PHYSICAL REVIEW B VOLUME 56, NUMBER 14 1 OCTOBER 1997-II

Local lattice distortions and thermal transport in perovskite manganites

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(Received 11 June 1997)

Measurements of thermal conductivity versus temperature and magnetic field are reported for perovskite manganites that exhibit ferromagnetic (FM), charge-ordering (CO), antiferromagnetic, and/or structural phase transitions. The data reveal a dominant lattice contribution to the heat conductivity with $\kappa \sim 1-2$ W/mK near room temperature. The rather low values, implying a phonon mean free path on the order of a lattice spacing, are shown to correlate with static local distortions of the MnO_6 octahedra. Modifications of the local structure are responsible for abrupt anomalies in the zero-field κ at the FM, CO, and structural transitions, and for colossal magnetothermal resistance near the FM transition. [S0163-1829(97)51738-3]

It has been recognized recently that colossal magnetoresistance (CMR) in the perovskite manganites involves electron-phonon interactions in addition to the double exchange mechanism.[1] Local distortions of the MnO_6 octahedra[2,3] appear to play an important role in determining the transport of doped holes and the complex magnetic and structural phase behavior. While the electronic transport has been the focus of considerable attention, the heat conductivity (κ) has not been systematically investigated.[4] The rather high electrical resistivity of the manganites implies that the lattice heat conduction should dominate that of the charge carriers even in the ferromagnetic metallic phase, thus offering an alternative probe of the interplay between the lattice, charge, and spin degrees of freedom.

Here we report measurements of κ in doped manganites that demonstrate the influence of structural, ferromagnetic (FM), charge-ordering (CO), and antiferromagnetic (AFM) transitions on the lattice transport. Our results indicate that the lattice thermal resistance is governed by local distortions of the MnO_6 octahedra that are substantially altered by the phase transitions and in applied magnetic fields.

The $La_{0.83}Sr_{0.17}MnO_3$ (LSMO) crystal was grown with the optical-float-zone technique using polycrystalline LSMO feed and seed rods in air at ambient pressure at the melting temperature of 1500 °C. The crystal was oriented by Laue diffraction for transport measurements along the [100] direction. $La_{1-x}Ca_xMnO_3$ (LCMO) and $Pr_{0.5}Sr_{0.5}MnO_3$ (PSMO) polycrystals were prepared by standard solid-state reaction; their characterization, along with resistivity and thermopower measurements on similar specimens, have been reported previously.[5,6] The structures of the LCMO $x=0.15$ and 0.30 specimens were refined from powder x-ray diffraction patterns using Reitveld analysis. Magnetization measurements were performed using a commercial superconducting quantum interference device magnetometer. The thermal conductivity, and in some cases thermopower and resistivity, were measured in a radiation-shielded vacuum probe with a standard steady-state technique. Typical specimen dimensions were $1\times1\times3$ mm^3. Corrections for heat losses via radiation and conduction through the leads, measured in separate experiments, were $\sim$10–15 % of the measured κ at room temperature and $\leqslant$3% for $T<100$ K. Magnetic fields were applied perpendicular to the heat flow with a superconducting solenoid and corrections for the field dependence of the chromel/constantan thermocouple applied.[7]

Figures 1 and 2 show $\kappa(T)$ for the various compounds. κ increases abruptly upon cooling through the respective FM transitions in the CMR compounds at $T_C=275$ K (LSMO), 265 K (PSMO), 255 K (LCMO, $x=0.30$), and decreases sharply below the CO transition[8] at $T_{CO}=275$ K (LCMO, $x=0.65$) and CO/AFM transition[9] at 150 K (PSMO). For the LSMO compound, which is just on the metallic side of the metal-insulator transition, a structural transition from rhombohedral to orthorhombic[3] occurs at $T_S\simeq230$ K for zero-field and 216 K for $H=9$ T. Thermal hysteresis in κ is evident at the structural and CO transitions. All of the κ values are quite low for crystalline solids, with the data for lightly doped LCMO near room temperature falling below values found in some glasses.

