Low-temperature specific heat of $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$

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We report measurements of the specific heat of $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$ for temperatures $2<T<15$ K. These materials are ferromagnetic metallic oxides which exhibit colossal magnetoresistance. We find that above 3 K the specific heat has terms proportional to T and T^3, but a $T^{3/2}$ term, as might be expected from the excitation of ferromagnetic spin waves, cannot be resolved outside of the precision of the data. The cubic term gives Debye temperatures of 400±17 K, and the linear term gives electron densities of states which are enhanced over band-structure estimates. [S0163-1829(96)04545-6]

Recently colossal magnetoresistance (CMR) in various perovskite oxide manganites has become a topic of considerable research interest.[1–11] CMR has been found near the ferromagnetic ordering temperature T_c of Mn spins in oxides of the general chemical formula $R_{1-x}A_xMnO_3$, where R is trivalent La, Pr, or Nd, and A is divalent Ba, Sr, or Ca. The typical composition where this has been most studied is $x\sim1/3$, although the effect can be seen in a wider range of composition with $x\geqslant0.1$.[9,12] The electronic transport, ferromagnetism, and CMR depend on the concentration of Mn^{4+} ions which are created by substitution of trivalent R ions with divalent A ions. These oxides exhibit semiconducting behavior in the paramagnetic state and metallic behavior in the ferromagnetic state. The transition from semiconducting to metallic behavior occurs near T_c. As a result, the resistivity peaks at a temperature $T\sim T_c$. The fundamental origin of the semiconductor-metal transition and the large CMR effect are not well understood at present. Traditionally, the electronic and magnetic properties of the manganites were explained by the "double-exchange" (DE) model.[13,14] However, a recent calculation[15] showed that the resistivity change in an applied magnetic field could not be explained by the DE model alone and the authors proposed that a Jahn-Teller-type electron-phonon coupling must also play an important role.

To better understand the electronic properties of these materials and to make contact with various proposed models, it is crucial to measure the fundamental properties of the ferromagnetic state. In this article we report measurements of the specific heat of $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$ in the ferromagnetic state well below T_c. The measurements allow us to probe fundamental parameters of the manganites, namely the density of states at the Fermi level $N(E_F)$, the Debye temperature θ_D, and the stiffness constant D corresponding to the ferromagnetic spin waves. D is defined by the spin-wave dispersion relation $\epsilon=Dq^2$, where ϵ is the energy and q is the momentum wave vector.

We made specific-heat measurements on three ceramic samples: one of $La_{0.8}Ca_{0.2}MnO_3$ and two of $La_{0.67}Ba_{0.33}MnO_3$. The mass range was 10–50 mg, and the samples were annealed for 12 h in air at 1000 °C after fabrication. The samples were further characterized by x-ray diffraction and iodometric titration, which showed that the samples contained less than 3% impurity phases, and that the oxygen content was $3\pm y$ where $y\leqslant\sim0.01$. Magnetization curves showed T_c's of 330–340 K for the Ba-doped samples, and 250 K for the Ca-doped sample, and the saturation moments implied fully magnetized and homogeneous samples. The specific heat was measured in the temperature range 2–15 K by relaxation calorimetry, with an absolute accuracy, as measured against a copper calibration sample, of 10%.

In Fig. 1 we show the specific heat C as a function of temperature for all three samples. We considered a temperature dependence of the form

$$C=\gamma T+\delta T^{3/2}+\beta T^3 \tag{1}$$

where γ, δ, and β are constants. These three terms are expected to arise from, respectively, charge carriers, ferromagnetic spin waves, and the lattice. In Fig. 2 the same data are shown in the form of C/T vs T^2 in the range of 2–8 K. The linearity of the curves in Fig. 2 above ~3 K indicates that the data fit Eq. (1) very well with the value of $\delta=0$. Below 3 K, the specific heat departs from this behavior showing an excess of unknown origin. Above 8 K, higher-order lattice terms can be expected to contribute. The degree to which the data can be used to rule out nonzero values of δ will be discussed in more detail below.

