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Scaling behavior of nearly first order magnetic phase transitions

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Abstract

A scaling behavior between heat capacity C_P^* and thermal expansion coefficient times temperature $\Omega T\lambda$, where λ is a scale factor, is obtained for ferromagnetic $La_{1-x}Ca_xMnO_3$ with $x = 0.20$, 0.25, 0.30, 0.34, 0.40, and 0.45 compounds. The pressure derivative of the magnetic phase transition temperature obtained through a scaling method is in good agreement with experimental results for all samples. The critical exponents associated with the specific heat (α) for $x = 0.25$, 0.30, and 0.34 are very close to the phase boundary where continuous phase transitions become discontinuous. This is attributed to strong coupling among the spin, charge, and lattice degrees of freedom, which indicates that the magnetization alone would be a poor choice for the order parameter in these systems. Based on thermodynamic arguments, a phase diagram with diverging, cusp-like, near first order, and first order phase transitions is presented.

1. Introduction

The theory of phase transitions and critical phenomena is one of the most important topics of condensed matter physics. In general, phase transitions are brought about by cooperative interaction between spins, charge, and phonons and they range from magnetization of ferromagnets and boiling of water to superconductivity [1, 2]. A change in the order parameter (OP) magnetization in ferromagnets, defining a phase transition, can be induced by thermodynamic parameters such as temperature, pressure, or magnetic field, and leads to a long-range ordering of the system.

According to thermodynamics, a first order phase transition leads to a discontinuity in the first derivative of the Gibbs free energy with respect to some thermodynamic variable. At the phase transition point, two phases have equal free energies but different entropy values. A latent heat is necessary to convert one phase into another phase by increasing the entropy of the system. Simultaneously, the two phases are separated by an energy barrier in a way they can coexist within a certain temperature interval. As a consequence, the correlation length remains finite and universality is no longer observed in discontinuous phase transitions [1, 2].

On the other hand, continuous phase transitions exhibit critical phenomena and they can be characterized by parameters known as critical exponents. The behavior of the system near the phase transition is described by divergences in the correlation length which leads to variation in physically measurable quantities. It has been shown that, for continuous phase transitions, the molar heat capacity at constant pressure C_P is an asymptotically linear function of the volumetric thermal expansion coefficient times the temperature ΩT [3]. Accordingly, a continuous phase transition must exhibit good overlap between C_P^* and $\Omega T\lambda$ data, where λ is a scale factor [3, 4]. An estimate of the pressure derivative of the phase transition temperature involving these parameters may also be done. Furthermore, in the vicinity of a continuous phase transition, C_P^* and ΩT scale with the same critical exponent [3, 4].

We applied this scaling method to diverging transitions [3, 5, 6] ($\alpha > 0$) using a high-resolution thermal expansion technique [7]. Afterward, we showed that it can be extended to cusp-like continuous phase transitions ($\alpha < 0$) observed in the antiferromagnets $LaMnO_3$ and $CaMnO_3$ revealing exponents $\alpha = -0.13(3)$ and $-0.12(2)$, respectively [4]. Here, we apply this method for spin–charge–lattice coupled ferromagnetic $La_{1-x}Ca_xMnO_3$, with $x = 0.20$, 0.25, 0.30, 0.34, 0.40, and 0.45 compounds, where the colossal magnetoresistance effect is pronounced. The critical exponents of the samples with $x = 0.25$, 0.30, and 0.34 are very close to the first order boundary. We have shown on a thermodynamic basis a phase diagram where diverging, cusp-like, near first order, and first order phase transitions are present.

