Thermal Conductivity of Manganite Perovskites: Colossal Magnetoresistance as a Lattice-Dynamics Transition

D. W. Visser* and A. P. Ramirez†

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

M. A. Subramanian

DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328

(Received 20 February 1997)

We present the thermal conductivity (κ) of several manganite perovskite compounds at temperatures 10–350 K and fields up to 6 T. In the metallic phase, κ behaves as expected for a crystalline solid. In the high-temperature insulating phase, however, $d\kappa/dT > 0$, the behavior of an amorphous solid. Unlike amorphous solids, $d\kappa/dT > 0$ here is related not to quenched structural disorder but rather to unusually large dynamic lattice distortions accompanying charge transport. Thus, "colossal magnetoresistance" in the manganite perovskites is characterized as a transition between regimes of different lattice dynamics. [S0031-9007(97)03158-X]

PACS numbers: 75.50.Cc, 63.90.+t, 72.15.Eb

The manganite perovskite compounds which display colossal magnetoresistance (CMR) [1] have attracted much attention for their possible use in magnetic reading applications. The effect which gives rise to CMR in these compounds is also a unique type of metal-insulator (M-I) transition. Although the electronic transport has been well studied in these systems, the thermal transport is less well understood. Several measurements, including the Debye-Waller factor [2], the pair distribution function [3], and the isotopic-substitution T_c shift [4] demonstrate the role of electron-lattice coupling in CMR. Such coupling should also be evident in thermal transport, and we have measured the thermal conductivity κ as a function of temperature and magnetic field to investigate the dual effects of electrons and phonons at what is usually characterized as either a magnetic-nonmagnetic or metal-insulator transition leading to CMR.

The samples studied have the general formula $T_{1-x}D_X$-MnO$_3$, where T is trivalent, and D a divalent cation. Away from the ferromagnetic critical region, we find two distinct types of behavior. In the low-temperature metallic state, κ displays the usual behavior of an *ordered* solid—a rise in $\kappa(T)$ as temperature is lowered below the Debye value θ_D. In the high-temperature insulating state, however, $\kappa(T)$ displays behavior characteristic of phonon scattering in an *amorphous* solid ($d\kappa/dT > 0$) [5]. Because it occurs in single crystals, however, the behavior cannot be due to quenched structural disorder as in amorphous materials. Instead, $d\kappa/dT > 0$ can be related empirically to the very large anharmonic lattice distortions inferred from the Debye-Waller factor. These results place the manganites in a unique class of materials from the standpoint of lattice dynamics. We also find that on entering the metallic state, $\kappa(T)$ rises sharply and this rise is strongly modified by an applied magnetic field.

Single crystals of (La, Pb)MnO$_3$ and (La, Nd, Pb)MnO$_3$ were grown from 3:1 wt % of PbO and PbF$_2$ flux [6]. The stoichiometries of the crystals, determined by electron microprobe analysis and wet chemical analysis, are La$_{0.62(2)}$Pb$_{0.38(2)}$MnO$_3$ and La$_{0.20(1)}$Nd$_{0.40(2)}$Pb$_{0.42(2)}$MnO$_3$, and agree well with the stoichiometries expected from starting compositions La$_{0.6}$Pb$_{0.4}$MnO$_3$ and La$_{0.2}$Nd$_{0.4}$-Pb$_{0.4}$MnO$_3$. Single crystal x-ray diffraction studies show that La$_{0.6}$Pb$_{0.4}$MnO$_3$ crystallizes in trigonal symmetry (space group $R\bar{3}C$; $a = 5.502(2)$, $c = 13.397$ Å; cell volume/formula unit: 61.03 Å^3) whereas La$_{0.2}$Nd$_{0.4}$-Pb$_{0.4}$MnO$_3$ crystallizes in an orthorhombic structure (space group $Pnma$; $a = 5.460(1)$; $b = 5.499(2)$; and $c = 7.740(4)$; cell volume/formula unit $= 58.09$ Å^3). The La$_{0.2}$Nd$_{0.4}$Pb$_{0.4}$MnO$_3$ and La$_{0.6}$Pb$_{0.4}$MnO$_3$ crystals have $T_c = 270$ and 350 K, respectively and the relationship between T_c and lattice constant is consistent with previous work [7,8]. The polycrystalline samples of La$_{1-x}$Ca$_x$MnO$_3$ were synthesized by standard solid state reaction at 1200 °C starting from high purity La$_2$O$_3$, SrCO$_3$, and MnO$_2$. These samples have $T_c = 170$ and 270 for $x = 0.1$ and 0.2, respectively. The Ca-doped samples contain different amounts of the dopant ion Ca^{2+}, so they differ in the degree of *band filling* [9]. In contrast, the Pb-doped samples contain the same amount of Pb dopant but different amounts of Nd^{3+} which modifies only the lattice constant—hence they differ by their *bandwidth*.