Let us first discuss the electronic contribution (κ_e) to the total thermal conductivity. The electronic properties of the paramagnetic phase of the manganites are consistent with

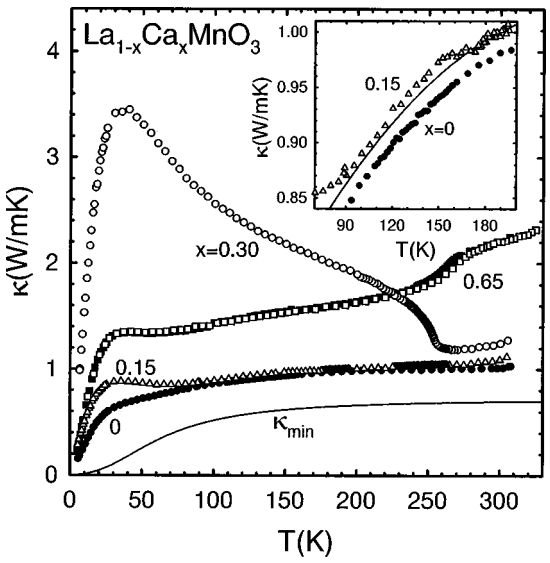

FIG. 1. Thermal conductivity vs temperature for LCMO polycrystals. The inset shows a magnified view of the data for $x=0$, 0.15 showing the anomaly observed near $T_C \simeq 170$ K for $x=0.15$. The solid line represents the data for $x=0$ shifted upward by 0.02 W/mK.

thermally assisted hopping of adiabatic small polarons.[10–12] The thermal conductivity of adiabatic small polarons is expected to be much smaller than implied by the free-electron Wiedemann-Franz law (WFL),[13] and κ_e is negligible in the paramagnetic phase. At $T \leqslant T_C$ the insulator-metal transition should yield an increasing κ_e, following the expected abrupt decrease in polaron binding energy and increase in the intersite transfer energy if the transition is viewed as a small-large polaron crossover.[14] Large polarons move itinerantly and the Wiedemann-Franz ratio has the free-electron value.[15] Thus regardless of the appropriate physical picture for the transition and the resulting FM ground state, the free-electron WFL provides a reasonable upper bound on κ_e. The measured electrical resistivities imply $\kappa_e/\kappa \leqslant 0.2$ at all T in the FM regime for the LCMO ($x=0.30$), LSMO, and PSMO specimens, and considerably less than this near T_C.

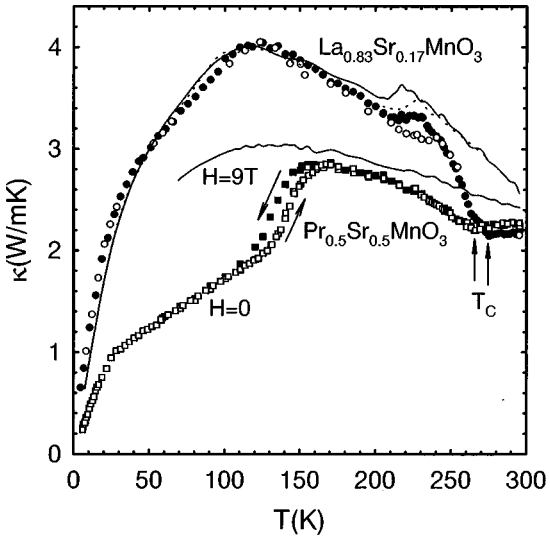

FIG. 2. Thermal conductivity vs temperature for the LSMO crystal and PSMO polycrystal. Solid (open) symbols represent cooling (warming) data for $H=0$. The solid (dashed) lines are for cooling (warming) in $H=9$ T.

