PHYSICAL REVIEW B **66**, 100404(R) (2002)

Heat conduction and magnetic phase behavior in electron-doped $Ca_{1-x}La_xMnO_3$ ($0 \leqslant x \leqslant 0.2$)

J. L. Cohn[1] and J. J. Neumeier[2]
[1]*Department of Physics, University of Miami, Coral Gables, Florida 33124*
[2]*Department of Physics, Florida Atlantic University, Boca Raton, Florida*
(Received 31 May 2002; published 9 September 2002)

Measurements of thermal conductivity (κ) vs temperature are reported for a series of $Ca_{1-x}La_xMnO_3$ ($0 \leqslant x \leqslant 0.2$) specimens. For the undoped ($x=0$), *G*-type antiferromagnetic compound a large enhancement of κ below the Neél temperature ($T_N \sim 125$ *K*) 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 $x \leqslant 0.02$.

DOI: 10.1103/PhysRevB.66.100404 PACS number(s): 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.[1] 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[2] revealed anomalous magnetic properties and drew attention to these compounds. Subsequent investigations[3–9] suggested electron-doped manganites to be interesting systems for studies of phase separation and polaron physics.

Undoped $CaMnO_3$ exhibits a *G*-type antiferromagnetic (AFM) order below $T_N \approx 125$ K. With $\sim 20\%$ trivalent substitution for divalent Ca, the system adopts a *C*-type, orbitally ordered AFM ground state with $T_N \sim 150$–200 K, depending on the dopant ions. For Mn^{3+} concentrations between these end points a small ferromagnetic (FM) moment is observed with $T_C = T_N(G)$ and a nonmonotonic doping behavior; data from Ref. 3 on $Ca_{1-x}La_xMnO_3$ ($0 \leqslant x \leqslant 0.2$) are shown in the inset of Fig. 1.

A fundamental issue is whether this FM component reflects a homogeneous canting of AFM moments for all *x* in this regime, as originally proposed by deGennes,[10] or whether some portion of the phase behavior can be attributed to FM droplets or polarons as found for the hole-doped compounds.[11] A very recent neutron scattering study[12] of $Ca_{1-x}La_xMnO_3$ constrains models for the regime $0.06 \leqslant x \leqslant 0.16$: (1) the FM moment is perpendicular to the *G*-AFM moment, consistent with homogeneous canting, and (2) FM clusters with sizes smaller than ~ 800 Å do not exist. Similar experiments at low doping $x \leqslant 0.05$ have not been reported, but this regime has been investigated theoretically.[13,14]

The present study of thermal conductivity (κ) vs temperature on $Ca_{1-x}La_xMnO_3$ ($0 \leqslant x \leqslant 0.2$) was motivated by the novel phase behavior of electron-doped manganites and by prior work[15,16] demonstrating 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 ($x \leqslant 0.02$) the evolution of κ and the magnetization suggests a competition between long-range antiferromagnetism and magnetoelastic polaron formation.

$Ca_{1-x}La_xMnO_3$ polycrystals were prepared by standard solid-state reaction; the preparation methods along with magnetization and resistivity measurements were reported elsewhere.[3] 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 $1 \times 1 \times 3$ mm^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 $\leqslant 2\%$ for $T \leqslant 150$ K. The specimens have a density of 78 ± 4 % that of

