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Anomalous Phonon-Spin Scattering in $La_{1-x}Sr_xMnO_3$

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The temperature dependence of the phonon thermal conductivity $\kappa(T)$ of $La_{1-x}Sr_xMnO_3$ ($0.11 \leq x \leq 0.20$) polycrystals was measured from 60 K to 360 K. For $x = 0.155$ and 0.170, $\kappa(T)$ is markedly reduced over a wide temperature range near the ferromagnetic transition temperature T_c. The analyses of $\kappa(T)$ have revealed the existence of anomalously strong phonon scattering caused by the coupling of spin fluctuations and the lattice instability in this double exchange coupled system.

KEYWORDS: $La_{1-x}Sr_xMnO_3$, thermal conductivity, ferromagnetic order, phonon-spin scattering, sound velocity

Carrier-doped lanthanum manganites with perovskite-based structures have renewed the interest of researchers. Although numerous studies were performed a long time ago,[1-3] the physical properties of these compounds are quite novel even at present.[4-8] The electrical resistivity $\rho(T)$ of $La_{1-x}Sr_xMnO_3$ conspicuously decreases below the ferromagnetic transition temperature T_c, sometimes displaying a kind of metal-insulator transition. This has been explained as being due to the double exchange mechanism between doped carriers and localized Mn spins, resulting in the effective ferromagnetic interaction between Mn^{3+} and Mn^{4+} ion pairs. The fundamental properties of this system may be explained by the double exchange mechanism, but dramatic physical properties such as colossal magnetoresistance[4-8] and magnetic field induced structural transition[9, 10] are staged as a result of the competition between various mechanisms, i.e., the antiferromagnetic superexchange, Jahn-Teller effect, structural instability due to ion-radius mismatching, charge-ordering and orbit-ordering besides the double exchange mechanism. However, the most important competition might be that between the electron system (itinerant or localized) and the lattice system. In a previous paper,[11] we reported sound velocity (v_s) anomalies associated with the charge-ordering and the magnetic ordering in $La_{1-x}Sr_xMnO_3$. In this paper, we report an anomalous enhancement in phonon scattering by spin fluctuations in a wide temperature range around T_c. The anomalous phonon scattering enhancement occurs for the Sr concentration x near the structural instability from the orthorhombic to rhombohedral phase.

$La_{1-x}Sr_xMnO_3$ ($x = 0.11$–0.20) samples were prepared from stoichiometric mixtures of La_2O_3, $SrCO_3$ and Mn_3O_4 powders. The mixtures were calcined at 1000°C for 24 h in air, pressed into pellets and then sintered at 1500°C for 8 h in air. The measured densities of each sample are higher than 80% of that of the ideal one. All the samples were confirmed by means of X-ray diffraction to be in a single phase at room temperature. The thermal conductivity $\kappa(T)$ was measured by a steady-state heat flow method between 60 K and 360 K. For $\kappa(T)$ measurement below 280 K, a Gifford-McMahon cycle helium refrigerator was used. For measurement above 280 K, the samples were remounted on a temperature controlled hot stage in a vacuum chamber. AuFe(0.07 at.%)-chromel and chromel-alumel thermocouples were used as thermometers for below and above 280 K, respectively.

Figures 1(a)–1(c) show the thermal conductivity of $La_{1-x}Sr_xMnO_3$ for $x = 0.170$, 0.155 and 0.145 as a function of temperature T. The sound velocity $v_s(T)$, taken from ref. 11, is also shown in these figures. We can see that both $\kappa(T)$ and $v_s(T)$ take local minimums at around T_c. T_c was determined from the sharp drop in the $\rho(T)$ curves of respective samples,[11] which is almost in accordance with that determined from the magnetization measurement. As shown in ref. 11, the electrical resistivity of these samples is rather large and the electronic contribution κ_e of heat conduction estimated from Wiedemann-Franz law is negligible. Thus the heat conduction is almost entirely due to phonons in the present $La_{1-x}Sr_xMnO_3$.

The phonon thermal conductivity is generally given by[12]

$$\kappa_{ph} = \frac{3\rho_0 nRT^3}{M\Theta_D^3} v_s^2 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} \tau_{ph}\, dx, \qquad (1)$$

where ρ_0 is the mass density, M the mass of one mole, n (=5 for $La_{1-x}Sr_xMnO_3$) the number of atoms in the chemical formula, R the gas constant, Θ_D the Debye temperature and x is the reduced phonon frequency. Assuming a kind of Matthiessen's rule for the phonon scattering rate, the phonon relaxation time τ_{ph} is given by[12]

$$\tau_{ph}^{-1} = \tau_b^{-1} + d(Tx) + s(Tx)^2 + p(Tx)^4 + \Delta\tau_{mag}^{-1}. \qquad (2)$$

Here τ_b is the scattering time due to grain boundaries and d, s and p refer to the strength of the phonon scattering by dislocations, sheet-like faults and point defects, respectively.[13] In the following, we try to quantify the strength of the enhancement in phonon scattering around T_c by the use of eqs. (1) and (2).