Thermal conductivity was measured using differential E-type thermocouples and a thin-film heater. Typical sample dimensions were $1 \times 1 \times 4$ mm^3. The maximum temperature gradient across the sample was 1% of the base temperature. We estimate a ±5% uncertainty in the geometrical factor used to convert conductance to conductivity.

In Fig. 1, $\kappa(T)$ is shown for each of the compounds. The first thing to notice is the magnitude of $\kappa(T)$ which lies in the range 0.5–5 W/mK typical for amorphous materials [5]. The magnitude of κ in the two high-κ samples is approximately equal in the paramagnetic region.

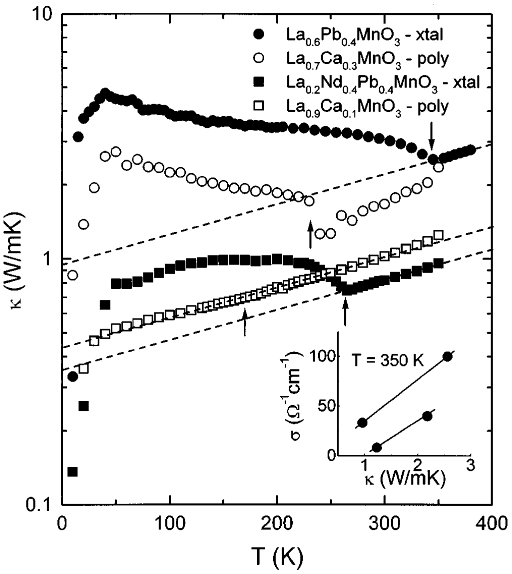

FIG. 1. Thermal conductivity κ for four different manganite perovskite samples. The arrows denote the ferromagnetic transition temperature. The three samples possessing a sharp change in $\kappa(T)$ at T_c also undergo a metal-insulator transition. The dashed lines represent an exponential temperature dependence $\kappa = \kappa_0 \exp(T/350)$, with κ_0 values described in the text. The inset shows the electrical conductivity σ versus κ, at 350 K for the four samples.

Since these are both the optimally doped members of their respective families, this agreement suggests that the measured κ's are intrinsic and not severely affected by grain-boundary scattering. The slope of $\log(\kappa)$ vs T in the high-temperature region is similar among three of the samples and can be parametrized by the expression $\kappa = \kappa_0 \exp(T/T_\kappa)$, where $T_\kappa = 355$ K and $\kappa_0 = 0.95$, 0.36, and 0.29 (W/mK), as shown by dashed lines in Fig. 1.

We discuss first, $\kappa(T)$ for $T > T_c$. A positive $d\kappa/dT$ at temperatures of order θ_D is unusual since the high-temperature thermal conductivity in crystalline insulators is almost always a decreasing function of temperature. This follows from the kinetic expression for thermal conductivity,

$$\kappa = NCvl\,, \tag{1}$$

where N is the number of thermal carriers, C the specific heat, v the group velocity (usually assumed to be constant), and l the mean free path. Above θ_D, phonons give $d\kappa/dT \sim 1/T^q$ where $q \approx 1$–2, due to phonon-density dependence of l and a constant $C(T) = C_{\mathrm{DP}}$, the Dulong-Petit value. For metals, the electrons usually dominate, hence $\kappa(T > \theta_D) \propto$ const, since $C(T) \propto T$ [5]. Clearly, $\kappa(T > T_c)$ in the manganites is not described by the usual high-temperature electron or phonon processes.

