The magnetic and electrical properties of “colossal magnetoresistance” (CMR) materials were reported in 1950. The double-exchange (DE) model was proposed the following year, but recent attempts to explain the exceedingly large magnetoresistive changes in these oxide materials led to the conclusion that the DE interaction must be augmented by an interaction between charge carriers and lattice distortions. Such an interaction suggests the possibility of both a first-order transition at the Curie temperature ($T_C$), which would be very unusual for ferromagnetic ordering, and an isotope effect. A thermodynamic analysis of thermal expansion ($\beta$) data, based on a comparison with measurements, made on other samples, of the specific heat ($C$) and the dependence of $T_C$ on pressure ($P$) has been interpreted as showing a second-order transition. Although there are other features that suggest first-order character, they do not constitute thermodynamic proof of the nature of the transition, and it is frequently assumed that the transition is typical of ferromagnets and second order. The isotope effect has been observed\textsuperscript{7,11,12} but its magnitude remains at issue. In this paper we report measurements of $C$ and $\beta$ for the same, well-characterized $^{16}$O and $^{18}$O samples of La$_{0.65}$Ca$_{0.35}$MnO$_3$ (LCMO). We show that in zero magnetic field [$H$] the transition at $T_C$ is a slightly broadened first-order transition, with the broadening quantitatively accounted for by the random substitution of Ca on the La sites. With increasing $H$, there is a dramatic diminution in the isotope effect, for which there is no apparent theoretical explanation, and a shift and broadening of the anomalies in both $C(H)$ and $\beta(H)$, which, although also very unusual for ferromagnetic ordering, is in qualitative agreement with a polaron/bipolaron model. In combination with low-$T$ data, the $C$ data suggest that a substantial fraction of the magnetic entropy is recovered only well above $T_C$, in agreement with the same model.\textsuperscript{13}

The procedures for making the samples are similar to those used earlier by Franck et al.,\textsuperscript{14} but with 12 sintering and regrinding steps. The density of the samples is 90% of the x-ray density. $^{18}$O gas exchange was performed at 1200 °C, resulting in an $^{18}$O concentration (by weight) of 91.3%. The larger samples, ~0.5–1 g, were used for zero-field continuous-heating measurements of $C$ on $^{16}$O and $^{18}$O samples. A piece from an $^{16}$O sample was used for similar measurements in fields to 70 kOe. These measurements were important in confirming the validity of in-field ac measurements and continuous-heating results on smaller samples. These smaller samples, ~100 mg, or pieces cut from them, were used for zero-field continuous-heating measurements of $C$ for $85<T<300$ K and for ac measurements on 5-mg samples between 250 and 320 K in fields to 70 kOe. Pieces of these samples were also used for magnetization ($M$) measurements\textsuperscript{14} and measurements of $\beta$ (Ref. 15) that will be reported in more detail elsewhere. The ac measurements of $C$, which have high precision but inaccurate absolute values, were scaled by using the continuous-heating data on the same samples. Changes in the heating rate by a factor of 2 had no effect on the continuous-heating data, but in the vicinity of $T_C$ the ac measurements did show an effect of sweep rate for $H\approx 2.5$ kOe. That effect was probably associated with hysteresis, which can affect ac data at a first-order transition. The measurements reported here were for sweep rates that gave results consistent with the continuous-heating data, implying that they correspond to thermal equilibrium.

Continuous-heating data for $C(0)$ and fits (see below) are shown in Fig. 1, and compared with $\beta(0)$, which closely mirrors the features in $C(0)$. The anomalies in $C$ at $T_C$ (taken to be the temperature of the maximum in $C$), unlike those associated with typical ferromagnetic (FM) transitions, are very nearly symmetric, although $C$ is larger on the low-
small magnetic and electronic contributions; terms, and by changes in the interval of the fit, did not im-
broadened by the distribution in \( T_C \).

\( C = C_B + C_{\text{mag}} + C_a + C_s \), where \( C_B \) is a smoothly varying background term that corresponds to the lattice specific heat \( (C_{\text{lat}}) \) plus possible small magnetic and electronic contributions; \( C_{\text{mag}} = C_a + C_s \) is the major "magnetic" contribution; \( C_a \) is the broadened latent-heat peak. \( C_s \), which represents the difference in \( C \) between these two phases, is constrained to be zero well below \( T_C \) rises to a maximum value at \( T_C \), and is also broadened by the distribution in \( T_{\text{C}} \). Over the temperature range \( 85 < T < 310 \text{ K} \), \( C_B \) could be well represented by \( C_B = B_0 + B_1 T + B_2 T^2 \). (Variations in the fitting expression for \( C_B \) by inclusion of harmonic-lattice \(^{17}\) and/or spin-wave terms, and by changes in the interval of the fit, did not improve the fit.) \( C_s \) can be represented by either a Gaussian or a Lorentzian function. As the Lorentzian function was more tractable in the nonlinear least-squares fitting, the empirical representation \( C_a = a b^2 (y^2 + b^2) \) was chosen, where \( y = (T/T_C - 1) \), \( a \) = height, and \( b \) = the half width of the Lorentzian peak. A simple representation for the step in \( C \) at the transition is \( C_s = d \exp(-f(y)b)F(y/b) \), where \( d \) and \( f \) are parameters and \( F(y/b) \) is a function reflecting the broadening.