As can be seen in Figs. 1(a)–1(c), the sound velocity v_s shows a considerable change around T_c. By the change of $v_s(\Delta v_s)$, $\kappa_{ph}(T)$ is affected in two competitive ways; (i) through the factor v_s^2 in eq. (1) and (ii) through the

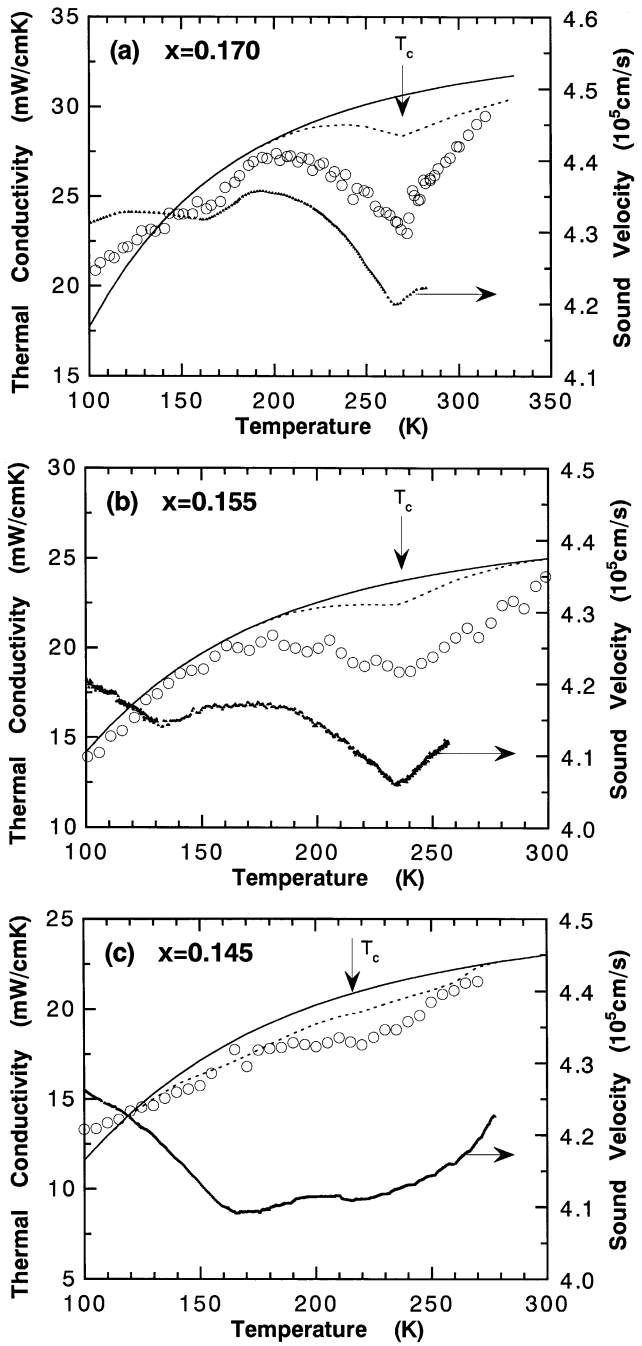

Fig. 1. (a) Data of thermal conductivity $\kappa(T)$ (○) and sound velocity $v_s(T)$[11] of $La_{1-x}Sr_xMnO_3$ for $x = 0.170$. Solid line represents the base line of $\kappa(T)$ which is estimated by use of the parameter values in Table I. The dotted line represents Δv_s corrections to $\kappa(T)$ due to the v_s^2 factor in eq. (1). (b) Similar data and curves to (a) for $x = 0.155$. (c) Similar data and curves for $x = 0.145$.