It is tempting to attribute the anomalous $\kappa(T > T_c)$ to electrons. In fact, $\kappa(T)$ and $\sigma(T) \equiv 1/\rho(T)$ (ρ is resistivity) scale with each other at 350 K (inset Fig. 1), within their respective doping families, suggesting they are related through the electron density. By attributing $\sigma(T)$ to changes in electron density and using Eq. (1) one finds that $\kappa(T)$ is proportional to $\exp(-\Delta_{\mathrm{tr}}/T)$ where $\Delta_{\mathrm{tr}} \sim 0.1 - 0.3$ eV is the transport gap. Fitting $\kappa(T)$ to such an expression yields extremely poor fits to the high temperature data. Another possible contribution to $\kappa(T)$ is from magnons, but the absence of any feature in $\kappa(T)$ at T_c in $La_{0.9}Ca_{0.1}MnO_3$ suggests that such a contribution is negligible.

A clue to the positive $d\kappa/dT$ at high temperatures is found in recent measurements of the neutron scattering pair distribution function (PDF) [3]. These show that for $La_{1-x}Ca_xMnO_3$ ($x = 0.20, 0.25$) a transition from a high-temperature state with disordered Mn-O and O-O bond lengths to a low-temperature state with a uniform bond length distribution. The bond disorder is ascribed to electron hopping, a process which involves real-space displacement of large Jahn-Teller distorted (d^4) Mn-O octahedra by undistorted (d^3) octahedra. In the FM state, on the other hand, the carriers are delocalized, and any distortion will be uniformly averaged over Mn-O sites. This study complements the neutron scattering study of the Debye-Waller factor [2], which shows that anharmonic distortions exist in both metallic and insulating regimes. While the PDF measurements address the static distribution of bond lengths (on the time scale of the scattering event), one expects dynamic effects as well. In particular, since the Jahn-Teller distortion is large but destabilized by doping it is natural to expect strong phonon-phonon as well as electron-phonon scattering at short wavelengths. The effect of such scattering on thermal conductivity can be made in contrast to amorphous solids such as vitreous silica or stainless steel, where a monotonic temperature dependence with $d\kappa/dT > 0$ is ascribed to quenched disorder extending down to the inter-atomic length scale [5]. Such disorder drastically inhibits the evolution of l with T—this is reflected in the tracking of $C(T)$ and $\kappa(T)$ above a "plateau" region ($\sim$100 K, where l is comparable to a structural correlation length [5,10]). In fact, in the manganites, $C(T)$ and $\kappa(T)$ do have similar temperature dependences in the region above 250 K [11]. However, these are also single crystals, so there is no reason to believe that the C-κ correspondence arises from effects of *quenched* disorder. In addition, the $d\kappa/dT > 0$ behavior disappears abruptly at T_c, where the unit cell undergoes only a modest size change, instead of the gross changes expected for an amorphous-crystalline transition.

We now show that the diffraction data suggest a description of the high-temperature behavior of $\kappa(T)$ solely in terms of phonons. A natural extension of Eq. (1) relates *anharmonic* lattice vibrations to a phonon-phonon scattering time. Leibfried and Schlömann have shown that for $T \geq \theta_D$, cubic terms in the lattice potential energy lead to an expression of the form

$$\kappa \propto \frac{aMC_{\mathrm{DP}}\theta_D^3}{\gamma^2 T}\,, \tag{2}$$

where a is the lattice constant, M is the mass per atom, and γ the Gruneisen coefficient [12]. This expression has been used to describe dependences of κ on θ_D among different materials and yields estimates correct within factors of 2–4 for a broad range of materials and κ values [5,13] where γ is usually assumed to be a constant between 2 and 3. However, neutron scattering measurements of $La_{0.65}Ca_{0.35}MnO_3$ by Dai *et al.* show that an effective γ extracted from the Debye-Waller factor W, is not only much larger than usual, but also varies strongly with temperature [2]. One can estimate $\gamma(T)$ using the relationship $\gamma = p\,\partial \ln W/\partial \ln V$ where V is the unit-cell volume and the constant $p = 1$ (0.5) in the limit where $T \ll \theta_D$ ($\gg \theta_D$) [14]. Using experimental values of $W(T)$ and $V(T)$ [15] for $La_{0.65}Ca_{0.35}MnO_3$, and the high-temperature value of p, one finds that γ decreases from 180 ± 10 to 120 ± 10 between 250 and 350 K. This leads to a 50% increase in $(\gamma^2 T)^{-1}$ in rough agreement with the observed (30–70)% increase in $\kappa(T)$ over the same temperature range. Many approximations have gone into the derivation of Eq. (2), and therefore its strict quantitative validity in the case of the manganite perovskites is questionable. However, it does strongly suggest that the anomalous temperature dependence of $\kappa(T > T_c)$ can be related to local anharmonic lattice distortions.

