Strongly Correlated Electrons with Orbital Degrees of Freedom (ORBITAL2001)
J. Phys. Soc. Jpn. Vol. 71 (2002) Suppl. pp. 142–144

Heat Transport Enhancement in Ferromagnetic Metallic Phase of $La_{1-X}Ba_XMnO_3$

Hiroyuki FUJISHIRO, Shingo KANOH and Manabu IKEBE

Faculty of Engineering, Iwate University, Morioka 020-8551, Japan

The phonon thermal conduction in $La_{1-X}Ba_XMnO_3$ (LBMO) has been investigated for the Ba concentration $X \leq 0.45$, where single phase samples can be prepared. The dominant phonon scatterer in this system is the Jahn-Teller local lattice distortions, which are relaxed in the ferromagnetic metallic phase with increasing charge carrier mobility. In comparison with other manganite systems, the phonon conductivity enhancement below T_c is rather moderate in LBMO and the metallic behavior of LBMO is not so ideal, contrary to the anticipation based on the tolerance factor Γ values.

KEYWORDS: $La_{1-X}Ba_XMnO_3$, manganites, thermal conductivity, tolerance factor

§1. Introduction

Recent revived studies on hole-doped rare-earth manganites have revealed a variety of dramatic phenomena associated with the metal-insulator transition.[1,2] The most fundamental driving force for the novel phenomena is the strong correlation between 3d (e_g) electrons, but it is also widely admitted that the electron-phonon interaction is very important as well. The well-known colossal magnetoresistance (CMR), for example, cannot be quantitatively explained by the double exchange mechanism only, and electron-phonon interaction and/or lattice effects must be taken account of.[3] The two key factors may be important as for the lattice effect in the $(RE_{1-X}AE_X)MnO_3$ system (RE=trivalent rare-earth ions, AE=divalent alkaline-earth ions). One is the Jahn-Teller (J-T) effect of Mn^{3+} ions which controls the e_g electron transport through the formation of the polarons. The other is the average $(RE_{1-X}AE_X)$ ionic radius which controls the single electron band width W through the distortion of the lattice from the cubic. Generally, the wider W is expected for the smaller distortion. A useful measure for the distortion of the perovskite structure is so-called tolerance factor Γ, which is defined by

$$\Gamma = \frac{r_A + r_B}{\sqrt{2}(r_B + r_O)}, \tag{1.1}$$

where r_A, r_B and r_O are the atomic radii of A-site $(RE_{1-X}AE_X)$ ion, B-site (Mn) ion and oxygen ion, respectively. For cubic structure Γ=1 and the lattice distortion is enhanced as the Γ value deviates from 1. The phonon thermal conductivity (κ_{ph}) provides a valuable measure for the phonon dynamics and for the phonon scattering mechanisms in a crystal. The electrical resistivity $\rho(T)$ of $(RE_{1-X}AE_X)MnO_3$ is pretty large even in the metallic phase and the Wiedemann-Franz law suggests that the heat-conduction is overwhelmingly due to phonons ($\kappa \cong \kappa_{ph}$). We have already studied the thermal conductivity κ of $La_{1-X}Ca_XMnO_3$ (LCMO)[4] and $La_{1-X}Sr_XMnO_3$ (LSMO)[5] and found characteristic κ_{ph} enhancement in the ferromagnetic metallic (FM-M) phase. The phonon heat conduction in these systems was limited by the phonon scattering by the local J-T lattice distortion and the κ_{ph} enhancement originated from the release in the J-T distortion in the metallic phase. The ionic radius of Ba^{2+} (=1.47Å) is larger than those of Ca^{2+} (1.18Å), Sr^{2+} (1.31Å) and La^{3+} (1.216Å). The tolerance factor Γ of $LaMnO_3$ is 0.938 and it is to increase toward 1 most rapidly by Ba substitution for La. Thus, from the view point of the Γ value, LBMO is expected to provide more ideal FM-M specimens than the other manganite systems. In this paper, we report the phonon and the electron transport in $La_{1-X}Ba_XMnO_3$ (LBMO) and compare with the results of the LCMO and LSMO systems.

