Critical behavior near room temperature in La$_{0.75}$Ca$_{0.05}$Na$_{0.20}$MnO$_3$ sample

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The critical behavior of La$_{0.75}$Ca$_{0.05}$Na$_{0.20}$MnO$_3$ was studied at around room temperature via magnetization measurements. From the relative slope, we deduced that the Tricritical Mean-Field model was the most suitable model. The estimated critical exponents were found to be $\beta = 0.24 \pm 0.004$, $\gamma = 0.98 \pm 0.065$ and $\delta = 5.08$ at $T_C = 300$ K. These critical exponents satisfied the Widom scaling relation $\delta = 1 + \gamma/\beta$, implying the reliability of our values. Based on the critical exponents, the magnetization–field–temperature ($M\text{-}\mu H\text{-}T$) data around $T_C$ collapsed into two curves, obeying the single scaling equation

$$M(H, \epsilon) = \epsilon^{\beta_0} \left( \frac{H}{T_{g0}} \right)^{\gamma_0}$$

with $\epsilon = (T - T_C)/T_C$ being the reduced temperature. These results suggest short-range interaction in our sample.

1. Introduction

Over the past few years, the colossal magnetoresistance (CMR) effect in doped manganites has attracted the attention of many researchers owing to their promising physical properties and potential applications around the Curie temperature $T_C$, such as memory recording, field sensors and magnetic reading heads. In general, the perovskite structure shows a distortion from the ideal structure (cubic) to a rhombohedral or orthorhombic structure, which is mainly caused by the Jahn–Teller (JT) effect following the deformation of the MnO$_6$ octahedron. Particularly, the low-doped La$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Ca$_x$MnO$_3$ samples have extraordinary electronic and magnetic properties and are good candidates for technological applications. These materials are characterized by an insulator–metal (I–M) transition and paramagnetic (PM)–ferromagnetic (FM) transition, which leads to the CMR effect. These properties have been explained by the double-exchange (DE) interaction, phase separation and JT effects, which represent the strong electron–phonon interaction. Recently, many studies have investigated the critical behaviors of manganites around the Curie temperature ($T_C$) to understand their transition nature (first or second order) and the universality class. Historically, the transition from PM-I to the FM-M state has been elucidated by the Zener DE theory. The analysis of the critical behaviors around the $T_C$ is a powerful tool to understand the interaction mechanism responsible for the transition. Therefore, it is important to study in detail the critical exponents in the PM–FM region. Initially, critical phenomena in the DE model were associated with the long-range Mean-Field theory. Subsequently, Motome and Furulawa proposed that the critical behavior could be associated to the short-range Heisenberg universality class. Several experimental studies on critical phenomena are still controversial concerning their Mean-Field values, short-range Heisenberg interaction, 3-D Ising values, and others models which are not classified into any universality class ever known. In general, the critical exponent $\beta$ varied from 0.3 to 0.5, while the reported values for exponent $\gamma$ varied from 1 to 1.4. Currently, there are four models that can be defined and used to explain the critical properties in magnetic compounds. These models are the 3D-Heisenberg ($\beta = 0.365$), Mean-Field ($\beta = 0.5$), Tricritical Mean Field ($\beta = 0.25$) and 3D-Ising ($\beta = 0.325$) models. It is noteworthy that the critical phenomenon in the PM–FM region raised important fundamental discussions. Previously, we studied the magnetic and magnetocaloric properties of La$_{0.75}$Ca$_{0.05}$Na$_{0.20}$MnO$_3$ samples. We noticed that our sample displays a FM–PM transition around room temperature. According to the magnetocaloric study, a large magnetic entropy change was observed, with a maximum of 6.01 J kg$^{-1}$ K$^{-1}$. In addition, it has an important relative cooling ability, which was found to be 225 J kg$^{-1}$. These results indicate that the material can be a good potential candidate in the refrigeration domain.

