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Anomalous low-temperature specific heat of charge-ordered $La_{0.5}Ca_{0.5}MnO_3$

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We report a study of the specific heat, resistivity, and magnetization of $La_{1-x}Ca_xMnO_x$ for $x=0.47$, 0.5, 0.53 with and without an applied magnetic field. In zero (earth) field we find that the charge-ordered materials ($x=0.5$,0.53) have extra entropy of nonmagnetic origin at low temperature when compared to metallic and ferromagnetic compositions ($x=0.47$,0.2). For the $x=0.5$ compound the specific heat does not change in a 8.5 T field even though the resistivity decreases ten orders of magnitude. [S0163-1829(98)51546-9]

Recently, mixed-valent perovskite manganese oxides ($A_{1-x}B_xMnO_3$: $A=$La, Pr, Nd; $B=$Ca, Sr, Ba) have attracted considerable attention because of their unusual magnetic and electronic properties.[1–10] Charge, spin, and lattice interactions all appear to play a significant role in determining these properties. At certain doping levels (x) a real space ordering of charge carriers has been observed at low temperatures.[10–12] Rather surprisingly, this charge-ordered state can be destroyed by a modest external magnetic field[4,13–15] resulting in a ferromagnetic metallic state! A detailed understanding of the charge ordering (CO) transition, the low-temperature ground state, and the effect of magnetic field is presently lacking.

In this paper we report a study of the low-temperature specific heat of a charge-ordered manganese oxide, with and without applied magnetic field. These measurements allow us to probe the low-temperature charge, spin, and lattice excitations of the CO ground state and the magnetic-field induced metallic state. We find an unexpected large, field independent contribution to the specific heat in the CO state. Our results, in conjunction with the other experiments, should help in reaching a theoretical understanding of the CO state and its anomalous field dependence.

For our study we chose the $La_{1-x}Ca_xMnO_3$ system since the La ion has no magnetic moment to complicate the low-temperature specific heat with a Schottky contribution. Moreover, the $La_{1-x}Ca_xMnO_3$ phase diagram is well established for all x.[5] The low-temperature phase of $La_{1-x}Ca_xMnO_3$ is ferromagnetic (FM) and metallic for $0.18<x<0.5$ and antiferromagnetic (AFM) and insulating within the concentration range $0.5<x<1$. For $0.5<x<1$ the long-range Coulomb interaction among the carriers overcomes the kinetic energy of the carriers and a charge ordering of $Mn^{3+}-Mn^{4+}$ occurs at a finite temperature.[10,16–18] Here we focus on samples with concentration at, or just above, $x=0.5$ where $La_{1-x}Ca_xMnO_3$ first undergoes a FM transition at $T\approx225$ K, then a CO transition accompanied by a FM-AMF transition at $T\approx150$ K (Ref. 5) and compare them to the samples with $x<0.5$.

Polycrystalline samples of $La_{0.53}Ca_{0.47}MnO_3$, $La_{0.5}Ca_{0.5}MnO_3$, and $La_{0.47}Ca_{0.53}MnO_3$ were prepared from stoichiometric amounts of La_2O_3, $CaCO_3$, and $MnCO_3$ by a standard solid-state reaction technique. X-ray powder diffraction and neutron diffraction show single-phase structure with no detectable impurity phases. The specific heat was measured in the temperature range 2–12 K and magnetic field range 0–8.5 T by relaxation calorimetry. This method has a relative accuracy of $\pm3\%$. Magnetization was measured with a commercial superconducting quantum interference device magnetometer, and resistivity was measured by a standard four-probe technique.

As shown in Fig. 1(a), the resistivity of $La_{0.5}Ca_{0.5}MnO_3$ increases sharply at the charge ordering temperature $T_{CO}\approx140$ K in zero magnetic field. At the same temperature the onset of AFM ordering is indicated by the drop magnetization [Fig. 1(c)]. Both magnetization (M) and resistivity (ρ) are hysteretic with similar transition temperatures in cooling as well as in warming. These results are in agreement with prior work.[13] Our study of $La_{0.47}Ca_{0.53}MnO_3$ shows [Fig. 1(a)] a nonmetallic temperature dependence of resistivity. As suggested by Fig. 1(c) it undergoes a FM transition and then an AFM transition similar to $La_{0.5}Ca_{0.5}MnO_3$. The 5 K value of M is too large to be explained by the magnetization of an antiferromagnet or canted antiferromagnet but can be explained by the presence of a small amount of FM phase. This has been confirmed by a neutron-diffraction study.[19] We find [Fig. 1(a)] that $La_{0.53}Ca_{0.47}MnO_3$ has a metallic $\rho(T)$ at low temperatures. Below $T_C=255$ K (from low field data) it is in the FM state with a low-temperature value of magnetization 97 emu/g close to saturation ($M_{sat}=g\mu_BS=100$ emu/g). Hence $La_{0.53}Ca_{0.47}MnO_3$ is below the Ca concentration where charge ordering occurs and the properties are similar to the well studied $x=0.3$ and 0.2 colossal magnetoresistive composition.[20]