In the critical region $\kappa(T)$ abruptly increases on entering the metallic state. If this is this solely due to conduction electrons there should be a Wiedemann-Franz (W-F) correspondence between $\rho(T)$ and the change in $\kappa(T)$ near T_c. In Fig. 2 we plot $\rho(T)$ and $\kappa(T)$ for $La_{0.2}Nd_{0.4}Pb_{0.4}MnO_3$ and notice a large temperature region near T_c where ρ and κ behave contrary to the W-F expression $\kappa\rho = (\pi^2/3)(k_B/e)^2 T$. One also finds that the measured Lorenz number $L_{\text{meas}} = \kappa\rho/T$ varies by over an order of magnitude, from 10^{-7} to 10^{-6} W/Ω K^2 in the region 200 to 250 K, always exceeding the Fermi gas value (2.4×10^{-8} W/Ω K^2). This is probably due to the resistivity which exceeds the Ioffe-Regel criterion. Thus, the large change in κ is, most likely, only *indirectly* related to the decrease in ρ.

The above discussion leads to the following description of $\kappa(T)$ in the region below T_c. Here there can be two different processes leading to the rise in $\kappa(T)$ as T decreases for $T \lesssim T_c$. The first is due to the reduction in phonon-phonon scattering due to local Jahn-Teller disorder as suggested by the PDF data. The second is an enhanced electron contribution due to the reduction in electron-phonon scattering. Both of these effects reflect the restoration of crystallinity as Jahn-Teller distortions become delocalized along with the charge carriers. As T decreases further, the more gradual rise in $\kappa(T)$ is most likely due to a reduction in umklapp scattering. The rise is much weaker than in very pure crystals, presumably due to disorder on the lanthanide site. A maximum in $\kappa(T)$ is reached at $T \approx 50$ K, and by analogy to studies of the effect of impurities in crystals [5,16], we attribute this peak to a crossover from umklapp-limited to defect-limited scattering [17]. At 50 K, l equals a characteristic inter-defect spacing and stops evolving as T is lowered. Below 50 K (Casimir limit) $\kappa(T)$ is dominated by $C(T)$ via Eq. (1).

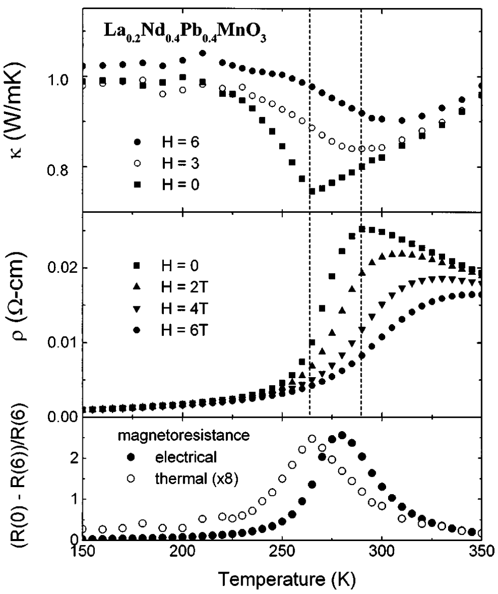

FIG. 2. Upper frame: Thermal conductivity κ versus temperature for $La_{0.2}Nd_{0.4}Pb_{0.4}MnO_3$ at three different values of applied magnetic field. Middle frame: Electrical resistivity $\rho(T)$ versus temperature for four different values of applied magnetic field. The vertical dashed lines span a temperature range where $\kappa(T)$ and $\rho(T)$ display behavior opposite to that of the Wiedemann-Franz law. Bottom frame: The electrical and thermal magnetoresistance, at 6 T, normalized to the high-field value.