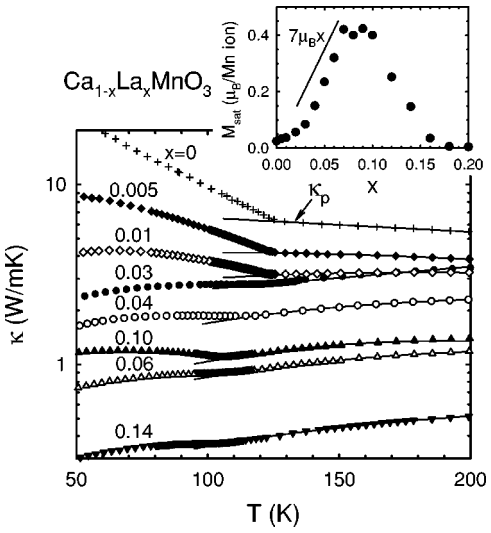

FIG. 1. Thermal conductivity vs temperature for $Ca_{1-x}La_xMnO_3$ polycrystals. The solid curves are polynomial fits to data in the paramagnetic phase. Inset: $T=5$ K saturation magnetization vs *x* for $Ca_{1-x}La_xMnO_3$ polycrystals from Ref. 3. The solid line represents $M_{sat} = 7\mu_B$/Mn-ion-electron.

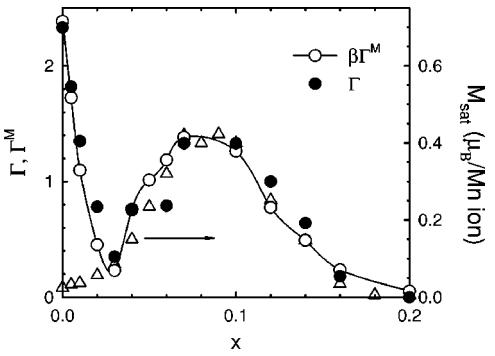

FIG. 2. Doping dependence of the dimensionless thermal conductivity slope change at T_N (Γ, defined in the text), and of the $T=5$ K saturation magnetization from Ref. 3 (open triangles, right ordinate). Open circles with solid lines are computed from magnetization data as discussed in the text and Eq. (1).

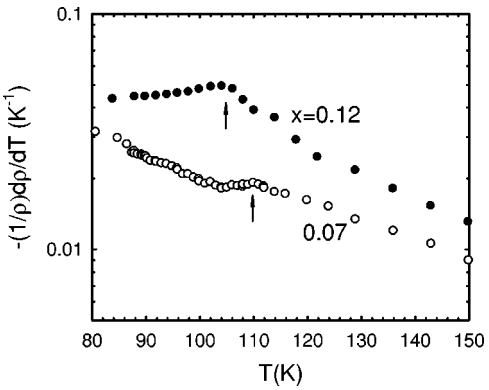

FIG. 3. Temperature derivative of electrical resistivity vs temperature for $Ca_{1-x}La_xMnO_3$ specimens with x near 0.10. Features marked by arrows indicate electronic delocalization below $T_N \approx 110$ K.

fully dense material, with no systematic dependence on doping; no porosity corrections have been applied.

Figure 1 shows $\kappa(T)$ for a series of specimens. The data for $CaMnO_3(x=0)$ indicate a large enhancement of κ at temperatures below $T_N(G)=125$ K [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[3] and the 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 $\Gamma \equiv -d(\kappa/\kappa_p)/dt|_{t\to 1}$, where κ_p is the T-dependent thermal conductivity in the paramagnetic state ($T>T_N$) and $t=T/T_N$. The behavior of κ_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, Fig. 2) operative for $x \gtrsim 0.03$.

Increases in κ at AF transitions have been observed previously in MnO (Ref. 17) and $LaMnO_3$ (Ref. 18) 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 its κ enhancement. Lattice anomalies associated with magneto or exchange striction are quite small for[19] $LaMnO_3$ and[20–22] $CaMnO_3$. Nevertheless, prior work[15,16] demonstrated that the lattice thermal resistivity of manganites at $T \leqslant 300$ K 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 κ near T_C for ferromagnetic compositions.[15] The subsequent analysis supports a lattice response to magnetic order as the mechanism for Γ in these compounds.

The observation $\Gamma \propto M_{sat}$ for $x \gtrsim 0.03$ is reminiscent of the behavior found for CMR compounds.[15] The lattice contribution to κ 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 $La_{0.83}Sr_{0.17}MnO_3$ is a simple magnetization dependence,[15] $W(M)-W(0) \propto -M^2(H,T)$.