§2. Experimental

$La_{1-X}Ba_XMnO_3$ samples were prepared by a standard solid-state reaction method. The sintering temperature was 1500°C. From the X-ray analyses, the lattice structure was consistent with orthorhombic for $0 \leq X \leq 0.10$, rhombohedral for $0.12 \leq X \leq 0.30$ and cubic for $0.34 \leq X \leq 0.45$. For $X \geq 0.50$, an impurity phase appeared and single phase crystals could not be achieved. The thermal conductivity $\kappa(T)$ was measured by a steady-state heat flow method between 10 K and 300 K by use of a Gifford-McMahon type as a cryostat. The thermal diffusivity $\alpha(T)$ was measured by an arbitrary heating method under an identical setup as the $\kappa(T)$ measurement. The magnetization $M(T)$ measured by a SQUID magnetometer confirmed that the LBMO samples are all the ferromagnets for $0.06 \leq X \leq 0.45$.

§3. Results and Discussion

Figure 1 shows the temperature dependence of the electrical resistivity $\rho(T)$ for $X \leq 0.18$ (Fig. 1(a)) and for $X \geq 0.25$ (Fig. 1(b)). $\rho(T)$ of the ferromagnetic samples ($X \geq 0.06$) shows a reduction at around the Curie temperature T_c. Below T_c, $\rho(T)$ clearly increases for

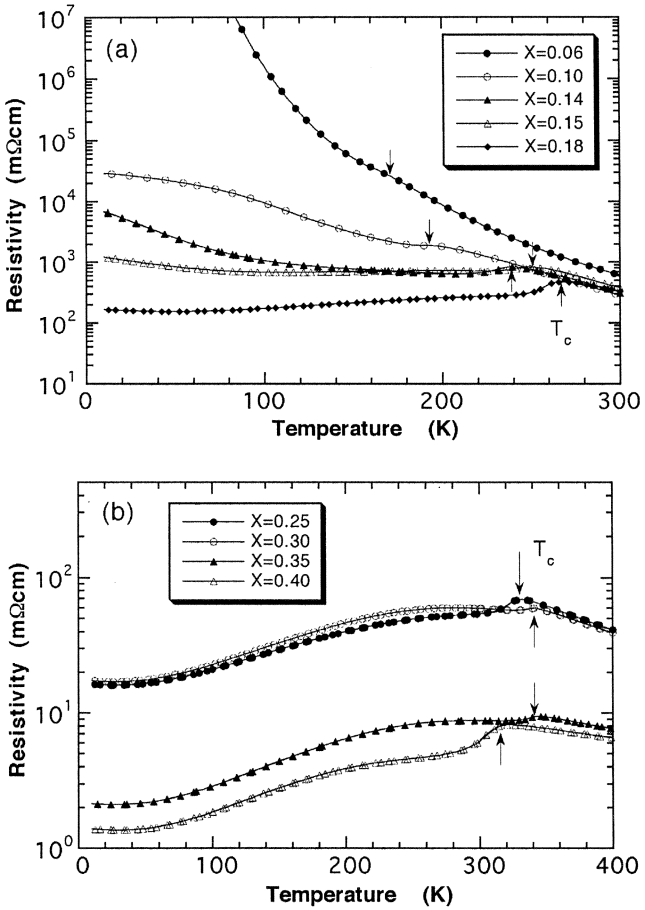

Fig. 1. $\rho(T)$ of $La_{1-X}Ba_XMnO_3$ for (a) $X \leq 0.18$ and (b) $X \geq 0.25$ as a function of T.