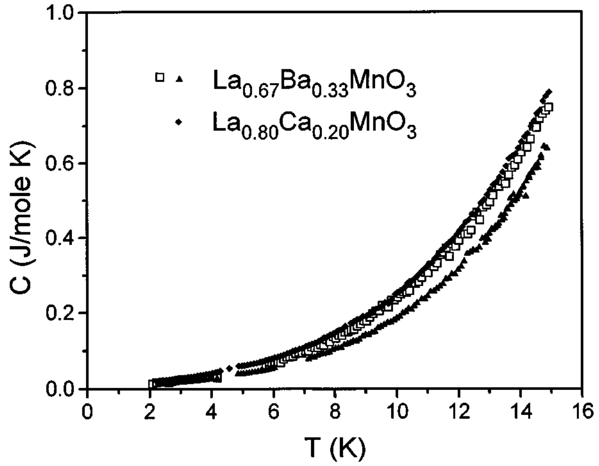

FIG. 1. Low-temperature specific heat of various CMR ceramic samples.

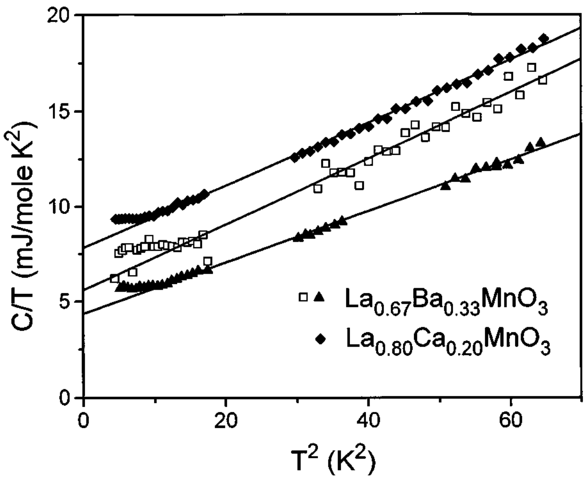

FIG. 2. Specific heat plotted as C/T vs T^2. Lines are best fits to the form $C=\gamma T+\beta T^3$.

Values of γ turn out to be 4.4±0.1 and 5.6±0.15 mJ/mole K^2 for the Ba-doped samples, and 7.8±0.07 mJ/mol K^2 for the Ca-doped sample. For β we obtain 0.13±0.005 and 0.173±0.005 mJ/mole K^4 (Ba-doped), and 0.164 ±0.0015 mJ/mole K^4 (Ca doped). Recently, Coey *et al.* found $\gamma=6.1$ mJ/mole K^2 and $\beta=0.263$ mJ/mole K^4 for $\mathrm{La_{0.7}Ba_{0.3}MnO_3}$.[16] It is not understood why our two Ba-doped samples are different, since they are from the same batch and had the same heat treatments. More study is needed to resolve this question, as well as the differences with Coey's data on nominally the same sample.

From β we obtain the Debye temperature by using the standard expression

$$\theta_D=\left(\frac{12\pi^4 pR}{5\beta}\right)^{1/3}, \tag{2}$$

where R is the ideal gas constant and $p=5$ is the number of atoms per formula unit. We get $\theta_D=383\pm2$ and 416 ± 2 K for the Ba-doped samples, and $\theta_D=390\pm1$ K for the Ca-doped sample. These values are comparable to the Debye temperatures often found in oxides of the $AB\mathrm{O}_3$-type structure. For example, in $\mathrm{LaNiO_3}$, $\theta_D=400\pm20$ K,[17] and in the much studied high-temperature superconductor $\mathrm{YBa_2Cu_3O_7}$, $\theta_D=380\pm10$ K.[18]

If we assume that the linear term in the specific heat arises entirely from the presence of the charge carriers,[19] then we can compute the density of states $N(E)$ at the Fermi energy $E=E_F$ according to

$$\gamma=\frac{\pi^2}{3}k_B^2 N(E_F), \tag{3}$$

where k_B is Boltzmann's constant. We find $N(E_F)=1.12\pm0.02$ and $1.41\pm0.04\times10^{24}$ $\mathrm{eV^{-1}\,mole^{-1}}$ (Ba doped), and $N(E_F)=2.0\pm0.02\times10^{24}$ $\mathrm{eV^{-1}\,mole^{-1}}$ (Ca doped). If we further assume that all holes introduced by the dopant are mobile carriers, with the dopant concentration x per formula unit, then with a molar volume V of 36 cm^3, we find a charge density of $n(x)=1.7\times10^{22}x$ carriers/cm^3. The free-electron value for γ, γ_0, is given by

$$\gamma_0=\left(\frac{4\pi^3 m_e k_B^2 V}{3h^2}\right)\left(\frac{3n}{\pi}\right)^{1/3}, \tag{4}$$

where m_e is the free-electron mass and h is Planck's constant. We find that $\gamma_0=1.0$ mJ/mole K^2 ($x=0.33$) or 0.9 mJ/mole K^2 ($x=0.2$). Thus, $\gamma/\gamma_0\sim5$ for the Ba-doped samples, and ~8 for the Ca-doped sample. However, the conduction band in these materials arises from the hybridization of Mn $3d$ and O $2p$ orbitals,[20–22] and the density of states is enhanced over the simple free-electron estimate. In addition, we expect an enhancement from many-body effects such as electron-electron correlations and the electron-phonon interaction.

