Heat Conduction and Magnetic Phase Behavior in Electron-Doped Ca$_{1-x}$La$_x$MnO$_3$

(0 ≤ x ≤ 0.2)

J. L. Cohn$^1$ and J. J. Neumeier$^2$

$^1$ Department of Physics, University of Miami, Coral Gables, Florida 33124 and
$^2$ Department of Physics, Florida Atlantic University, Boca Raton, Florida

Measurements of thermal conductivity (κ) vs temperature are reported for a series of Ca$_{1-x}$La$_x$MnO$_3$ (0 ≤ x ≤ 0.2) specimens. For the undoped (x = 0), G-type antiferromagnetic compound a large enhancement of κ below the Neél temperature ($T_N$ ∼ 125K) indicates a strong coupling of heat-carrying phonons to the spin system. This enhancement exhibits a nonmonotonic behavior with increasing x and correlates remarkably well with the small ferromagnetic component of the magnetization reported previously [Neumeier and Cohn, Phys. Rev. B 61 14319 (2000).] Magnetoelastic polaron formation appears to underly the behavior of κ and the magnetization at x ≤ 0.02.

PACS numbers: 75.50.-y, 66.70.+f, 71.38.-k, 75.30.-m

Electronic phase separation has emerged as a paradigm for describing the ground state of strongly correlated electron systems. It may underly the phenomenon of colossal magnetoresistance (CMR) in hole-doped (Mn$^{3+}$-rich) perovskite manganites studied extensively in recent years. A few studies of electron-doped (Mn$^{4+}$-rich) manganites revealed anomalous magnetic properties and drew attention to these compounds. Subsequent investigations suggested that this phase separation in electron-doped manganites may be of technological importance because of the resultant colossal magnetoresistance (CMR) in hole-doped (Mn$^{3+}$-rich) manganites.

Manganites and by prior work $^{15}$ motivated by the novel phase behavior of electron-doped manganites, and by the discovery that the lattice thermal resistivity of manganites is a sensitive measure of bond disorder arising from distorted MnO$_6$ octahedra. Electron hopping via double exchange couples the spins to these octahedral distortions. For the present system the thermal conductivity clearly reflects the lattice response to the FM moment throughout the doping range. At low doping (x ≤ 0.02) the evolution of κ and the magnetization suggests a competition between long-range antiferromagnetism and magnetoelastic polaron formation.

Ca$_{1-x}$La$_x$MnO$_3$ polycrystals were prepared by standard solid-state reaction; the preparation methods along with magnetization and resistivity measurements are reported elsewhere. Iodometric titration indicated the oxygen content of all specimens fell within the range 3.00±0.01. The thermal conductivity was measured in a radiation-shielded vacuum probe using a differential chromel/constantan thermocouple and steady-state technique. Typical specimen dimensions were 1×1×3mm$^3$. Heat losses via radiation and conduction through leads were measured in separate experiments and the data corrected accordingly. This correction was typically 10-15% near room temperature and ≤ 2% for T ≤ 150 K. The specimens have a density of 78±4% that of fully dense material, with no systematic dependence on doping; no porosity corrections have been applied.

Fig. 1 shows κ(T) for a series of specimens. The data for Ca$_{1-x}$La$_x$MnO$_3$ (x = 0) indicate a large enhancement of κ at temperatures below $T_N(G)$ = 130K (for the remainder of the paper we write $T_N$ to mean $T_N(G)$). The other compounds also show an enhancement, but with a diminished magnitude. For all values of x the electronic contribution to κ at T < 150 K, as inferred from the electrical resistivity and Wiedemann-Franz relation, is less than 5% of the measured value. Furthermore, no substantial changes were observed in resistivities through T$_N$. Thus the enhancement is associated with either a magnon or phonon contribution to heat conduction.

To characterize the enhancement, we define the dimensionless change in slope, evaluated just below $T_N$, as $\Gamma \equiv -d(\kappa/T)/dT |_{T\rightarrow T_N}$, where $\kappa_p$ is the $T$-dependent thermal conductivity in the paramagnetic

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The behavior of $\kappa_p$ at $T < T_N$ is taken as the extrapolation of polynomial fits to data at $T > T_N$ (solid curves in Fig. 1). The doping behavior $\Gamma(x)$ is shown in Fig. 2 of particular interest is the nonmonotonic behavior. $\Gamma(x)$ appears to be composed of two contributions: a term strongly decreasing with $x$ and operative for $x \lesssim 0.02$, and a term proportional to the FM saturation moment (open triangles and right ordinate). Open circles with solid lines are computed from magnetization data as discussed in the text and Eq. (1).