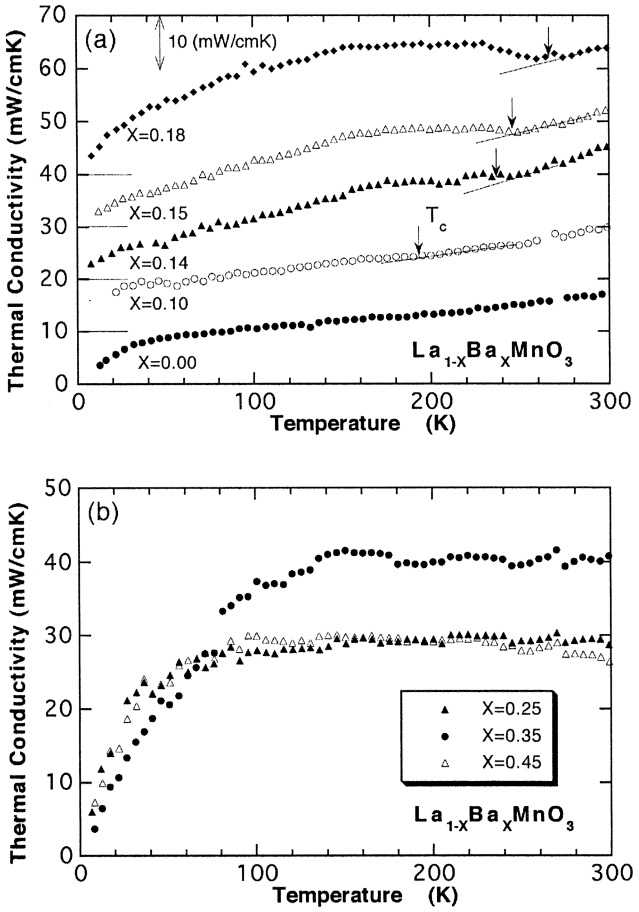

Fig. 2. $\kappa(T)$ of $La_{1-X}Ba_XMnO_3$ for (a) $X \leq 0.18$ and (b) $X \geq 0.25$ as a function of T.

X=0.14 and it clearly decreases for X=0.18 with decreasing temperature, while $\rho(T)$ remains almost constant for X=0.15. This fact indicates that the phase boundary between ferromagnetic metal (FM-M) and ferromagnetic insulator (FM-I) is located in the vicinity of the Ba concentration X=0.15. Figure 2(a) shows the thermal conductivity $\kappa(T)$ for X=0.00, 0.10, 0.14, 0.15 and 0.18. $\kappa(T)$ of the X=0.00 (A-type antiferromagnetic) and the X=0.10 sample is very small and monotonically decreases with decreasing temperature. $\kappa(T)$ of the X=0.18 (FM-M) sample shows clear enhancement below T_c taking a local minimum at T_c. As we have pointed out for the LCMO and LSMO systems, the enhanced phonon heat conduction in the FM-M phase below T_c is a common peculiarity of the perovskite manganite systems.[4,5] It is to be noticed that the X=0.15 sample also shows the enhancement similar to that of X=0.18. The X=0.14 and 0.15 samples, which are located near the phase boundary between the FM-I and FM-M phases from the $\rho(T)$ behavior, belongs to the FM-M phases from the $\kappa(T)$ behavior. Figure 2(b) shows $\kappa(T)$ for the X=0.25, 0.35 and 0.45 samples which belong to the typical FM-M LBMO group. The thermal conductivity takes a maximum for X=0.35. As we have reported, the most important phonon scattering mechanism is due to the J-T local lattice distortion, which is reduced significantly with increasing mobility of holes.[5] From this view point, the best metal is realized in LBMO for X=0.35, where κ takes a maximum. Figure 3 presents the thermal diffusivity $\alpha(T)$ vs. T for X=0.10, 0.165, 0.18 and 0.25. In the case that thermal conduction is overwhelmingly due to phonons, the thermal diffusivity is given by

$$\alpha = \frac{\kappa_{ph}}{C_{ph}} \simeq \frac{1}{3} v_{ph} l_{ph}, \tag{3.1}$$