The contribution to heat conduction from spin waves (κ_m) at $T \leqslant T_C$ must also be considered for these materials. For other ferromagnetic insulators,[16] κ_m is negligible compared to the lattice term at all but the lowest temperatures ($T \ll \Theta_D$). However, the rather low κ values of the manganites imply a more substantial relative spin-wave contribution, particularly in the regime of interest near T_C where the magnetic specific-heat anomaly (ΔC) represents a considerable fraction of the total specific heat.[8,17] In the region of the anomaly it is reasonable to assume the magnon mean free path is independent of T so that $\Delta\kappa_m \propto \Delta C$. The inset of Fig. 1 shows an enlarged view of the κ data for the LCMO $x=0.15$ sample in the region near its FM transition at $T_C \simeq 170$ K where just such an anomaly is observed. The $x=0$ compound, which has the same lattice contribution to within experimental accuracy at $T > 170$ K, is shown for comparison (no anomaly is seen at its AFM transition, $T_N \simeq 130$ K). This $x=0.15$ composition is on the insulating side of the CMR regime[5] ($0.2 \leqslant x \leqslant 0.5$) where, unlike for CMR compositions, changes in the local structure that can also influence κ are not observed through the FM transition.[2] We see that $\Delta\kappa_m \approx 1.3 \times 10^{-2}$ W/mK. Using the kinetic theory expression, $\Delta\kappa_m = (1/3)\Delta C v_m^2 \tau_m$, and the values $\Delta C = 1.7 \times 10^5$ J/m^{3}K (for $x=0.1$),[8] $v_m = 600$ m/s, and $\tau_m = 2 \times 10^{-12}$ s (v_m and τ_m are the long-wavelength spin-wave velocity and lifetime, respectively[18]), yields $\kappa_m = 4 \times 10^{-2}$ W/mK, in quite reasonable agreement with the data. To estimate the corresponding spin-wave contribution in the CMR region for $x=0.30$ we assume that $\Delta\kappa_m$ scales with the specific heat-anomaly. Using[8] $\Delta C(x=0.33)/\Delta C(x=0.1) = 8$ implies $\Delta\kappa_m(x=0.30) \simeq 0.1$ W/mK. Thus spin waves contribute about 5–10 % of the measured κ at T_C in the CMR compounds and do not account for the much larger zero-field enhancements that extend to lower temperatures.

Having established that κ is predominantly of lattice origin we now address the very small values. Using the model of Cahill *et al.*[19] and a Debye temperature,[20] $\Theta_D = 300$ K, we compute the minimum theoretical value for the lattice conductivity of $LaMnO_3$, $\kappa_{\min}$ (solid line in Fig. 1). This curve corresponds to heat transport via random walk of energy between localized, uncorrelated oscillators, as describes the thermal conductivity of amorphous solids and disordered crystals.[19] For $T \geqslant 100$ K, $LaMnO_3$ has $\kappa/\kappa_{\min} \sim 1.5$, implying a phonon mean free path comparable to the Mn-Mn distance (~ 4 Å). Even for the LSMO crystal, κ(300 K) exceeds $\kappa_{\min}$ only by about a factor of 3. We thus conclude that grain boundary scattering is not a significant source of thermal resistance in the polycrystals. These low values of κ are not simply a consequence of the complex unit cell (with 20 atoms); the closely related lightly doped cuprates have κ values an order of magnitude higher.[21]

Radaelli *et al.*[2] have established a correlation between charge mobility and local distortions of the MnO_6 octahedra (both static and dynamic) in these compounds. These distortions are likely sources of strong phonon scattering and κ values near $\kappa_{\min}$. The structural data[2,9,22] support this proposal for the orthorhombic specimens[23] as shown in Fig. 3