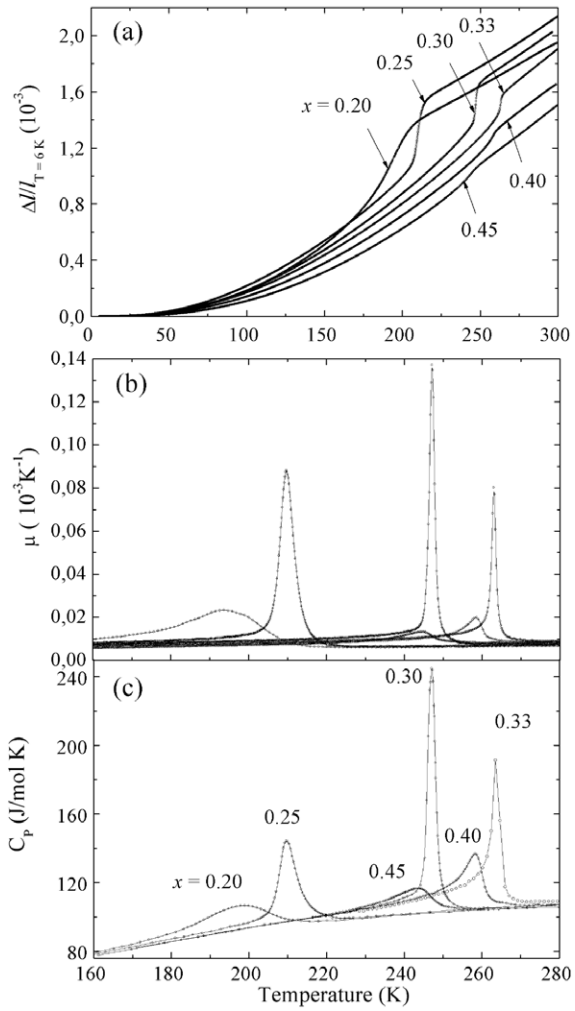

Figure 1. (a) Linear thermal expansion $\Delta l/l$, normalized to its value at 6 K, (b) linear thermal expansion coefficient $\mu(T) = \mathrm{d}(\Delta l/l)/\mathrm{d}T$, and (c) heat capacity C_P for $La_{1-x}Ca_xMnO_3$.

2. Experimental details

The doped samples, $La_{1-x}Ca_xMnO_3$, were prepared by the sol–gel method. The x-ray powder diffraction confirmed the single-phase nature of all samples. Heat capacity was measured using a Quantum Design physical properties measurement system (PPMS) employing a thermal relaxation technique. High-resolution thermal expansion measurements were performed using a fused quartz capacitive cell with a sensitivity [7] in Δl of 0.1 Å.

3. Results and discussion

Figure 1 shows the linear thermal expansion, linear thermal expansion coefficient, and heat capacity for $La_{1-x}Ca_xMnO_3$ with $x = 0.20$, 0.25, 0.30, 0.34, 0.40, and 0.45. A contraction in the volume across the phase transition temperature T_c due to a ferromagnetic ordering leads to a diverging behavior in C_P and μ in all of these compositions. For the samples with $x = 0.25$, 0.30, and 0.34, the peak in C_P and μ is very high and narrow while for $x = 0.20$, 0.40, and 0.45, it is smaller and broad. This is illustrated in figure 2, where it is clearly shown that the width at half maximum decreases, passing through $x = 0.33$ which is the narrowest, and increases again as charge carriers are introduced. The very narrow transition of $x = 0.33$ indicates that the fluctuation-induced ordered domains grow to macroscopic size very close to T_c. This overall behavior is inversely proportional to the T_c values that increase to $T_c = 265$ K ($x = 0.33$) and decrease as revealed by the phase diagram [8]. On the other hand, the change in the unit-cell volume across T_c decreases monotonically as shown in figure 2. As we shall see, the pressure derivative $\mathrm{d}T_c/\mathrm{d}P$ follows the same trend as charge carriers are introduced.

In order to apply the scaling method, we first subtract a linear contribution $(a + b'T)$ [where $b' = (b + (\partial S/\partial T)_c)$] from $C_P(T)$ mimicking a conventional background and find a rough value for the scale factor λ. By doing that C_P^* and $\mu T\lambda$ will be collapsed onto one curve. Afterwards, the constant a, linear coefficient b', and λ values are refined to enlarge the overlap range between C_P^* and $\mu T\lambda$.

Figure 3 shows the good overlap between C_P^* and $\mu T\lambda$, suggesting a continuous phase transition for all doped samples. It is important to mention that thermal hysteresis is absent in these samples which suggests a second order nature of the phase transition. The values for λ are shown in figure 4. The predicted $\mathrm{d}T_c/\mathrm{d}P$ values, using the scaling method ($v = 3.57 \times 10^{-5}$ m^3 mol^{-1}), for each sample are also plotted in figure 4. They are in good agreement with experimental values for all samples [9]. We note that the overlap between

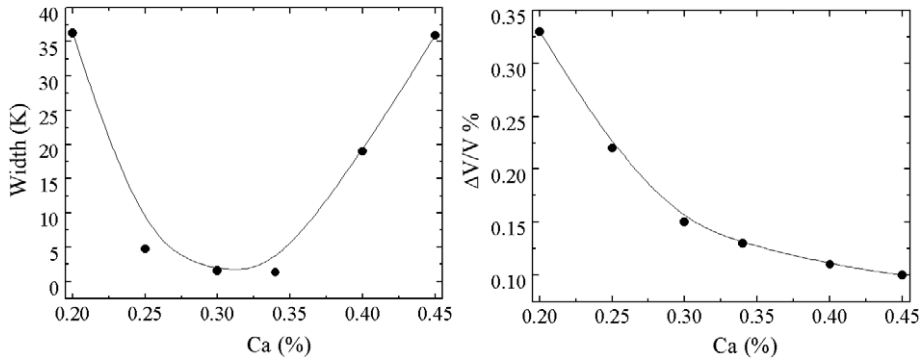

Figure 2. The width at half maximum, obtained from thermal expansion data, and $\Delta V/V$ across T_c as a function of Ca concentration.

