Analysis of the critical behavior associated with the antiferromagnetic transitions of $LaMnO_3$ and $CaMnO_3$

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We apply a method for analyzing phase transitions to the well-known antiferromagnets $LaMnO_3$ and $CaMnO_3$ using high-resolution thermal-expansion data. The critical exponents associated with the specific heat (α) are obtained. Within experimental error, the results suggest that $LaMnO_3$ and $CaMnO_3$ belong to the same universality class. An additional byproduct of our analysis is estimates for the pressure derivative of the magnetic phase transition temperature.

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I. INTRODUCTION

For the majority of systems, a thermodynamic phase transition results in a change in the order parameter (OP).[1,3] Cooperative interaction between magnetic spins, in the special case of a magnetic transition, leads to long-range ordering of the spins and the OP is generally taken to be the magnetization in ferromagnets (M), or the sublattice magnetization in the case of antiferromagnets. Its nonzero value in the ordered phase corresponds to symmetry breaking of the system. In a so-called continuous (i.e., second-order) phase transition, the OP rises continuously from zero at the critical temperature (T_c), while for those discontinuous transitions (i.e., first order), for which an OP can be defined, a jump is observed.[1] In both cases, an anomaly appears in basic thermodynamic quantities at T_c. Continuous phase transitions are characterized by the buildup of fluctuations in the OP *near* T_c and the subsequent divergence of them *at* T_c. The fluctuations correspond to short-range clusters of the ordered phase, which are not correlated with regard to their mutual position. The behavior of the system near T_c is described by divergences in the correlation length (ξ), which in turn leads to divergences in physically measurable quantities such as the magnetic susceptibility. The molar heat capacity at constant pressure (C_P) either diverges or experiences a jump or exhibits a cusp at T_c. In contrast, at a discontinuous phase transition ξ remains finite and C_P exhibits a spike[2] at T_c.

For continuous phase transitions, which are the subject of this work, the behavior of physical quantities such as spontaneous magnetization $[M=M(H=0)]$, magnetic susceptibility $[\chi=(\partial M/\partial H)_{H\to 0}]$, ξ, and C_P obey power laws of the reduced temperature, $t\equiv(T-T_c)/T_c$, governed by the critical exponents, β, γ, ν, and α, respectively, near T_c.[1,3] Herein, we are primarily interested in the critical exponent α. The volume thermal-expansion coefficient times temperature (ΩT) and isothermal compressibility coefficient (κ) scale with the same critical exponent[4] as C_P, ($|t|^{-\alpha}$). The critical region is loosely defined by the reduced temperature range which is dominated by a power-law behavior characterized by a single critical exponent α. Empirical observation has shown that for magnetic systems, the critical region begins around $\log|t|\sim -1$, which coincides approximately with the break down of molecular-field theory at about the same point.[5]

The critical exponents are universal in the sense that a wide range of materials exhibit the same exponents.[1,3] These universality classes depend on the spatial dimensionality of the system, its symmetry, the number of components which comprise the OP, and the range of the microscopic interaction responsible for the phase transition.[1]

In previous work,[4] we proposed a method for the simultaneous analysis of C_P and the volumetric thermal expansion coefficient Ω at constant applied magnetic field B. This method reveals that C_P is an asymptotically linear function of ΩT and for continuous phase transitions they scale according to

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_c + v\Omega T\left(\frac{\partial P}{\partial T}\right)_c. \tag{1}$$

In this equation, S is the molar entropy, v is the molar volume, and the derivatives $(\partial S/\partial T)_c$ and $(\partial P/\partial T)_c$ are along the transition line. This relation holds for temperatures in the vicinity of T_c and reveals that in this region, C_P^* and ΩT scale with the *same* critical exponent. In practice, C_P^* is defined as $C_P^*\equiv C_P-[a+bT+T(\partial S/\partial T)_c]$. The linear term reflects contributions from degrees of freedom decoupled from the lattice expansion associated with the phase transition. According to Eq. (1), a continuous phase transition must exhibit good overlap between C_P^* and $\Omega T\lambda$, where λ is a scale factor; note that v does not change significantly in the region where the overlap is physically significant. After subtraction of the linear term, Eq. (1) may be rewritten as[4]

$$\frac{dT_c}{dP} = \frac{v\Omega T}{C_P^*}. \tag{2}$$

Thus, this method can predict the pressure derivative dT_c/dP.