change of Θ_D. The temperature range in which $\kappa(T)$ of the present samples exhibits peculiar reductions belongs to a rather high-temperature region ($T_c \geq \Theta_D/2$, $\Theta_D \cong 450\,K$). In such a case, $\kappa_{ph}(T)$ is mainly affected by the factor v_s^2 in eq. (1). This correction due to the factor v_s^2 to $\kappa(T)$ base lines is presented by the dotted line in Figs. 1(a)–1(c). The $\kappa(T)$ base lines given by the solid lines are calculated on the basis of eqs. (1) and (2) using the parameter values in Table I. The corrections for $\kappa(T)$ given by the dotted line are far too small to explain the observed reduction in $\kappa(T)$. In order to remedy the discrepancy, we introduced an additional term, $\Delta\tau_{mag}^{-1}$, in eq. (2) and calculated $\Delta\tau_{mag}^{-1}$ values necessary to fit the experimental $\kappa(T)$ by the use of eq. (1). The results of calculated $\Delta\tau_{mag}^{-1}$ values are shown in Fig. 2. The peaks of $\Delta\tau_{mag}^{-1}$ are centered at T_c and the values of $\Delta\tau_{mag}^{-1}$ seem to become larger with the order of increasing x for the present three samples. Figure 3 shows $\kappa(T)$ of $La_{1-x}Sr_xMnO_3$ for $x = 0.135$ and 0.20. The reduction in $\kappa(T)$ at T_c is very weak, although it is still clearly noticed for $La_{0.80}Sr_{0.20}MnO_3$. The $\kappa(T)$ of $La_{0.89}Sr_{0.11}MnO_3$ was also measured but the corresponding anomaly near T_c was almost completely wiped out.

Next, we briefly discuss the origin and the mechanism which result in the enhanced phonon scattering $\Delta\tau_{mag}^{-1}$. Since the enhancement occurs in a temperature range centered around T_c, it is quite clear that some mechanism closely related to spin magnetic moments is the origin of the enhancement. The observed enhancement $\Delta\tau_{mag}^{-1}$ is very large; by assuming $v_s \approx 4 \times 10^5\,cm/s$ and $\Delta\tau_{mag}^{-1} \approx 10^{-12}$ (the maximum value in Fig. 2), the phonon mean free path limited by this scattering is as small as $\sim$40 Å. Such a strong spin-phonon scattering has not been observed and usual spin-phonon interaction through the spin-orbit coupling is unlikely to be the origin. One possible scenario for the enhanced phonon scattering by the spin system may be as follows.

The $La_{1-x}Sr_xMnO_3$ system with a perovskite based structure has a lattice instability and the crystal structure changes from orthorhombic to rhombohedral with increasing x at around $x = 0.17$.[6] Our $La_{0.83}Sr_{0.17}MnO_3$ sample actually shows the structural transition at about $T = 180\,K$ as indicated by the hysteretic behavior in $v_s(T)$ and $\rho(T)$.[11] The $La_{1-x}Sr_xMnO_3$ sample considered here is orthorhombic below 180 K and rhombohedral above 180 K for $x = 0.170$ and orthorhombic for $x = 0.145$ and 0.155 over the entire temperature range.[6,11] The structural instability from orthorhombic to rhombohedral is intimately related with the stability of ferromagnetism through the double exchange mechanism and the ferromagnetic order favors a rhombohedral lattice.[14] This interplay of lattice structure and ferromagnetism is considered to be the origin of the characteristic field-induced structural transition observed in this system.[9,10] The observed anomalous enhancement in phonon scattering may similarly result from the strong coupling between the lattice and the spin system via the double exchange interaction.

Table I. Fitting parameters used to determine $\kappa_{ph}(T)$ base lines for various $La_{1-x}Sr_xMnO_3$ samples.

	$\tau_b^{-1}\,(s^{-1})$	$d\,(K^{-1}\,s^{-1})$	$s\,(K^{-2}\,s^{-1})$	$p\,(K^{-4}\,s^{-1})$	$\Theta_D\,(K)$	$\rho_0\,(g/cm^3)$
$x = 0.170$	3.2×10^8	1.6×10^{10}	3.2×10^5	3.2×10^1	450	5.28
$x = 0.155$	3.7×10^8	1.8×10^{10}	3.7×10^5	3.7×10^1	450	5.28
$x = 0.145$	4.2×10^8	2.1×10^{10}	4.2×10^5	4.2×10^1	450	5.31

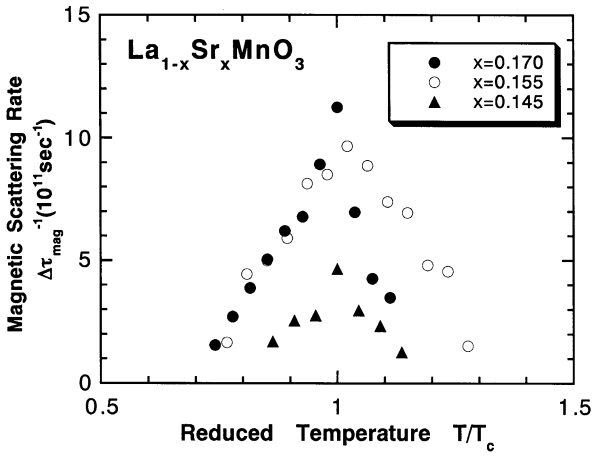

Fig. 2. The strength of additional phonon scattering $\Delta\tau_{\rm mag}^{-1}$ vs reduced temperature $T/T_{\rm c}$. $\Delta\tau_{\rm mag}^{-1}$ is estimated on the basis of eqs. (1) and (2) (see text).