Increases in $\kappa$ at AF transitions have been observed previously in MnO$_3$ and LaMnO$_3$ crystals. The former material undergoes a substantial crystallographic distortion below $T_N$ (magnetostriction), and this suggests changes in the lattice heat conduction as a likely mechanism for the $\kappa$ enhancement. Lattice anomalies associated with magneto or exchange striction are quite small for MnO$_3$ and LaMnO$_3$. Nevertheless, prior work demonstrated that the lattice thermal resistivity of manganites at $T \leq 300K$ is controlled principally by distortions of the MnO$_6$ octahedra through their influence on phonon scattering rates. The latter can be substantially more sensitive to internal structural modifications than are lattice or elastic constants. Heat conduction by magnons could contribute to the enhancement, but this seems less likely given that magnons contribute negligibly to $\kappa$ near $T_C$ for ferromagnetic compositions. The subsequent analysis supports a lattice response to magnetic order as the mechanism for $\Gamma$ in these compounds.

The observation $\Gamma \propto M_{sat}$ for $x \gtrsim 0.03$ is reminiscent of the behavior found for CMR compounds. The lattice contribution to $\kappa$ in CMR materials is enhanced below the zero-field FM transition temperature and in applied magnetic field at fixed $T$ near $T_C$. This lattice response correlates with a reduced distortion of the MnO$_6$ octahedra that accompanies double-exchange mediated charge delocalization. Underlying the field and $T$-dependent thermal resistivity ($W = 1/\kappa$) of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ is a simple magnetization dependence $W(M) \propto -M^2(H, T)$.

We now show that the nonmonotonic behavior of $\Gamma(x)$ for Ca$_{1-x}$La$_x$MnO$_3$ is remarkably well reproduced by a similar phenomenological assumption for $T < T_N$: $W(M, T) = W(0, T) \propto M(T) - M_p(T)$. $M_p(T)$ is the magnetization of the paramagnetic phase. For zero-field measurements, $M(T)$ is the spontaneous magnetization, $W(M, T) = \kappa^{-1}$ is the measured thermal resistivity, and $W(0, T) \equiv \kappa_p^{-1}$ (the hypothetical thermal resistivity in the absence of magnetic order). This assumption implies that $\Gamma$ should be proportional to the normalized change in slope of the magnetization, evaluated just below $T_N$,

$$\Gamma = -\beta \frac{T_N}{M(T_N)} \left( \frac{dM}{dT} \bigg|_{T \to T_N} - \frac{dM_p}{dT} \bigg|_{T \to T_N} \right) \equiv \beta \Gamma^M$$

(1)

Using the available $M(T)$ curves measured at $H = 2kOe$, excellent agreement of $\Gamma(x)$ with Eq. (1) was found for all $x$, with proportionality constant $\beta = 2.52 \times 10^{-4}$ (open circles and solid curve, Fig. 2).

This result is most easily interpreted in the regime $x \gtrsim 0.03$ where $\Gamma \propto M_{sat}$. Though no insulator-metal transition takes place at $T_N$ akin to that at $T_C$ in CMR
compounds, there is clear evidence in electrical resistivity measurements near $x = 0.10$ that some electron delocalization takes place below $T_N$; the slopes, $-(1/\rho)d\rho/dT$, exhibit an abrupt change at the transition (Fig. 3). In analogy with the case of CMR materials, the correlation between $\Gamma$ and magnetization in this regime is plausibly attributed to enhanced electron hopping mediated by double-exchange between aligned (FM droplet scenario) or partially aligned (canting scenario) spins. Enhanced electron transfer reduces the average distortion of the MnO$_6$ octahedra and associated phonon scattering within the FM regions of the specimen. That $\Gamma$ follows both $M_{sat}$ and $\Gamma^M$ is consistent with a conventional magnetization of the form $M = M_{sat}f(T)$ where $f(T)$ reflects the order parameter of the FM phase.

The regime $x \leq 0.02$ is more complicated since $M_{sat}$ has a very different $x$ dependence from that of $\Gamma^M$ (and $\Gamma$). These different doping behaviors entail a crossing of the $M(T)$ curves for different $x$ at $T < T_N$ (Fig. 3). The data suggest that two independent components contribute to the magnetization in this regime, one with $T_C = 125$ K, characterizing the undoped specimen, and the other with $T_C \approx 115$ K, characterizing $x \geq 0.04$. A smooth evolution between the two is reflected in the $M(T)$ data for the intervening compositions. This coexistence is most evident in the curve for $x = 0.02$ as an inflection near $T = 110$ K.