where C_{ph} is the phonon heat capacity, v_{ph} the phonon velocity and l_{ph} is the phonon mean free path. As a whole, the magnitude and temperature dependence of $\alpha(T)$ reflect those of $\kappa(T)$ in Fig. 2 with clear increase below T_c where $\kappa(T)$ is enhanced. What is to be noticed in Fig. 3 is very small $\alpha(T)$ values above T_c, which increases with increasing temperature. Usually, phonon scattering increases with increasing temperature, but the present $\alpha(T)$ results suggest the inverse. The decreasing phonon scattering with increasing temperature was confirmed up to very high temperatures for the LCMO system,[6] which provided a peculiar feature of the phonon scattering by small J-T polarons in the manganite system; the phonon scattering by the local J-T distortion is reduced with increasing mobility of polarons also in the paramagnetic phase.

In Fig. 4, we compare $\kappa(T)$ of typical metallic samples of LCMO, LSMO and LBMO systems. The κ values are the largest for $La_{0.75}Sr_{0.25}MnO_3$ and the κ enhancement is also the most conspicuous. In contrast, κ values and the κ enhance-

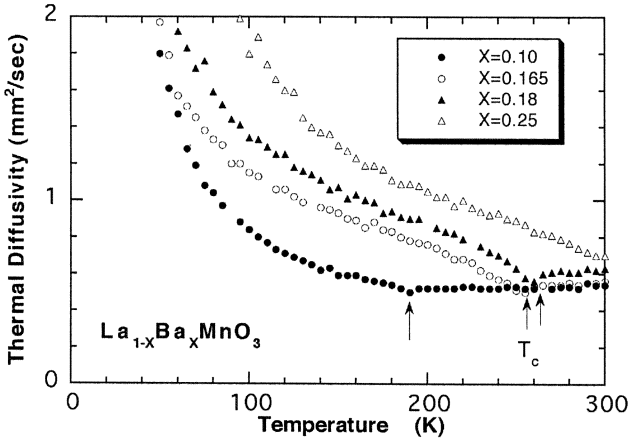

Fig. 3. The thermal diffusivity $\alpha(T)$ vs. T. $\alpha(T)$ slightlt increases above T_c.

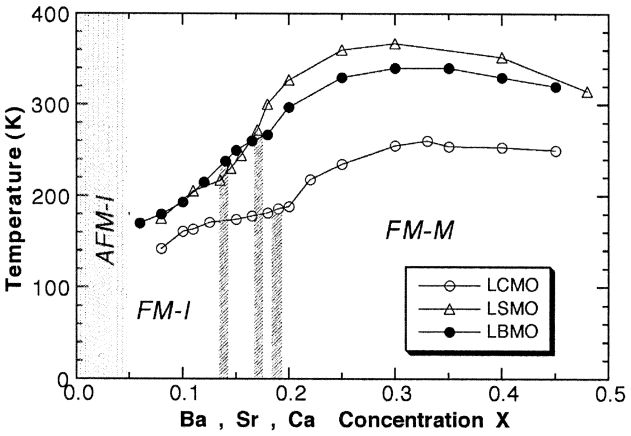

Fig. 5. The magnetic and electrical phase diagrams of the three systems. T_c was determined from the electrical resistivity. The hatches at $X \cong 0.14$, 0.17 and 0.19 represent the metal-insulator boundary for LCMO, LSMO and LBMO, respectively.

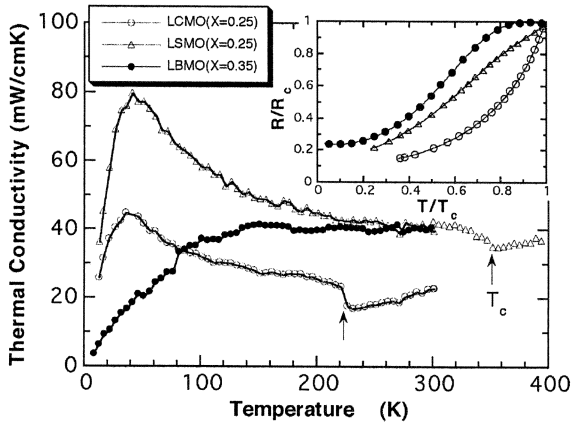

Fig. 4. Comparison of $\kappa(T)$ of $La_{0.75}Ca_{0.25}MnO_3$, $La_{0.75}Sr_{0.25}MnO_3$ and $La_{0.65}Ba_{0.35}MnO_3$, which are typical metallic samples of each system. The inset shows the normalized electrical resistivity R/R_c vs. the normalized temperature T/T_c.

