare value, and the renormalized phonon frequency $\tilde{\omega}_q$ is given by

$$\tilde{\omega}_q^2 = \omega_q^2 - 2\omega_q |M_q|^2 \frac{1}{\gamma(T)} \sum \frac{n_{\tilde{\xi}} - n_{\tilde{\xi} + \xi}}{t_{\tilde{\xi} + \xi} - t_{\tilde{\xi}}}$$

(2)

where $t_\xi$ and $n_\xi$ are the transfer integral and the electron number operator, respectively. Since the summation has a very weak temperature dependence, Eq. (2) can be written succinctly as $\tilde{\omega}_q = \sqrt{\omega_q^2 [1 - \tilde{\beta}/\gamma(T)]}$, where $\tilde{\beta}$ contains all the temperature independent terms. The essence of the physics contained in this expression is very simple, that is, the ability of electrons to screen the phonons varies as a function of temperature, since $\gamma(T)$, which determines the electron mobility, is temperature dependent.

Since the sound velocity is proportional to $\tilde{\omega}_q$, we can easily compare our data to the theoretical result. It should be noted that the above result would be valid for both acoustic and optical phonon modes; indeed, the optical phonon modes show a similar behavior as a function of $T$.$^{20}$ The measured sound velocity and theoretically calculated one are compared in Fig. 2(a). Both are the results at zero magnetic field. In generating the theoretical curve, $T_c$ was set at 240 K, and the value of $\tilde{\beta}$ was 0.33. It is seen that the velocity change with decreasing $T$, i.e., phonon-hardening, is qualitatively reproduced. Thus it seems that Lee and Min’s model captures the essential physics. However, it is also clear that the undeniable discrepancy between the experimental data and the theoretical curve persists at all temperatures. This discrepancy is a major problem, even if we take the mean field nature of the theory into consideration. Another problem of the model, which cannot be disregarded, is that the field dependence of $\gamma(T)$ is too weak to account for the shift of phonon-hardening to higher temperatures in the presence of a magnetic field. Fig. 2(b) illustrates this point: $\gamma(T)$ calculated from the mean field theory at two values of magnetic field, $B = 0$ T and $B = 1$ T, is plotted. The two curves are barely distinguishable except for the region around $T_c$. 

Fig. 2 (a) The relative change in the longitudinal sound velocity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ at zero field is plotted against temperature. The open circles denote experimental data, while the solid line does theoretical values. (b) $\gamma(T)$ calculated at two different field values from the theory is plotted. The magnetic field has only a weak effect on $\gamma(T)$.

From the present ultrasonic study, one can draw the following conclusion: notwithstanding the current available theory combining the DEM and the small polaron effect captures certain essential aspects of the CMR phenomena, it falls short in fully accounting for the experimental results. We suggest that one important ingredient, which should be incorporated into the theory, is the electron redistribution effect. The electron redistribution effect differs from the screening effect, represented by $\gamma(T)$, in that it takes into account the band structure of a material. Kittel noted that as the strains of the ultrasound propagating through a solid should cause a change in the band structure, electrons would try to redistribute themselves to lower its energy and this effect would lead to a change in sound velocity. The redistribution effect seems even more important for LCMO than for ordinary solids, considering the half-metallic nature of the LCMO band structure.

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References
14) Although the magnetic phase transition point $T_c$ is slightly lower than the temperature $T_p$ at which a maximum in resistivity occurs, these two can used interchangeably for our purpose. See S.H. Park, Y.H. Jeong, K.-B. Lee, and S.J. Kwon: *Phys. Rev. B.*, **56**, 67 (1997).