We now show that the nonmonotonic behavior of $\Gamma(x)$ for $Ca_{1-x}La_xMnO_3$ 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 Γ should be proportional to the normalized change in slope of the magnetization, evaluated just below T_N:

$$\Gamma = -\beta \frac{T_N}{M(T_N)} \left(\left. \frac{dM}{dT} \right|_{T\to T_N} - \left. \frac{dM_p}{dT} \right|_{T\to T_N} \right) \equiv \beta \Gamma^M \quad (1)$$

Using the available $M(T)$ curves[3] measured at $H=2$ kOe, excellent agreement[23] 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

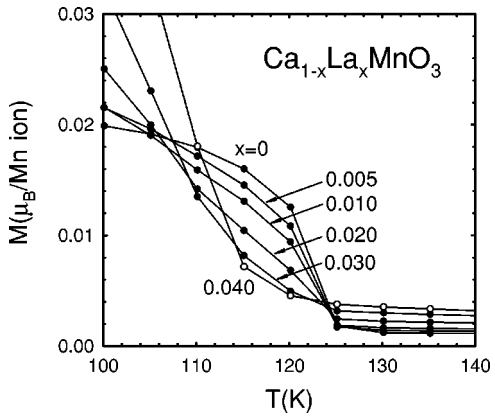

FIG. 4. Magnetization at $H=2000$ Oe for lightly doped specimens.

CMR materials, the correlation between Γ 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 Γ follows both M_{sat} and Γ^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 $x\leqslant 0.02$ is more complicated since M_{sat} has a very different x dependence from that of Γ^M (and Γ). These different doping behaviors entail a crossing of the $M(T)$ curves for different x at $T<T_N$ (Fig. 4). 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 $T_C\lesssim 115$ K, characterizing $x\geqslant 0.04$. 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.

Γ 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 $x\geqslant 0.03$. Supporting this hypothesis is a recent study of Raman scattering in similar compounds.[20] 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 Γ. 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.[24] 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. 1). It increases from $\sim 1\mu_B$/Mn-ion-electron for $x\leqslant 0.02$ to $\sim 7\mu_B$/Mn-ion-electron for $0.03\leqslant x\leqslant 0.08$. The latter is the value expected if each La dopant adds a symmetric seven-site FM polaron,[3] determined in calculations[14] to be the stable ground state for this system. The value $x\simeq 0.03$ appears to mark a crossover between regimes. The mean spacing between dopant ions is estimated as $r_{La}=(3V/16\pi x)^{1/3}$ ($V=207$ Å^3 is the unit cell volume,[12] containing four f.u.'s). For $x=0.03$, $r_{La}\simeq 7.4$ Å, equal to the third-nearest-neighbor Mn distance. This would be the distance between the centers of seven-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[14] (e.g., defects, next-nearest-neighbor exchange) play a role. For example, larger polarons with canted-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[12] for $x\geqslant 0.06$.

A model that distinguishes between isolated and clustered polarons describes the qualitative features of the experimental results. We propose that the $T_C=125$ K 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 two or more polarons to share a Mn site grows rapidly for seven-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 Γ and Γ^M with x at $x\leqslant 0.02$, and for their minima at $x\simeq 0.03$ where the FM transition is maximally nonuniform.

What is the origin of the small value for dM_{sat}/dx at $x\leqslant 0.02$ and its increase near $x\simeq 0.03$? 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 $x\leqslant 0.02$. 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[15,16] to the present system where the ground state

appears to consist of magnetoelastic polarons ($x \leqslant 0.02$) and a spin-canted phase ($x \geqslant 0.06$). 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 Nos. DMR-9631236 and DMR-0072276, and at Florida Atlantic University by Grant No. DMR-9982834.