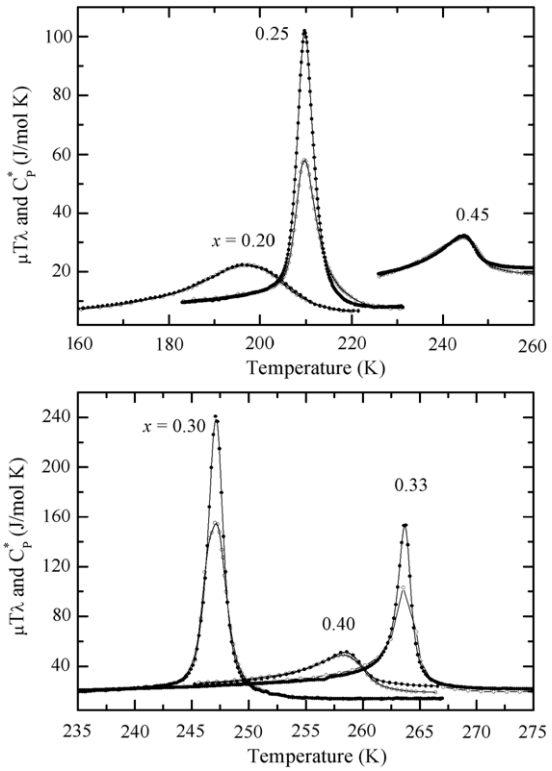

Figure 3. C_P^* (open symbols) and $\mu T\lambda$ (solid symbols) for $La_{1-x}Ca_xMnO_3$ samples at the indicated doping levels illustrating the overlap between them.

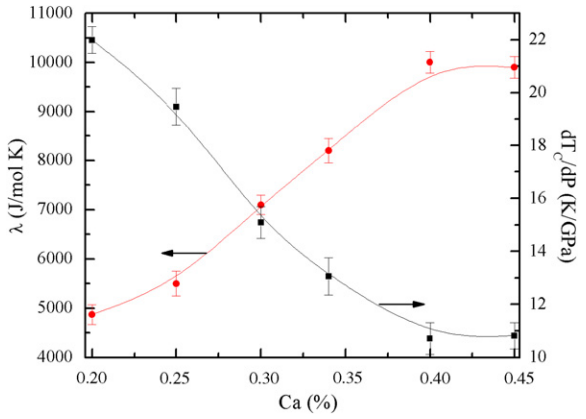

Figure 4. Scaling factor and the pressure derivative of dT_c/dP and critical exponent (b) as a function of Ca concentration.
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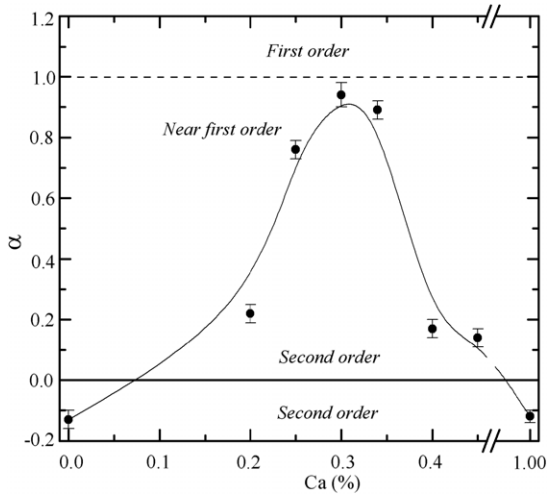

Figure 5. Critical exponent as a function of Ca concentration. The value for $x = 0.30$ is from [3] and for $x = 0$ and 1 [4]. The dashed line illustrates the boundary between first and second order phase transitions. The solid line is a guide to the eye.

C_P^* and $\mu T\lambda$ close to T_c for $x = 0.25$, 0.30, and 0.33 is not as good for these compositions as for the others. Note that the $x = 0.33$ composition has the sharpest transition in μ. For example, the full width at half maximum for $x = 0.33$ is $\Delta T = 1.3$ K while the C_P data reveal a width of 5.3 K. Indeed, figure 3 reveals that the sharpness of the feature at T_c for these samples observed through high-resolution thermal expansion is not detected by heat capacity measurements. The rounding of the peak in C_P measurements can be associated with sample inhomogeneity. Experimental contributions to the rounding of the peaks include the large measuring heat pulses in the relaxation technique [10]. This is absent in our thermal expansion measurements. Therefore, we have found the thermal expansion technique superior to C_P measurements in revealing this divergent behavior because it is less susceptible to finite-size effects [3, 11][1].