$\Gamma$ follows the diminution of the higher-$T$ transition and presumably has its origin in the same coupling between spins and octahedral distortions underlying the response at $x \geq 0.03$. Supporting this hypothesis is a recent study of Raman scattering in similar compounds. Sharply enhanced Raman intensities at $T < T_N$ for low-frequency, rotational and bending modes of the oxygen octahedra were observed for CaMnO$_3$. With increasing La doping this enhancement below $T_N$ was diminished, and was absent for $x = 0.03$, very similar to the trend observed here for $\Gamma$. It seems likely that the two phenomena are related.

Another important experimental result relevant to a description of the data at low $x$ comes from recent magnetic neutron scattering studies of an $x = 0.02$ compound in magnetic field. The field dependence of the AF scattering intensity was inconsistent with a FM component arising from either uniform spin canting or ferrimagnetism; the FM component is decoupled from the AF background in applied field.

These observations implicate magnetoelastic polarons in the FM and lattice response at low $x$. In this regard the behavior of the slope $dM_{sat}/dx$ is of interest (inset, Fig. 3). It increases from $\sim \mu_B$ to $\sim 7\mu_B$ for $0.03 \leq x \leq 0.08$. The latter is the value expected if each La dopant adds a symmetric 7-site FM polaron determined in calculations to be the stable ground state for this system. The value $x \approx 0.03$ appears to mark a crossover between regimes. The mean spacing between dopant ions is estimated as $r_{La} = (3V/16\pi x)^{1/3}$ (where $V = 207\AA^3$ is the unit cell volume containing 4 f.u.’s). For $x = 0.03$, $r_{La} \approx 7.4\AA$, equal to the 3rd-nearest neighbor Mn distance. This would be the distance between the centers of 7-site polarons sharing a single Mn site (a polaron “cluster”), but other polaron configurations are close in ground-state energy and might be favored if interactions not yet considered in calculations (e.g., defects, next-nearest neighbor exchange) play a role. For example, larger polarons with canting-spin arrangements are interesting candidates because the large-scale clusters anticipated at higher doping could evolve smoothly into the long-range, spin-canted state proposed on the basis of neutron scattering for $x \geq 0.06$.

A model that distinguishes between isolated and clustered polarons describes the qualitative features of the experimental results. We propose that $T_C = 125$ K

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**FIG. 3:** Temperature derivative of electrical resistivity vs temperature for Ca$_{1-x}$La$_x$MnO$_3$ specimens with $x$ near 0.10. Features marked by arrows indicate electronic delocalization below $T_N \approx 110$K.

**FIG. 4:** Magnetization at $H = 2000$Oe for lightly-doped specimens.
transition in Fig. 4 is associated with isolated polarons (i.e. those without adjacent polarons) and the lower-$T_C$ transition to clusters of two or more polarons. This is plausible since the balance between kinetic, lattice and spin energies, possibly different for a cluster, could yield a polaronic state less robust against thermal fluctuations. Presumably a small (principally isolated) polaron density at $x=0$ is associated with native defects (e.g. oxygen or Mn vacancies). With increasing La doping, polaron clusters are produced at the expense of isolated polarons. For a random distribution, the probability for 7-site or larger polarons given the large number of Mn sites over which electrons may be distributed to define a cluster. This provides a natural explanation for the rapid decrease of $\Gamma$ and $\Gamma^M$ with $x$ at $x \leq 0.02$, and for their minima at $x \approx 0.03$ where the FM transition is maximally nonuniform.

What is the origin of the small value for $dM_{sat}/dx$ at $x \leq 0.02$ and its increase near $x \approx 0.03$? One possibility is that these features reflect differing magnetic moments for isolated and clustered polarons (e.g. different canting angles for spin-canted polarons). Alternatively, these features might reflect a change in the number of polarons induced per dopant, e.g. if perturbations associated with defects (vacancies, La ions) suppress polaron formation at $x \leq 0.02$. Experimental investigations that better define the polaron characteristics are required to refine these ideas.

In summary, systematic changes in the behavior of the thermal conductivity at the AF transition in La-doped CaMnO$_3$ and their correlation with magnetization measurements indicate that the lattice thermal resistivity is a sensitive probe of FM interactions through the coupling of spins to local distortions of the MnO$_6$ octahedra. This extends similar conclusions obtained previously for hole-doped, CMR compounds [15] to the present system where the ground state appears to consist of magneto-elastic polarons ($x \leq 0.02$) and a spin-canted phase ($x \geq 0.06$). The crossover between these two regimes, clearly manifested in both the thermal conductivity and magnetization data, appears to reflect novel polaron physics and is of particular interest for further study.

The authors acknowledge experimental assistance from Dr. B. Zawilski and Dr. R. Maier. The work at the University of Miami was supported, in part, by NSF Grant No.’s DMR-9631236 and DMR-0072276, and at Florida Atlantic University by DMR-9982834.

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