This trend in γ is consistent with the DE model. In this model, T_c is proportional to an effective transfer integral t_{eff} for an electron hopping between Mn ions. In the tight-binding approximation $N(E_F)$ is inversely proportional to t_{eff}. Since γ is directly proportional to $N(E_F)$ we expect that the samples with the higher T_c's will be the ones with the lower γ's. Indeed, this is what was seen experimentally.

We can compare the density of states obtained from our measurements with those obtained from band-structure calculations. A recent calculation estimated a total $N(E_F)=5\times10^{23}$ $\mathrm{eV^{-1}\,mole^{-1}}$ in $\mathrm{La_{2/3}Ca_{1/3}MnO_3}$.[22] This value should be comparable to that for $\mathrm{La_{0.67}Ba_{0.33}MnO_3}$. Using this value of $N(E_F)$, we find that the band-structure-derived value of γ, denoted by γ_B, is 2.0 mJ/mole K^2. Hence the measured γ is ~2–3 γ_B. In the absence of a band-structure estimate for $N(E_F)$, we might anticipate a similar enhancement for $\mathrm{La_{0.8}Ca_{0.2}MnO_3}$. However, the electron-phonon interaction and electron correlations are not included in the band-structure calculation.[22] The measured γ can be written as

$$\frac{\gamma}{\gamma_B}=\left(\frac{m^*}{m_B}\right)(1+\lambda_{\mathrm{ep}}), \tag{5}$$

where m_B is the band mass of the carrier, m^* is the effective mass due to electron-electron correlations, and λ_{ep} is the electron-phonon coupling constant. To estimate whether our observed enhancement of γ/γ_B arises from the first factor in Eq. (5), the second factor, or both, it is worthwhile to compare our results with the γ's found in similar $AB\mathrm{O}_3$-type transition-metal oxides with perovskite structure.[23] Specific-heat measurements are available for the $\mathrm{LaNiO_3}$ system[17] and the $\mathrm{La_{1-x}Sr_xTiO_3}$ system, made metallic by Sr doping.[24] In $\mathrm{LaNiO_3}$ the observed γ is 15 mJ/mole K^2, and $N(E_F)\approx4.6\times10^{23}$ $\mathrm{eV^{-1}\,mole^{-1}}$. Thus $\gamma/\gamma_0=10$ and $\gamma/\gamma_B\approx4$. In the $\mathrm{La_{1-x}Sr_xTiO_3}$ system, γ and γ/γ_0 depend on x. For $x=1/3$, $\gamma=7.5$ mJ/mole K^2 and $\gamma/\gamma_0=1.5$. For $x<0.05$ the material is a Mott insulator, but for $x=0.05$, $\gamma=16$ mJ/mole K^2 and $\gamma/\gamma_0=2.56$. In this system, the enhancement of γ arises mainly from correlation effects in that $m^*/m_c\approx2.5$.[24] If a similar enhancement is present in our samples, i.e., $m^*/m_B\approx2.5$, then this alone is enough to account for our observed value of $\gamma/\gamma_B\approx2.5$ in $\mathrm{La_{0.67}Ba_{0.33}MnO_3}$. However, further experiments will be necessary to determine the relative contributions of correlations and electron-phonon interactions to the enhanced γ. Presumably, λ_{ep} would be characteristic of a Jahn-Teller material.[20]

Finally we would like to address the question of the spin-wave contribution to the specific heat. If the spin-wave stiffness constant is D, and there is no gap in the excitation spectrum, then we would expect a contribution to the low-temperature specific heat of $\delta T^{3/2}$ where[25]

$$\delta = 0.113 V k_B \left(\frac{k_B}{D}\right)^{3/2}. \qquad (6)$$

Recent neutron-scattering measurements on $La_{0.67}Ca_{0.33}MnO_3$,[26] and standing spin-wave resonance measurements on $La_{0.67}Ba_{0.33}MnO_3$,[27] have determined D to be 150–170 meV Å^2, with a gap of less than 0.04 meV, consistent with zero. From this value, we estimate that a spin-wave term should be present and should contribute ~15–20 % to our heat-capacity signal for temperatures between, say, 4–8 K. However, the neutron-scattering results of Perring *et al.* indicate a gap of 2.5±0.5 meV in $La_{0.7}Sr_{0.3}MnO_3$.[28] A gap of this magnitude in our samples would prevent us from seeing a spin-wave contribution at temperatures below ~28 K.