Near T_c, C_P^* and $\Omega T\lambda$ can be fitted by the expression

$$\Omega T\lambda \propto C_P^* = (A_\pm/\alpha_\pm)|t|^{-\alpha_\pm} + B_\pm + Dt, \tag{3}$$

where $(A_\pm/\alpha)|t|^{-\alpha}$ represents the leading contribution to the singularity of C_P and the linear term $B_\pm+Dt$ represents a background contribution. The one-parameter scaling theory requires that $\alpha_-=\alpha_+$ for continuous phase transition. If $\alpha<0$, C_P shows a cusplike transition, remains finite, and has

the value of B at T_c. In this case, B should be the same above and below T_c, $[B_+ = B_-]$. On the other hand, if $\alpha > 0$, C_P shows diverging behavior, becoming infinite at T_c. In that case, one should consider corrections to scaling due to nonlinear scaling fields at $t=0$.[6] In essence, this arises because the second derivative of the free energy is not required, from a theoretical standpoint, to be continuous in the absence of the magnetic field. Therefore, the constant B may contain contributions associated with the phase transition (or decoupled from the regular background) and it may acquire different values[6–8] above and below T_c. When $\alpha=0$, C_P can show a simple discontinuity or a logarithmic divergence at T_c, with no power-law dependence.[1]

We applied this method to magnetic transitions[4,9,10] on three occasions to determine α using a high-resolution thermal-expansion technique.[11] In those cases, α was found to be positive ($\alpha > 0$). Here, we apply it to the antiferromagnets $LaMnO_3$ and $CaMnO_3$ revealing exponents $\alpha = -0.13(3)$ and $-0.12(2)$, respectively.

$LaMnO_3$ and $CaMnO_3$ samples were prepared using the conventional solid-state method. Heat capacity was measured using a Quantum Design physical properties measurement system employing a thermal relaxation technique.[12] High-resolution thermal-expansion measurements were performed using a fused quartz capacitive cell with a sensitivity[11] in Δl of 0.1 Å. The relative sensitivity is at least 3 orders of magnitude better than that of diffraction methods. This resolution provides the high-quality data required for critical analysis. The average manganese valence was measured using iodometric titration. Under the assumption that La, Ca, and O have the valences of +3, +2, and −2, respectively, we found the oxygen content of $LaMnO_3$ to be 3.04 ± 0.01 and $CaMnO_3$ to be 3.00 ± 0.01.

Heat capacity at constant pressure C_P and linear thermal-expansion coefficient $\mu = [1/L(300\ \mathrm{K})][d\Delta L/dT]$, where L is the sample length (we have assumed that for our polycrystalline samples $\Omega = 3\mu$), for $LaMnO_3$ and $CaMnO_3$, are shown in Fig. 1. A distinct peak with λ shape in both C_P and μ is observed at the paramagnetic to antiferromagnetic (AF) phase transition occurring at the Néel temperatures $T_N = 135.5$ K and 122.6 K for $LaMnO_3$ and $CaMnO_3$, respectively. A λ-shaped peak (or cusp) along with the absence of hysteresis[13] suggest a continuous phase transition. The rounding of the peak, most pronounced for $LaMnO_3$ (see Fig. 1), can be associated with sample inhomogeneity. This effect is observed even in single crystals and is likely attributable to Mn, La, and/or oxygen defects.[14,15] Experimental contributions to the rounding of the peaks include the large measuring heat pulses in the relaxation technique.[12] Although this is absent in our thermal-expansion measurements, the temperature spacing between data points also contributes to rounding when we calculate μ by numerical, point-by-point differentiation, from our sample length versus T data. However, 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.

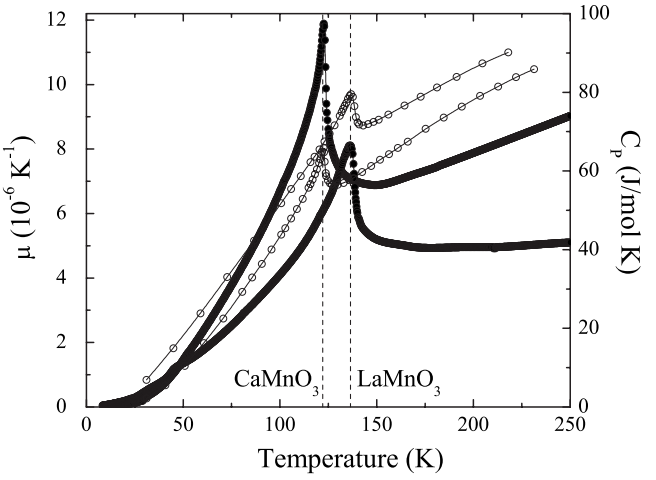

FIG. 1. Linear thermal-expansion coefficient $\mu = \Omega/3$ (solid symbols) and heat capacity C_P (open symbols) for $CaMnO_3$ and $LaMnO_3$. Dashed lines indicate phase transition temperatures.