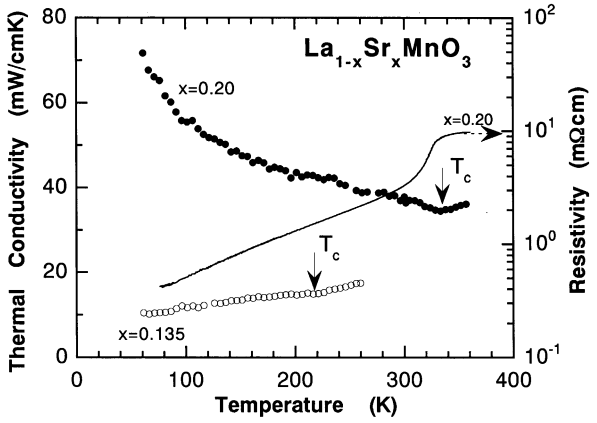

Fig. 3. Thermal conductivity $\kappa(T)$ of $La_{1-x}Sr_xMnO_3$ for $x = 0.135$ and 0.20. Anomalous reduction in $\kappa(T)$ is small at these Sr concentrations. The electrical resistivity $\rho(T)$ is also shown for $x = 0.20$ (see ref. 11 for $\rho(T)$ of $x = 0.135$).

It is well-known that many types of relaxation effects show characteristic anomalies near the second order phase transition $T_{\rm c}$.[15] This is caused by the divergent fluctuations of the order parameter and the fluctuations of the spin magnetic moments also intensely develop at around the ferromagnetic transition temperatures. Associated with the fluctuations of the magnetic short range order in $La_{1-x}Sr_xMnO_3$, the crystal structure may also tend to fluctuate locally between orthorhombic and rhombohedral lattices. From the viewpoint of phonon transport, the local fluctuations of lattice structure may act as effective phonon scattering centers, providing a resultant strong phonon-spin scattering mechanism in $La_{1-x}Sr_xMnO_3$ crystals. The local structural fluctuations are expected to be stronger for the Sr concentration x near the orthorhombic to rhombohedral lattice transition and will become weaker for x far from the transition line. In Fig. 2, we see that $\Delta\tau_{\rm mag}^{-1}$ is the largest for rhombohedral $La_{0.83}Sr_{0.17}MnO_3$ which just crosses the lattice transition line at 180 K. The values of $\Delta\tau_{\rm mag}^{-1}$ are also large for orthorhombic $La_{0.845}Sr_{0.155}MnO_3$ with Sr concentration pretty near the structural transition. For $x = 0.145$, which is fairly separated from the lattice transition line, $\Delta\tau_{\rm mag}^{-1}$ values are much suppressed in comparison with $x = 0.170$ and $x = 0.155$ samples. Thus the anomalous phonon-spin scattering shows a clear correlation with the structural instability in the $La_{1-x}Sr_xMnO_3$ system at around $x = 0.170$. This local lattice fluctuation model bears some common features to the two-level model of amorphous solids,[16] where phonons are scattered by tunneling motions of atoms between two metastable atomic sites. In the present model, the motion between two atomic sites (orthorhombic and rhombohedral) is mediated by fluctuations of the ferromagnetic order.

In summary, our thermal conductivity measurement revealed anomalously strong phonon scattering around $T_{\rm c}$ ("giant" phonon-spin scattering) in $La_{1-x}Sr_xMnO_3$ crystals with Sr composition x in the vicinity of the orthorhombic to rhombohedral structural transition. We have proposed one possible mechanism for "giant" phonon-spin scattering based on the double exchange mechanism. The proposed mechanism reflects, however, only one phenomenological aspect of the problem. Theoretical studies which more rigorously take account of various competitive or cooperative mechanisms in this system, especially the (dynamical) Jahn-Teller effect are urgently required. It is also worth noting that the "giant" phonon-spin scattering occurs over a very wide temperature range around $T_{\rm c}$ in spite of the three-dimensional nature of the $La_{1-x}Sr_xMnO_3$ system.

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