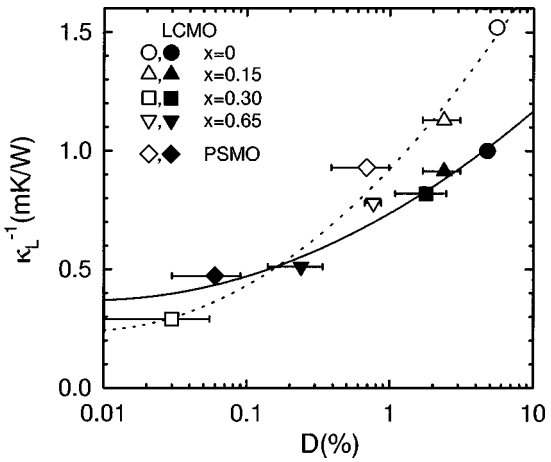

FIG. 3. Lattice thermal resistivity (from free-electron WFL and measured resistivities) at $T=35$ K (open symbols) and 300 K (closed symbols) vs corresponding low- and high-T Mn-O bond distortion (computed from our own refinements and those of Refs. 2, 9, and 22). The solid and dashed lines are guides to the eye.

where the lattice thermal resistivity, κ_L^{-1}, is seen to correlate with the MnO_6 distortion as defined by $D \equiv (1/3)\Sigma_{i=1}{}^{3}|(u_i - \overline{u})/\overline{u}| \times 100$, with u_i the Mn-O bond lengths, and $\overline{u} = (u_1 u_2 u_3)^{1/3}$. That κ_L^{-1} scales with D at both high and low T indicates that the thermal resistance in these materials is primarily controlled by the *static* rather than the *dynamic* MnO_6 distortions since the latter, as reflected in Debye-Waller factors, are larger in CMR compounds at $T > T_C$ but are independent of doping at low T (Booth *et al.*[2]). The correlation is especially convincing given that D is dramatically altered by the FM and CO transitions. For example, PSMO has the smallest D at 300 K, but one of the largest at 35 K; the reverse is true for LCMO $x=0.30$. The decrease in κ upon cooling through the structural transition in LSMO is also consistent with the known increase in the distortion of the octahedra.[3]

The influence of the FM and CO transitions on the lattice transport may be further characterized by examining the sound velocity (v) enhancements observed below T_C and T_{CO} by Ramirez *et al.*[8] for LCMO $x=0.33$ and $x=0.63$, respectively. These authors observed, at $T/T_C = T/T_{CO} \sim 0.8$, relative increases from the values at T_C and T_{CO} of $\Delta v/v \sim 4\%$ and 11%, respectively. In spite of this considerable hardening of the lattice, κ for $x=0.65$ actually *decreases* below T_{CO}; the implication is that the phonon lifetime τ is substantially *reduced*. The kinetic theory expression implies $\Delta\tau/\tau \sim 44\%$ and -30% over the same temperature intervals for $x=0.30$ and $x=0.65$, respectively. Thus the phonon scattering rate correlates with the static MnO_6 distortion, and this scattering underlies the behavior of the thermal resistivity (Fig. 3). That T_C and T_{CO} also represent charge delocalization and localization transitions, respectively, indicates that the lattice distortions are associated with localized charge, possibly a manifestation of small polarons.

Further insight into the close correspondence between the lattice and charge transport is provided by the magnetic-field dependence of κ for the LSMO crystal, shown in Fig. 4(a) at three temperatures in the CMR regime. The field effect is very large, $\Delta\kappa(H)/\kappa \simeq 34\%$ at $H=9$ T for $T \approx T_C = 275$ K.