To apply Eq. (1), 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 to collapse C_P^* and $\mu T\lambda$ 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 2 shows the resulting overlap between C_P^* and $\mu T\lambda$ suggesting a continuous phase transition for $LaMnO_3$ and $CaMnO_3$. The scale factors λ are found to be $27\,000 \pm 300$ J/mol K and $26\,000 \pm 300$ J/mol K, respectively. Using Eq. (2) ($v = 3.57 \times 10^{-5}$ m^3/mol), values of $dT_N/dP = 3.9(6)$ K/GPa and 4.1(6) K/GPa are obtained for $CaMnO_3$ and $LaMnO_3$, respectively. These pressure derivatives obtained using our scaling method are in agreement with those measured experimentally (3.4 K/GPa and 5.4 K/GPa for $CaMnO_3$ and $LaMnO_3$, respectively).[16]

The critical exponent for each sample is obtained using the thermal-expansion data which have higher density of points and exhibit less rounding of the transition than the heat-capacity data. This difference is likely associated with finite-size effects.[4,12,17,18] Although more complicated fitting may be employed, we allow only a background subtraction using $(\mu T\lambda - B_\pm - Dt) = (A_\pm/\alpha)|t|^{-\alpha}$. First, we assume that $\alpha > 0$ (C_P diverging transition) for $LaMnO_3$ and $CaMnO_3$ and choose $B_\pm$, D, and T_c that maximize the power-law fittable temperature range of $\mu T\lambda$ versus $|t|$ on a $\log_{10}$-$\log_{10}$

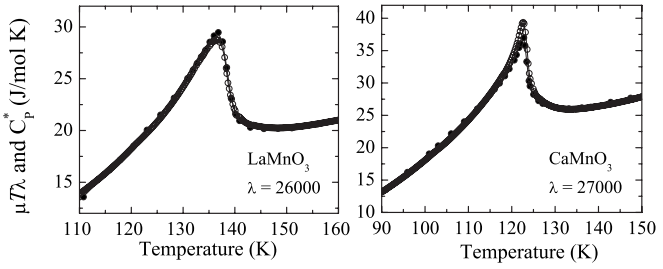

FIG. 2. C_P^* (solid symbols) and $\mu T\lambda$ (open symbols) versus T illustrating the overlap between them.

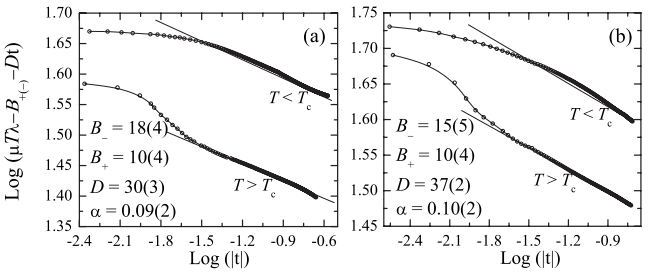

FIG. 3. $\mu T\lambda - B_{\pm} - Dt$ as a function of the reduced temperature $|t|$ on a $\log_{10}$-$\log_{10}$ scale above and below T_c for (a) $LaMnO_3$ and (b) $CaMnO_3$ assuming that α is positive. Values of B and D are in J/mol K.

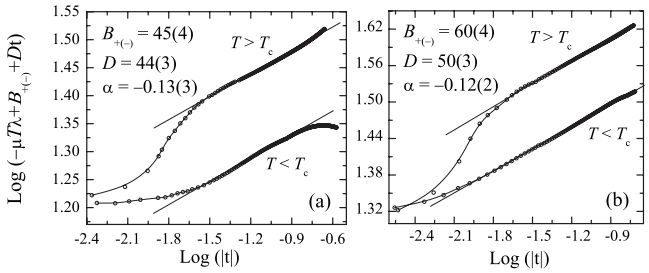

FIG. 4. $-\mu T\lambda + B_{\pm} + Dt$ as a function of the reduced temperature $|t|$ on a $\log_{10}$-$\log_{10}$ scale above and below T_c for (a) $LaMnO_3$ and (b) $CaMnO_3$ assuming that α is negative. Values of B and D are in J/mol K.