ment are the smallest for $La_{0.65}Ba_{0.35}MnO_3$ at low temperatures. The tolerance factor Γ=0.931, 0.964 and 0.993 for $La_{0.75}Ca_{0.25}MnO_3$, $La_{0.75}Sr_{0.25}MnO_3$ and $La_{0.65}Ba_{0.35}MnO_3$, respectively. The density of the hole carriers is the largest for $La_{0.65}Ba_{0.35}MnO_3$, which suggests that $La_{0.65}Ba_{0.35}MnO_3$ is the best metal among these samples. However, the small $\kappa(T)$ values and its small enhancement suggest that the metallic behavior is the worst for LBMO at least in the low temperature region. The normalized resistivity in the inset of Fig. 4 also supports that the metallic behavior of $La_{0.65}Ba_{0.35}MnO_3$ is not so good, contrary to our anticipation from the Γ value. In addition, the $\kappa(T)$ behavior of LBMO supports that the origin of $\kappa(T)$ maxima observed in LCMO and LSMO are not the phonon-phonon scattering because the phonon-phonon scattering should not be so drastically different among these systems. Figure 5 shows the phase diagram of the LBMO, LSMO and LCMO systems. The ferromagnetic phase of LBMO occurs at higher temperatures than LCMO but at slightly lower temperatures than LSMO. This result suggests that the double exchange interaction, which is the most fundamental origin for the FM-M phase, is the strongest for LSMO and supports again that the LBMO is not so good a metal as compared to LSMO. On the other hand, the metallic phase sets in for $X \geq 0.15$ in LBMO, for $X \geq 0.17$ for LSMO and for $X \geq 0.19$ for LCMO, and the FM-M region is the widest for LBMO in accord with the expectation based on the Γ value.

§4. Summary

The thermal conductivity $\kappa(T)$ and diffusivity $\alpha(T)$ of the ferromagnetic $La_{1-X}Ba_XMnO_3$ (LBMO) sintered crystals have been investigated and the results have been compared with those of $La_{0.75}Sr_{0.25}MnO_3$ (LSMO) and $La_{0.75}Ca_{0.25}MnO_3$ (LCMO), which have the smaller tolerance factor Γ. The positive $d\alpha(T)/dT$ for $T > T_c$ suggests that the dominant phonon scattering mechanism in LBMO is due to the Jahn-Teller (J-T) local lattice distortion in the insulating phase. The local J-T distortion is significantly relaxed in the ferromagnetic metallic (FM-M) phase with increasing mobility of charge carriers. But the κ enhancement in LBMO is small in comparison with that of LSMO and LCMO. Contrary to the speculation on the basis of the Γ value, the metallic behavior of LBMO is not so ideal as LSMO and LCMO. The FM-M phase, however, is stabilized for wider Ba content range $X \geq 0.15$.

1) Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara and Y. Tokura: Phys. Rev. Lett. **74** (1995) 5108.
2) Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido and N. Furukawa: J. Phys. Soc. Jpn. **63** (1994) 3931.
3) A.J. Millis, P.B. Littlewood and B.I. Shaiman: Phys. Rev. Lett. **74** (1995) 5144.
4) H. Fujishiro and M. Ikebe: *Physics in Local Lattice Distortions,* edited by H. Oyanagi and A. Bianconi, American Institute Physics, (2001) 433.
5) M. Ikebe, H. Fujishiro and Y. Konno: J. Phys. Soc. Jpn. **67** (1998) 1083.
6) H. Fujishiro, M. Ikebe, T. Akashi and T. Goto: to be published in Physica B (2002).