The eight parameters that appear in the fit are tractable in the nonlinear least-squares fitting, the empirical representation \( C_a = a b^2 (y^2 + b^2) \) was chosen, where \( y = (T/T_C - 1) \), \( a \) = height, and \( b \) = the half width of the Lorentzian peak. A simple representation for the step in \( C \) at the transition is \( C_s = d \exp(-f(y)b)F(y/b) \), where \( d \) and \( f \) are parameters and \( F(y/b) \) is a function reflecting the broadening. The eight parameters that appear in \( C \) are determined by fits to the data over the range \( 85 < T < 310 \text{ K} \). (Similar fitting procedures were used for the zero-field thermal-expansion data and for the normalized ac specific-heat data for \( H = 0 \).) The Lorentzian-broadened latent-heat term \( C_a \) has a half width \( \sim 1.5 \text{ K} \). This half width is roughly the same for samples ranging in size from \( \sim 5 \) to 1100 mg and comparable to the half width of the anomaly observed in \( \text{La}_0.65\text{Ca}_{0.35}\text{MnO}_3 \).

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at a first-order transition, they took the heights of the anomalies as $\Delta C$ and $\Delta \beta$ at a second-order transition. As expected on very general grounds, the anomalies in $C$ and $\beta$ are similar in shape and width. The heights are approximately proportional to the areas, ensuring that if $\Delta S$ and $\Delta V$ satisfy the Clapeyron equation, $\Delta C$ and $\Delta \beta$, when defined in that way, approximately satisfy the Ehrenfest equation. However, the shapes and widths of the anomalies in $C$ are consistent with a first-order transition, for which there would be a sharp symmetric “peak” (the latent heat) and a “step” $\Delta C$ (the difference in $C$ between the two phases); they are not consistent with an Ehrenfest second-order transition, for which there would be only the step. The data for $C$ correspond to the sum of a temperature-dependent difference in $C$ between the two phases and a latent heat, both broadened by the same distribution in $T_C$. $\Delta C$ contributes only $\sim 10\%$ to the height of the anomaly; the major component of the anomaly is symmetric and inconsistent with the $\Delta C$ at a second-order transition. Similar considerations apply to the data for $\beta$. The evidence of hysteresis, which frequently accompanies first-order transitions but is not expected for continuous transitions, in the ac measurements of $C$ for $H \approx \sim 2.5$ kOe, also suggests first-order character of the $H=0$ transition, which persists in low $H$. Several other measurements of $C(H)$ for $^{18}O$ samples of La$_{1-x}$Ca$_x$MnO$_3$ ($0.3 \leq x \leq 0.4$) (Refs. 18, 22, and 23) are qualitatively similar to those reported here, but are not suited for a quantitative discussion of the order of the phase transition, either because they are not absolute results, or because there are insufficient data near $T_C$ to reveal the symmetry of the anomaly.

Measurements of $M$ also give information on the nature of the transition: If the magnetic free energy ($G$) near $T_C$ is written as $G=G_0+a_1(T-T_C)M^2+a_2M^4+\ldots$, $a_4$ cannot be negative if the transition is second order. Since the slope of $H/M$ vs $M^2$ is $4a_4$, in this approximation, a test of the order of the transition can be obtained from such a plot. $H/M$ vs $M^2$ plots for small $H$ are shown in Fig. 3. These results, similar to those reported in Ref. 9, have a negative slope, and thus support the conclusion that the transition is first order for zero and small fields. The sharp rise in $M$ just below $T_{C^*}$, shown in the inset in Fig. 3, and similar results in electron-diffraction and neutron-scattering measurements, while not thermodynamic evidence, are more suggestive of a first-order transition than a continuous transition.