scale constraining $\alpha_- = \alpha_+$. Figures 3(a) and 3(b) display $(\mu T\lambda - B_{\pm} - Dt)$ versus $|t|$ on a $\log_{10}$-$\log_{10}$ scale above and below T_c for $LaMnO_3$ and $CaMnO_3$, respectively. Careful inspection of Fig. 3 reveals poor linearity for $T < T_c$ and a small linear temperature range. Since the above analysis with $\alpha > 0$ is not so convincing, we let $\alpha < 0$ implying $(-\mu T\lambda + B_{\pm} + Dt) = (A_{\pm}/|\alpha|)|t|^{|\alpha|}$ and repeat the same procedure choosing B, D, and T_c that maximize the linear temperature range. In this case, B is constrained to be the same above and below T_c. Figures 4(a) and 4(b) show the $(-\mu T\lambda + B_{\pm} + Dt)$ versus $|t|$ on a $\log_{10}$-$\log_{10}$ scale above and below T_c for $LaMnO_3$ and $CaMnO_3$, respectively. The agreement of $\alpha_+ = \alpha_-$ and the linear T range with one-parameter scaling theory is better. Notable is the improved linearity below T_c and a larger region of linearity (especially for $T < T_c$ in the case of $CaMnO_3$). The resulting parameters are, $B_{\pm} = 45(4)$ J/mol K and $D = 44(3)$ J/mol K for $LaMnO_3$ and $B_{\pm} = 60(4)$ J/mol K and $D = 50(3)$ J/mol K for $CaMnO_3$. The critical exponent is determined as the slope of the linear region. Therefore, the inherent rounding of the transition close to T_c and the deviation from linearity are not included in determination of the slope. Though the reduced temperature range wherein our experimental data obey the critical behavior expression is small, it is inside of the $|t| \leq -1$ boundary where the observation of true critical behavior is expected.[5] From the y intercept and the slope, we obtained the critical parameters: $\alpha = -0.13(3)$ and $A_+/A_- = 1.01(2)$ for $LaMnO_3$ and $\alpha = -0.12(2)$ and $A_+/A_- = 1.06(2)$ for $CaMnO_3$. As discussed below, the values of α and A_+/A_- suggest that both compounds are of the same universality class.

The negative values of α imply that C_P^* is finite at T_c (i.e., $C_P^* = B$). The experimental values of C_P^* at T_c shown in Fig. 2 are 29.4 J/mol K and 39.4 J/mol K which have the same order of magnitude as those obtained through the scaling analysis 45(4) J/mol K and 60(4) J/mol K for $LaMnO_3$ and $CaMnO_3$, respectively. We expect this agreement would be better if the inherent rounding were absent. The critical exponent for $LaMnO_3$ is in agreement with that obtained from thermal diffusivity [$\alpha = -0.11(1)$] measurements.[15] This is the first time that α is obtained for $CaMnO_3$. At present, there are no analytical calculations of critical exponents for antiferromagnetic systems with which to compare our results but the three-dimensional ferromagnetic Heisenberg model was determined[1] to have $\alpha = -0.11$ and $A_+/A_- = 1.5$. Numerous experimental determinations have been made including MnF_2 ($\alpha = -0.103 \pm 0.03$),[19] Co_3O_4 ($\alpha = -0.15 \pm 0.06$),[20] $RbMnF_3$ ($\alpha = -0.11 \pm 0.01$),[21] Sr_2FeMoO_6 ($\alpha = -0.12 \pm 0.01$),[22] CrO_2 ($\alpha = -0.17$),[23] $La_{0.9}Ag_{0.1}MnO_3$ ($\alpha = -0.127$),[24] NiO ($\alpha = -0.118 \pm 0.006$),[25] and Ni ($\alpha = -0.1 \pm 0.03$).[26] Comparing our results to these reveals that all values are negative and in the vicinity of -0.1.

$CaMnO_3$ orders with an isotropic G-type structure whereby each Mn magnetic moment is ordered antiferromagnetically with its nearest neighbor via superexchange interactions between Mn^{4+} ions.[27] The ordering in $LaMnO_3$ is more complex because Mn^{3+} has $4d$ electrons which leads to a Jahn-Teller effect and a tendency toward ferromagnetic order via the superexchange interaction.[27–29] It exhibits A-type AF order where the Mn magnetic moments in the a-b plane are ferromagnetically ordered but successive planes are coupled antiferromagnetically. Thus, our findings reveal that despite the difference in the antiferromagnetic structures[27,28] exhibited by $LaMnO_3$ and $CaMnO_3$, the critical exponents for both compounds, within experimental error, are identical as are the values of A_+/A_-. This indicates that $LaMnO_3$ and $CaMnO_3$ belong to the same universality class. On the other hand, another antiferromagnetic manganese oxide[10] $CaMn_2O_4$ exhibits $\alpha = 0.082 \pm 0.007$ suggesting a different universality class.

In summary, we have applied a method for analyzing continuous phase transitions to cusplike phase transitions ($\alpha < 0$) where the heat capacity is finite at T_c. The critical exponents are determined for $LaMnO_3$ and $CaMnO_3$. Within experimental error, both belong to the same universality class. This is somewhat surprising, given the differences in the antiferromagnetic ordered structures of the two compounds. Values for dT_c/dP were also determined.

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