The dependence of $\kappa(T)$ on magnetic field is shown for the $La_{0.2}Nd_{0.4}Pb_{0.4}MnO_3$ sample in Fig. 2. Here we see that near T_c, $\kappa(T)$ changes by about 30% in a 6 T field with respect to the zero-field value at $T = 265$ K. This is, to our knowledge, the largest field-induced change in thermal conductivity of any system near room temperature. For $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.6}Pb_{0.4}MnO_3$ the changes in κ at 6 T are 50% at 240 K and 10% at 340 K, respectively. Clearly the field effect varies with T_c, similar to the electrical magnetoresistance. This can be understood from the above discussion. As T_c decreases, the amount of structural disorder due to localized carriers also increases and therefore $\kappa(T_c)$ decreases. When the system transforms into a metal, either by lowering temperature or by applying a magnetic field, the reduction in disorder is therefore greater, the lower the T_c. In the bottom part of Fig. 2 we compare the field-induced changes in the resistance, both thermal and electrical. As already implied by the zero-field behavior, the peaks occur at different temperatures, illustrating that the two scattering processes are indirectly related via electron-phonon coupling, not directly via a Wiedemann-Franz relationship.

In conclusion, we have shown that the manganite perovskites display a large anomaly in κ, associated with the M-I transition. This anomaly signals a transition between regimes of different lattice dynamics which implies that the CMR transition is not purely electronic in origin.

We would like to acknowledge T. G. Calvarese (DuPont) for his assistance in the crystal growth experiments. We acknowledge useful discussions with P. Dai, P. Littlewood, A. Millis, P. Majumdar, P. Schiffer, C. M. Varma, and J. Zhang.

---

*Present address: Department of Physics, Yale University, New Haven, CT 06520.

†Author to whom correspondence should be addressed.

[1] R. von Helmholt *et al.*, Phys. Rev. Lett. **71**, 2331 (1993); S. Jin *et al.*, Science **264**, 413 (1994); K. Chahara *et al.*, Appl. Phys. Lett. **63**, 1990 (1993); R. M. Kusters *et al.*, Physica (Amsterdam) **155B**, 362 (1989).

[2] P. Dai, J. Zhang, H. A. Mook, S-J. Liou, P. A. Dowben, and E. W. Plummer, Phys. Rev. B **54**, 3694 (1996); P. Dai *et al.*, Solid State Commun. **100**, 865 (1996); P. G. Radaelli *et al.*, Phys. Rev. B **54**, 8992 (1996).

[3] S. J. L. Billinge, R. G. DiFrancesco, G. H. Kwei, J. J. Neumeier, and J. D. Thompson, Phys. Rev. Lett. **77**, 715 (1996).

[4] G. Zhao, K. Conder, H. Keller, and K. A. Müller, Nature (London) **381**, 676 (1996).

[5] R. Berman, *Thermal Conduction in Solids* (Oxford University Press, Oxford, 1976), p. 105.

[6] A. H. Morrish, B. J. Evans, J. A. Eaton, and L. K. Leung, Can. J. Phys. **47**, 2691 (1969).

[7] H. Hwang, S-W. Cheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).

[8] C. W. Searle and S. T. Wang, Can. J. Phys. **48**, 2023 (1970).

[9] P. Schiffer, A. P. Ramirez, W. Bao, and S-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).

[10] J. J. Freeman and A. C. Anderson, Phys. Rev. B **34**, 5684 (1986); J. E. Graebner, B. Golding, and L. C. Allen, Phys. Rev. B **34**, 5696 (1986). For a theoretical discussion of κ in this temperature range, see A. Jagannathan, R. Orbach, and O. Entin-Wohlman, *Hopping Transport in Solids* (Elsevier Science Publishers, Amsterdam, 1991), p. 125.

[11] A. P. Ramirez, P. Schiffer, S-W. Cheong, W. Bao, T. T. M. Palstra, P. L. Gammel, D. J. Bishop, and B. Zegarski, Phys. Rev. Lett. **76**, 3188 (1996).

[12] G. Leibfried and E. Schlömann, Nachr. Akad. Wiss. Gött., Math.-Phys. Kl. **4**, 71 (1954).

[13] P. G. Klemens, in Solid State Phys. **7**, 1 (1958).

[14] J. M. Ziman, *Principle of the Theory of Solids* (Cambridge University Press, Cambridge, England, 1972), 2nd ed., Sect. 2.9.

[15] J. Zhang and P. Dai (private communication).

[16] V. Narayanamurti, W. D. Seward, and R. O. Pohl, Phys. Rev. **148**, 481 (1966).

[17] There is no pronounced structural anomaly near 50 K (Ref. [2]).