The critical exponent for the samples with $x = 0$, 0.30, and 1 was previously obtained [3, 4]. In order to estimate for the other samples $x = 0.20$, 0.25, 0.34, 0.40, and 0.45 we have used the same procedure as described elsewhere [3, 4]. Thermal expansion data which have higher density of points and exhibit less rounding of the transition than the heat capacity data were used. The behavior of α as a function of Ca concentration is illustrated in figure 5. The doped samples exhibit positive values with diverging behavior in C_P and μ at T_c. For the samples with $x = 0.25$, 0.30, and 0.34, the exponents are exceptionally large with magnitudes close to one, revealing an anomalous critical behavior of the continuous phase transition near T_c. The extremely large value of α near $x = 0.30$ implies smaller exponents for the magnetization (β) and magnetic susceptibility (γ) if the exponent identity $\alpha + 2\beta + \gamma = 2$ holds [12].

From a thermodynamic point of view, the significance of $\alpha \to 1$ can be appreciated by considering the leading power-law term $((A_\pm/\alpha)|t|^{-\alpha}$ where $t \equiv (T - T_c)/T_c)$ for C_P in the vicinity of the phase transition. In order to calculate the entropy difference between the state at $T_1 < T_c$ and $T_2 \to T_c^-$, one may integrate C_P/T from T_1 to T_2. The sign (+) means coming from above T_c and (−) coming from below T_c. When T_1 is close enough to T_c, the integral is given by

$$\delta S \propto \frac{A_-}{T_c}\int_{T_1}^{T_2}(T_c - T)^{-\alpha}\,dT = \frac{A_-}{T_c}\left[\frac{(T_c - T_1)^{1-\alpha} - (T_c - T_2)^{1-\alpha}}{1-\alpha}\right]. \quad (1)$$

[1] In the thermal expansion measurement, temperature is changed at 0.2 K min^{-1}, and any thermal averaging is associated with the derivative of $\Delta L/L$, which has a spacing of 0.2 K. In the heat capacity measurement, a heat-pulse technique is employed with a typical temperature rise of 1%.

When $\alpha \to 1^-$, δS diverges. This makes the criterion for continuous transition (S being continuous across T_c) impossible and suggests instead a first order phase transition.

When $\alpha < 1$, the phase transition is continuous and the entropy difference from a paramagnetic state ($T_3 > T_c$) to a ferromagnetic state ($T_1 < T_c$) $\Delta S \equiv S(T_3 > T_c) - S(T_1 < T_c)$ may be obtained as

$$\Delta S \propto \frac{1}{T_c}\int_{T_1}^{T_3}(T_c - T)^{-\alpha}\,dT = \frac{1}{T_c}\left[\frac{(T_c - T_3)^{1-\alpha} - (T_c - T_1)^{1-\alpha}}{1-\alpha}\right] \quad (2)$$

which vanishes when $T_1 \to T_c^-$ and $T_3 \to T_c^+$. That is, there will be no discontinuity of entropy across T_c. This is the fundamental requirement for a continuous phase transition ($\Delta S = 0$). This analysis indicates that a phase transition with an exponent close to one is in close proximity to the phase boundary where second order (continuous) transitions become first order, as illustrated in figure 5. In general, this close proximity to first order can induce a first order interpretation of phase transitions. On the other side of the phase diagram (figure 5) when $\alpha = -1$, the phase transition is continuous. An exponent $\alpha = -1$ is predicted in the three-dimensional spherical model [13] for a ferromagnet and is expected to occur in the extreme disorder limit [14].

We believe that the large α values reported herein reflect that the order parameter is more complex than typically assumed. In the clean limit of an ideal system (without disorder), the competing order parameters coming from the spin, charge, and lattice degree of freedom would produce a fluctuation-induced first order phase transition [15]. Other studies have shown that introducing an infinitesimal amount of disorder, inherent in solid solutions, drives the system to a continuous phase transition [16]. A general discussion of phase transitions for strongly correlated systems indicates that phase transitions in such systems may exhibit unusual critical behavior that is not simple to interpret in terms of the Landau–Ginzburg–Wilson paradigm [17]. They argue that many phase transitions thought to be first order are actually continuous. We believe that once an appropriate order parameter is found, a better understanding of the thermodynamic quantities near the phase transition will emerge.

4. Conclusion

In summary, we have applied a scaling method for analyzing continuous phase transitions in ferromagnets $La_{1-x}Ca_xMnO_3$ with $0.2 \leqslant x \leqslant 0.45$. The dT_c/dP are obtained for all samples. The critical exponent for $x = 0.25$, 0.30, and 0.34 is exceptionally large reflecting the close proximity to the boundary where second order (continuous) transitions become first order. It is suggested that the large α exponents may be associated with strong coupling between spin, lattice, and charge degrees of freedom that must be described through an order parameter that is more complex than just the magnetization. We have illustrated on a thermodynamic basis a phase diagram where diverging, cusp-like, near first order, and first order phase transitions are present.

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