In Fig. 2 we plot our specific heat data in the form of C/T vs T^2 over the temperature range 2–12 K for $La_{0.53}Ca_{0.47}MnO_3$, $La_{0.5}Ca_{0.5}MnO_3$, and $La_{0.53}Ca_{0.47}MnO_3$ with $H=0$. The error bars are the size of the data points shown. The low-temperature specific heat $C(T)$ of a magnetic insulator has a contribution from magnetic excitations (spin waves) and the lattice (βT^3). In the case of a metal there is an additional contribution to the specific heat from the charge carriers, γT, where γ is proportional to the density of states at the Fermi level [$N(E_F)$]. For the charge-ordered samples $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.47}Ca_{0.53}MnO_3$ we find $C/T\rightarrow0$ as $T\rightarrow0$, i.e., there is no γT term consistent with their insulating resistivity. For the FM and metallic $La_{0.53}Ca_{0.47}MnO_3$ we can see from Fig. 2 that there is a γT term[21] in the specific heat. This term is of the same order as

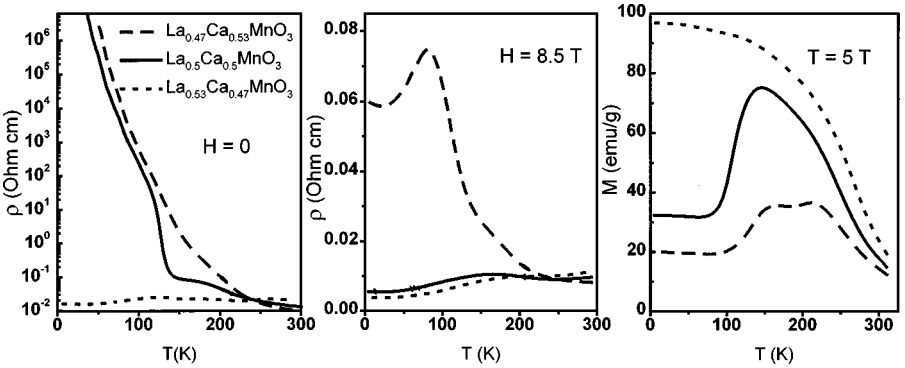

FIG. 1. The resistivity and magnetization of $La_{0.53}Ca_{0.47}MnO_3$, $La_{0.5}Ca_{0.5}MnO_3$, and $La_{0.47}Ca_{0.53}MnO_3$ as a function of temperature at various magnetic fields. All data shown were taken while decreasing the temperature.

found previously for $La_{0.8}Ca_{0.2}MnO_3$.[22] Surprisingly, over most of the temperature range measured, $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.47}Ca_{0.53}MnO_3$ have a much larger specific heat than metallic $La_{0.53}Ca_{0.47}MnO_3$. To understand the origin of this unusual extra entropy of the charge-ordered samples, the contribution to the specific heat from various excitations has to be estimated.

First we consider AFM spin waves with dispersion $\epsilon = (\Delta^2 + A^2q^2)^{1/2}$, where A is a coefficient proportional to the exchange energy and Δ is the anisotropy gap. For $\Delta \gg k_BT$ the spin-wave contribution to the specific heat C_{AFM} is exponentially small. For $\Delta \ll k_BT$,

$$C_{\mathrm{AFM}} = \frac{8\pi^2 R}{15}\left(\frac{T}{\Theta_C}\right)^3, \tag{1}$$

where R is the ideal gas constant and Θ_C is close to the Néel temperature T_N.[23,24] We take the temperature of the AFM-FM transition $T_{\mathrm{AFM\text{-}FM}}$ as our lowest estimate of T_N. With $T_{\mathrm{AFM\text{-}FM}} = 150$ K we have $C_{\mathrm{AFM}} = 0.013T^3$ mJ/mole K, which is about ten times smaller than the lattice contributions (βT^3) measured in the $La_{1-x}C_xMnO_3$ system.[22,25,26] Thus, the large excess specific heat cannot be explained by AFM spin wave excitations.