It is clear from Fig. 1 that there is ample experimental resolution for seeing a 15–20 % contribution to the specific heat. However, a more difficult and subtle question is whether or not the resolution is sufficient to cleanly separate the terms in Eq. (1) over the restricted temperature range where it applies. Moreover, it is not even clear that a magnetic contribution should follow a $T^{3/2}$ dependence in conducting ferromagnets. Snyder *et al.*[29] have presented evidence for a T^2-like temperature dependence of the magnetization of $La_{0.67}(Ca,Sr)_{0.33}MnO_3$. This is expected when single-particle excitations dominate over spin-wave excitations. The specific-heat contribution should then show the same T^2 temperature dependence. Our own magnetization data on one of the Ba-doped samples suggests a $T^{1.3\pm0.1}$ dependence.

To answer these questions, we show in Fig. 3 the expected form of C with the presence of a $T^{3/2}$ or T^2 term which contributes 20% of the signal at 6 K. Plotted is the fractional difference in C, $\Delta C/C$, from a best-fit $\gamma T + \beta T^3$ form for the Ca-doped sample in the temperature range 3–8 K. The Ba-doped samples are similar. While the size of the scatter in the data is comparable to the magnitude of the expected change in signal, the trend is clearly different. However, the trend can be accounted for by remnants of the excess specific heat below 3 K at the low end, and lattice deviations from the Debye function at the high end where temperatures approach $\theta_D/50$. So, the possibility exists that such a magnetic contribution is present, but cannot be resolved at the current level of precision in the data. In fact, variations in such a contribution from sample to sample might explain the apparent differences in γ and β mentioned above. In summary, the presence or absence of a $T^{3/2}$ or T^2 magnetic contribution to the specific heat cannot currently be settled. More experiments are clearly necessary to resolve this question, as well as the nature of the excess specific heat below 3 K.

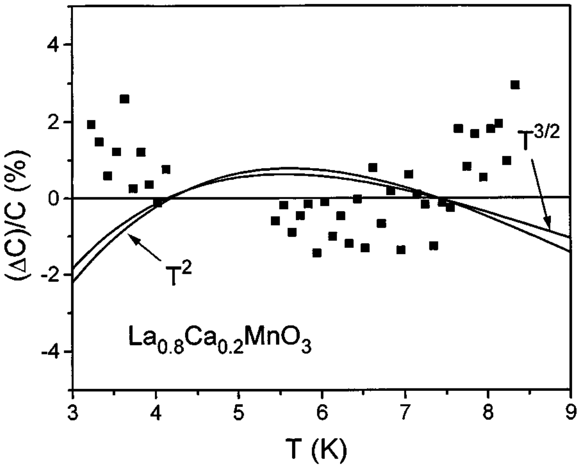

FIG. 3. Fractional specific-heat residuals, $\Delta C/C$ vs T for the Ca-doped sample. $\Delta C = C - (\gamma T + \beta T^3)$ where γ and β are best-fit values. Smooth curves show the expected residuals if C were to contain a term $\propto T^{3/2}$ or T^2 which contributes 20% of the signal at 6 K.

It should be realized that the history of trying to determine D from low-temperature specific-heat data in zero magnetic field has revealed many possible procedural difficulties, both for metallic[30] and insulating[31] ferromagnetic materials. There are many types of spurious contributions which can contaminate the heat-capacity signal and mask the presence of a spin-wave term. However, it has been shown that reliable values of D can be obtained from specific-heat measurements in nonzero magnetic fields for the iron garnets.[31] We plan to add magnetic-field capability to our cryostat in the near future.

In conclusion, we have measured the low-temperature specific heat of lanthanum-manganites $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$. We found that the temperature dependence has an electronic linear term and a lattice cubic term. Observed Debye temperatures are typical of perovskites, and the carrier density of states is found to be enhanced over free-electron and band-structure estimates. However, the nature of any possible magnetic contribution to C is presently not understood.

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