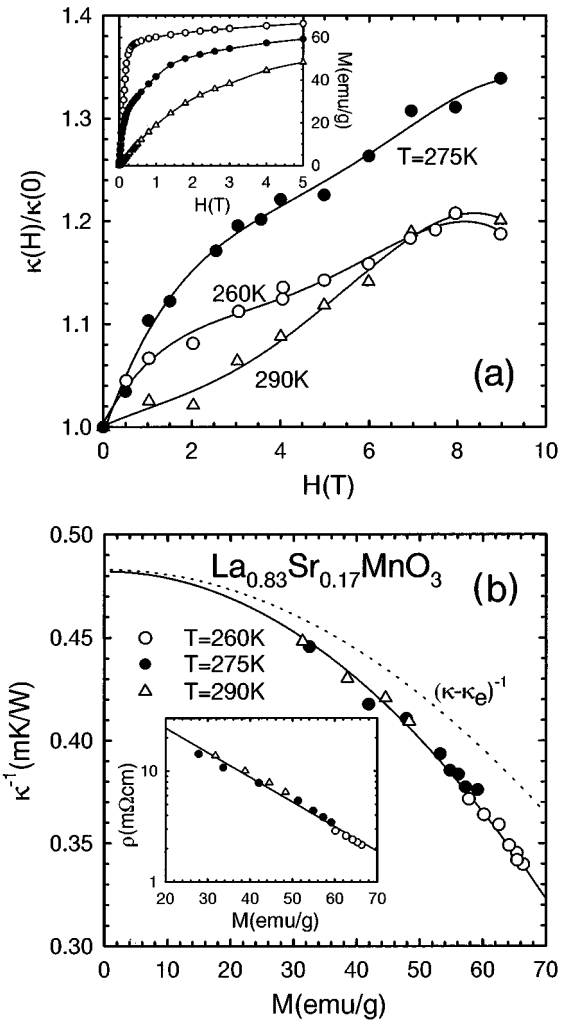

FIG. 4. (a) Normalized magnetothermal conductivity vs applied field for the LSMO crystal. The inset shows magnetization data at the same temperatures. Solid lines are guides to the eye. (b) Thermal resistivity vs magnetization computed from the data in (a). The solid line is a fit to the form, $\kappa^{-1} = A - BM^2$. The Wiedemann-Franz estimate of the electronic contribution is subtracted to yield the dashed curve. The inset shows ρ vs M at the same temperatures with a fit (solid line) to the exponential relation discussed in the text.

More compelling is Fig. 4(b) where we plot κ^{-1} vs M by employing the magnetization curves, $M(H)$ [inset, Fig. 4(a)]. We see that κ^{-1} is a single function of $M(H,T)$, with $\kappa^{-1}(H,T) = A - BM^2(H,T)$ providing a good fit [solid line in Fig. 4(b)]. Similar to Hundley *et al.*[10] we find that the electrical resistivity for our LSMO crystal also correlates with M [inset, Fig. 4(b)], following the exponential relation, $\rho(H,T) = \rho_0 \exp[-M(H,T)/M_0]$, with $\rho_0 = 68$ mΩ cm and $M_0 = 19.5$ emu/g. The change in the lattice contribution [dashed line, Fig. 4(b)] predominates in the magnetothermal resistivity. These results indicate that both the lattice and charge mobilities are governed by the same local physics. Double-exchange and strong electron-phonon interactions[1] appear to yield the appropriate framework wherein M is a measure of the intersite electron transfer energy, and the latter determines both the degree of electronic localization and associated local MnO_6 distortions. Our results complement

measurements of magnetovolume effects[3,24] which indicate that substantial field-induced structural changes occur in these materials, even in the rhombohedral phase.

Finally we note that anomalous spin fluctuations associated with electron diffusion[18] near T_C suggest the interesting possibility that an applied field of several teslas enhances the magnon heat conduction, an unconventional effect since the conventional spin-wave thermal conductivity[16] is unaffected at low fields ($g\mu_B H/k_B T \ll 1$). The neutron-scattering results of Lynn *et al.*[18] indicate that in such fields the diffusive spectral weight is transferred into the spin waves, enhancing their contribution by nearly an order of magnitude at T_C. Further studies are required to address this possible contribution to $\kappa(H)$.

The authors gratefully acknowledge B. Fisher for providing PSMO and helpful comments, G. Kwei for structural parameters of LCMO $x=0.65$, and D. Emin for informative discussions. The work at the University of Miami was supported by NSF Grant No. DMR-9631236.

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