A recent neutron-diffraction study[19] on $La_{0.5}Ca_{0.5}MnO_3$ found about 20% of FM phase at low temperature which is consistent with our magnetization data (Fig. 1). The associated FM spin-wave contribution to the specific heat would be $C_{\mathrm{FM}} = 0.2 \times [0.113Vk_B(k_BT/D)^{3/2}]$,[27] where V is a molar volume, D is a spin-wave stiffness, and k_B is Boltzmann's constant. Since the stiffness D is proportional to T_CS,[27] where T_C is the Curie temperature and S is the average value of the spin, we have $D_{x=0.5}/D_{x=0.33} = (T_C/S)_{x=0.5}/(T_CS)_{x=0.33}$. Using the value of $D_{x=0.33} = 170$ meV Å^2 (Ref. 8) and the corresponding T_C and S values, we estimate $D_{x=0.5} = 145$ meV Å^2 and consequently $C_{\mathrm{FM}} = 0.15T^{3/2}$ mJ/mole K for 20% of a FM phase. This is only about 3% of the lattice contribution at $T = 10$ K and is too small to explain the large excess specific heat we find for the charge ordered samples.

Since magnetic excitations cannot fit our specific-heat data we next consider low-energy optical phonons as have been observed in perovskite ferroelectric oxides.[28] We take $C = C'(T) + \beta T^3$ with $\beta = 0.14$ mJ/mole K^4 for the lattice term. This value of β is representative of that found previously in similar manganese oxides.[22,25,26] What about $C'(T)$? If we take optical phonon excitations with a dispersion relation $\epsilon = \Delta + Bq^2$ the corresponding specific heat is[29]

$$C' = k_BV\left(\frac{k_BT}{4\pi B}\right)^{3/2}\left(\frac{15}{4}f_{5/2}(y) + 3f_{3/2}(y) + y^2f_{1/2}(y)\right), \tag{2}$$

where $y = \Delta/k_BT$ and $f_p(y)$ is given by

$$f_P(y) = \sum_{n=1}^{\infty}\frac{e^{-ny}}{n^P}. \tag{3}$$

Using this, the best fit to our specific-heat data is with $\Delta = 6.7$ K, $B = 23.3$ meV Å^2 for $La_{0.15}Ca_{0.5}MnO_3$ [see Fig. 2 (Ref. 30)] and $\Delta = 6.7$ K, $B = 31.4$ meV Å^2 for $La_{0.47}Ca_{0.53}MnO_3$. However, such a low-energy excitation would be unusual since our value of $\Delta \approx 7$ K is lower than was observed in $BaTiO_3$ ($\Delta \approx 17$ K).[28] Other experiments, such as measurements of a dielectric constant, will be necessary to see if such low-energy optical phonons exist in $La_{0.5}Ca_{0.5}MnO_3$.

What else could give this anomalous specific heat? In $La_{0.5}Ca_{0.5}MnO_3$ an orbital orientational ordering of d_{z^2} orbitals in Mn^{3+} accompanies the charge ordering.[10,18,20] It is possible that orbital excitations of some kind could give a contribution to the specific heat, however, there is no theo-

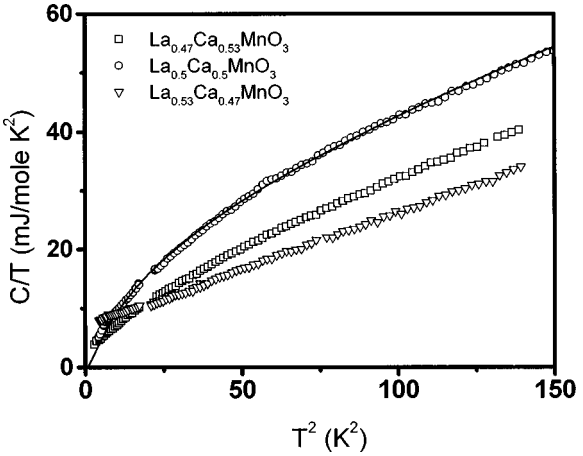

FIG. 2. Specific heat plotted as C/T vs T^2 at $H = 0$. Solid line is fit for $La_{0.5}Ca_{0.5}MnO_3$ described in text.