Using $C_B$ obtained from the $H=0$ data, fits to $C_{\text{mag}}(H)=[C(H)-C_B]$ were made for $H=2.5$, 5, 10, 20, 40, and 60 kOe. The $^{16}O$ and $^{18}O$ ac data and the fits are shown in Fig. 2. The fits provide a systematic procedure for obtaining the mean values of $T_C$, which correspond to the maxima in $C_{\alpha}$, and their quality supports the general validity of the assumptions that underlie them. Perhaps the most striking property that reflects a sizable electron-phonon interaction is the large oxygen isotope effect ($\sim 10$ K), usually observed in the magnetic transition in low field, but also in the resistive transition, including high-field measurements. The isotope effect in the thermodynamic transitions for $C$ and $\beta$ is evident in Figs. 1 and 2. The isotope exponent is given by $\alpha_{\text{iso}} = -d \ln(T_C)/d \ln(m_O)$, where $m_O$ is the oxygen isotopic mass. $\alpha_{\text{iso}}$ is $\sim 0.3$ for $H=0$ and decreases significantly in higher fields. $T_C$ values shown in Fig. 4 are obtained from the maxima in the $C$ and $\beta$ data, as well as from $C_{\alpha}$. Values of $T_C$ for 60 kOe show some scatter because the maxima in that field are poorly defined, and because the fitting function is less satisfactory when $H=60$ kOe. The general decrease in $\alpha_{\text{iso}}$ with $H$ is unmistakable. The shape and field dependence of the anomalies in Figs. 1 and 2 are similar to the predictions of the Alexandrov and Bratkovsky bipolaron model, which also predicts a possible first-order FM transition at $T_C$ for $H=0$, and continuous transitions for larger fields. The $T_C$ vs $H$ results are quite similar to $T_C$ vs $P$ data obtained from pressure-dependent zero-field resistivity measurements made on the same samples.

The specific-heat data make it possible to estimate $S_{\text{mag}}(300)$, the magnetic entropy change from 0 to 300 K. Let $S_{\text{mag}}(300)-S_{\text{mag}}(200)=\int C'/TdT+\int C'/TdT$,
the magnetic entropy between 200 and 300 K. Plots of $S_n(0), S_s(0),$ and $S_{mag}(0)$ vs $T$ for $H=0$ are shown as insets in Fig. 2. As can be seen from the insets, $S_{mag}(300)-S_{mag}(200)=2.75 \pm 0.05 \text{ J K}^{-1} \text{ mol}^{-1}$ for both the $^{16}$O and $^{18}$O materials. Below $\sim 200 \text{ K}$ $C_B$ is indistinguishable from $C$. However, we can use the data of Fisher et al.\textsuperscript{24} to make a rough estimate of $S_{mag}(200)$. They find that for $1<T<12 \text{ K}$ the electronic ($\gamma T$) and spin-wave ($B_{sw}T^{3/2}$) contributions to $C$ have $\gamma=4 \text{ mJ K}^{-2} \text{ mol}^{-1}$ and $B_{sw}=0.7 \text{ mJ K}^{-5/2} \text{ mol}^{-1}$, and therefore $S_{mag}(200)$ is $\sim 2 \text{ J K}^{-1} \text{ mol}^{-1}$. (The entropy associated with the anomaly in the lattice expansion at $T_C$ is estimated to be $\sim 0.1 \text{ J K}^{-1} \text{ mol}^{-1}$, well within the overall uncertainty of the measurements.) Then $S_{mag}(300)-4.7 \text{ J K}^{-1} \text{ mol}^{-1}$, or $\sim 40\%$ of $12.7 \text{ J K}^{-1} \text{ mol}^{-1}$, the entropy of the “free” Mn$^{3+}$ (spin-2) and Mn$^{4+}$ (spin-$\frac{3}{2}$) ions at high $T$. This result implies either that $C_{lat}$ is considerably smaller than $C_B$,\textsuperscript{25} or that $\sim 60\%$ of the magnetic entropy in LCMO is removed above 300 K. This latter possibility is consistent with Mn$^{3+}/\text{Mn}^{4+}$ moments combining at temperatures well above $T_C$ to form clusters,\textsuperscript{26} FM inclusions,\textsuperscript{27,28} polarons\textsuperscript{28} and/or bipolarons,\textsuperscript{13} or some combination of these, in dynamic equilibrium. For example, assume that 0.35 moles of Mn$^{3+}$/Mn$^{4+}$, randomly oriented at very high $T$, gradually combine, as $T$ is lowered, to form 0.175 moles of FM bipolarons well above $T_C$. If either these bipolarons or the remaining 0.3 moles of Mn$^{3+}$ (or some combination of the two) are progressively ordered as the temperature approaches 300 K, the reduction in entropy between very high $T$ and 300 K is $\sim 8.7 \text{ J K}^{-1} \text{ mol}^{-1}$. The remaining $\sim 4 \text{ J K}^{-1} \text{ mol}^{-1}$ of entropy is sufficiently close to $S_{mag}(300)-4.7 \text{ J K}^{-1} \text{ mol}^{-1}$ to suggest that these interactions (or comparable ones) among the moments approximate what actually occurs in LCMO well above $T_C$. This picture is consistent with both the susceptibility and thermal-expansion measurements above $T_C$.\textsuperscript{14,15} It is also consistent with the more rigorous and detailed discussion of the entropy for CMR materials by Alexandrov and Bratkovsky.\textsuperscript{13}

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