[1] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
[2] H. Chiba, M. Kikuchi, K. Kasuba, Y. Muraoka, and Y. Syono, Solid State Commun. **99**, 499 (1996); I.O. Troyanchuk, N.V. Samsonenko, H. Szymezak, and A. Nabialek, J. Solid State Chem. **131**, 144 (1997); A. Maignan, C. Martin, F. Damay, B. Raveau, and J. Hejtmánek, Phys. Rev. B **58**, 2758 (1998).
[3] J.J. Neumeier and J.L. Cohn, Phys. Rev. B **61**, 14 319 (2000).
[4] C. Martin, A. Maignan, M. Hervieu, B. Raveau, Z. Jirák, M. Savosta, A. Kurbakov, V. Trounov, G. André, and F. Bourée, Phys. Rev. B **62**, 6442 (2000).
[5] M.M. Savosta, P. Novák, M. Marysko, Z. Jirák, J. Hejtmánek, J. Englich, J. Kohout, C. Martin, and B. Raveau, Phys. Rev. B **62**, 9532 (2000).
[6] R. Mahendiran, A. Maignan, C. Martin, M. Hervieu, and B. Raveau, Phys. Rev. B **62**, 11 644 (2000).
[7] P.N. Santhosh, J. Goldberger, P.M. Woodward, T. Vogt, W.P. Lee, and A.J. Epstein, Phys. Rev. B **62**, 14 928 (2000).
[8] M. Respaud, J.M. Broto, H. Rakoto, J. Vanacken, P. Wagner, C. Martin, A. Maignan, and B. Raveau, Phys. Rev. B **63**, 144426 (2001).
[9] H. Aliaga, M.T. Causa, H. Salva, M. Tovar, A. Butera, B. Alascio, D. Vega, G. Polla, G. Leyva, and P. Konig, cond-mat/0010295 (unpublished).
[10] P.-G. deGennes, Phys. Rev. **118**, 141 (1960).
[11] M. Hennion, F. Moussa, G. Biotteau, J. Rodriguez-Carvajal, L. Pinsard, and A. Revcolevschi, Phys. Rev. Lett. **81**, 1957 (1998).
[12] C. D. Ling, J. J. Neumeier, E. Granado, J. W. Lynn, D. N. Argyriou, and P. L. Lee (unpublished).
[13] C.D. Batista, J. Eroles, M. Avignon, and B. Alascio, Phys. Rev. B **58**, R14 689 (1998).
[14] Y.-R. Chen and P.B. Allen, Phys. Rev. B **64**, 064401 (2001).
[15] J.L. Cohn, J.J. Neumeier, C.P. Popoviciu, K.J. McClellan, and Th. Leventouri, Phys. Rev. B **56**, R8495 (1997).
[16] J.L. Cohn, J. Supercond. : Incorp. Novel Magn. **13**, 291 (2000).
[17] G.A. Slack and R. Newman, Phys. Rev. Lett. **1**, 359 (1958).
[18] J.-S. Zhou and J.B. Goodenough, Phys. Rev. B **64**, 024421 (2001).
[19] C. Ritter, M.R. Ibarra, J.M. De Teresa, P.A. Algarabel, C. Marquina, J. Blasco, J. Garcia, S. Oseroff, and S.-W. Cheong, Phys. Rev. B **56**, 8902 (1997).
[20] E. Granado, N.O. Moreno, H. Martinho, A. Garcia, J.A. Sanjurjo, I. Torriani, C. Rettori, J.J. Neumeier, and S.B. Oseroff, Phys. Rev. Lett. **86**, 5385 (2001).
[21] R.K. Zheng, C.F. Zhu, J.Q. Xie, and X.G. Li, Phys. Rev. B **63**, 024427 (2001).
[22] J.J. Neumeier, A.L. Cornelius, and K. Andres, Phys. Rev. B **64**, 172406 (2001).
[23] That agreement with Eq. (1) is found using the *field-induced* rather than the *spontaneous* magnetization suggests that either both Γ and β are field independent, or that their field dependencies cancel in their product.
[24] E. Granado (private communication).