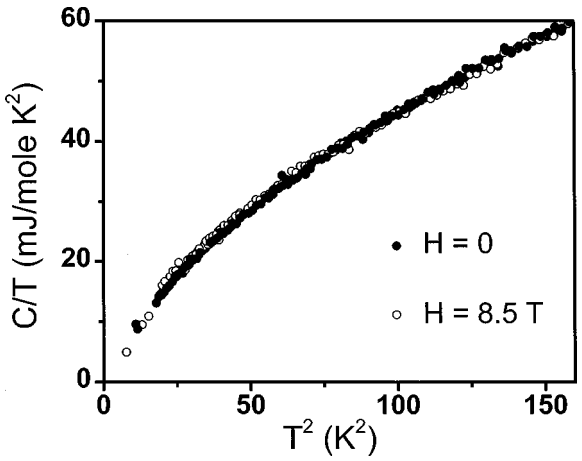

FIG. 3. Specific heat of $La_{0.5}Ca_{0.5}MnO_3$ at $H=0$ and $H=8.5$ T.

retical prediction for this to our knowledge. Some authors have proposed that polarons or bipolarons play an important role in the mechanism of the charge ordering.[31] Intersite bipolarons[32] might have a dispersion relation $\epsilon=\Delta+Bq^2$ and could give a contribution C' as we have found. However, without more direct evidence for bipolarons this is only a speculation.

In summary, we find an anomalous excess specific heat in charge-ordered samples $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.47}Ca_{0.53}MnO_3$ when compared to metallic compositions, such as $La_{0.53}Ca_{0.47}MnO_3$. This extra entropy has its origin in nonmagnetic excitations present in the charge-ordered state. Their origin is unknown but we believe they play an important role in the physics of the charge-ordered state.

Now we consider the effect of an applied magnetic field on the specific heat. In Fig. 3 the zero-field low-temperature specific-heat data and the $H=8.5$ T data are presented. The $H=8.5$ T data were taken after the sample was cooled down from room temperature in a magnetic field. Thus, the sample was in the ''metallic'' state at low temperature as judged by the resistivity data shown in Fig. 1(b). Surprisingly, the high-field specific heat is exactly the same as for $H=0$ and no γT term from conduction electrons is found within our accuracy, i.e., $C/T(H=0)=C/T(H=8.5\ \mathrm{T})\approx 0.5$ mJ/mole K^2. The same result has been obtained for zero-field cooled conditions.

What are some possible explanations for this unexpected result? According to Xiao *et al.*,[13] a magnetic field $H\sim 12$ T is necessary to induce the AFM-FM transition at 4.2 K in $La_{0.5}Ca_{0.5}MnO_3$. At our maximum field of 8.5 T the AFM ordering is only partially destroyed and the number of mobile charges induced may not be sufficient to be detected by specific heat within our present accuracy. Measurements at larger magnetic field are required to resolve this question.

Another possible explanation for the absence of the field dependence of $C(T)$ for our charge-ordered samples is the existence of localized states at the Fermi level. Suppose there is a finite $N(E_F)$ of localized states at $H=0$ which gives $\gamma<0.5$ mJ/mole K^2, i.e., below our resolution limit. The application of a magnetic field may delocalize charge carriers (by a mobility change) leading to reduced resistivity but the $N(E_F)$ would not change, hence γ would remain the same.

Since the estimated specific-heat contributions from AFM and FM spin waves are small and comparable to each other, a change from mostly AFM phase at $H=0$ to partly FM phase when cooled in $H=8.5$ T should not effect our specific-heat data.

The absence of a change in the specific heat in a magnetic field is additional evidence that the extra contribution to the low-temperature specific heat $C'(T)$ does not come from magnetic excitations. An external magnetic field introduces an additional gap $g\mu_B H$ into the dispersion relation of a magnetic system which would significantly change C'. We observe no change in specific heat which implies a nonmagnetic origin to the excess specific heat.

In conclusion, we have measured the specific heat of $La_{0.53}Ca_{0.47}MnO_3$, $La_{0.5}Ca_{0.5}MnO_3$, and $La_{0.47}Ca_{0.53}MnO_3$ from 2–12 K and up to 8.5 T and resistivity and magnetization of these samples in various magnetic fields. $La_{0.47}Ca_{0.53}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ are in the charge-ordered state accompanied by AFM ordering at $T<140$ K. $La_{0.53}La_{0.47}MnO_3$ is ferromagnetic and metallic at low temperature. Charge-ordered samples have a large excess specific heat compared to metallic and ferromagnetic $La_{0.53}Ca_{0.47}MnO_3$ which we showed must originate from excitations of nonmagnetic origin. The nature of these unusual excitations is unknown but they are likely related to the charge ordering. In a magnetic field of 8.5 T no evidence of a γT term from mobile charge carriers is found despite the fact that the resistivity has a metallic temperature dependence at this field at low temperature.

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