In this study, we present the first detailed dc magnetization study of the critical phenomena in a DE FM, La$_{0.75}$Ca$_{0.05}$Na$_{0.20}$MnO$_3$. We determined the $T_C$ and the critical exponents $\gamma$, $\beta$ and $\delta$ and tested them for scaling.
2. Experimental details

The \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \) polycrystalline sample was prepared by the flux method, using NaCl as a flux.\(^{13}\) The crystal structure of the studied powder was checked by X-ray diffraction, which confirmed that the sample crystallized in the rhombohedral structure with the \( R3c \) space group and had a detectable secondary phase of \( \text{Mn}_3\text{O}_4 \).\(^{14}\) The relative amount of \( \text{Mn}_3\text{O}_4 \) as determined from the XRD patterns of the sample was found to be 10\%. To extract the critical exponent of the samples accurately, the magnetic isotherm for the sample was measured in the range of \( 0–5 \) T, in the vicinity of the PM to FM phase transition. The isothermals were corrected by a demagnetization factor that was determined with the low-temperature \( \text{MnO}_3 \) sample.

Magnetization is associated with the spontaneous magnetization \( M_s \) and ferromagnetic equation of state can be expressed as

\[ M_s(T) = M_0(-e)^\delta, \quad e > 0, \quad T > T_C \]

\[ M_0(1/T - T_C) = M_0(H)_c, \quad T = T_C \]

where \( \beta \) is associated with the spontaneous magnetization \( M_{0 s} \), \( \gamma \) is associated with the initial magnetic susceptibility \( \chi_0 \). \( \delta \) is associated with the critical magnetization isotherm at \( T_C, e = (T - T_C)/T_C \) is the reduced temperature, \( \mu_0 H \) is the demagnetization adjusted magnetic field and \( M_0, h_0/M_0, \) and \( D \) the critical amplitudes.

3. Results and discussion

In our earlier work,\(^{15,16} \) we showed that for \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \), the field-cooled (FC) magnetization versus temperature under an applied magnetic field of 0.05 T demonstrated a magnetic transition from the PM to FM state at its transition temperature; the \( T_C \) value was found to be 300 K. To introduce the FM state in manganite oxides, the existence of the \( \text{Mn}^{3+}–\text{Mn}^{4+} \) mixed valence is necessary. Ferromagnetism is caused by the exchange energy; this favors electrons with parallel spins. A deeper insight into the magnetic phase transition may be obtained by analyzing the critical phenomena. Based on Banerjee’s criterion, a positive slope reflects a second order magnetic transition, while a negative one reflects a first order magnetic transition. From Eqn. 1, we obtained a positive slope for our sample. This indicates that \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \) undergoes a second order PM–FM transition. It is well known that a magnetic system showing a second order PM–FM transition, around \( T_C \), can be described by a set of interrelated critical exponents.

According to the scaling hypothesis, for a second-order phase transition around \( T_C \), the critical exponents \( \beta \) (associated with the spontaneous magnetization \( M_{0 s}(T) = \lim_{H \to 0} M \) just below \( T_C \)), \( \gamma \) (relevant to the initial magnetic susceptibility \( \chi_0 \), \( \chi_0^{-1}(T) = \lim_{H \to 0} (\mu_0 H/M) \) just above \( T_C \)), and \( \delta \) (associated with the critical isotherm \( M(T, \mu_0 H) \) at \( T_C \)) are given as:\(^{17,18}\)

\[ M_s(T) = M_0(-e)^\delta, \quad e < 0, \quad T < T_C \]

\[ M_0(1/T - T_C) = M_0(H)_c, \quad T = T_C \]

According to Banerjee’s criterion, a positive slope for our sample, and \( f \) for \( T > T_C \).

Eqn (4) implies that \( M/|\epsilon|^{1/\gamma} \) as a function of \( \mu_0 H/|\epsilon|^{-(\beta+\gamma)} \), falls on two universal curves, one for \( T > T_C \), and the other for \( T < T_C \).

In general, four models can be defined according to the values of the critical exponents; 3D-Heisenberg model (\( \beta = 0.365 \) and \( \gamma = 1.336 \)), Mean-Field model (\( \beta = 0.5 \) and \( \gamma = 1 \)), Tricritical Mean-Field model (\( \beta = 0.25 \) and \( \gamma = 1 \)) and the 3D-Ising model (\( \beta = 0.325 \) and \( \gamma = 1.24 \)). The different models are collected in Table 1.

![Fig. 1 A set of typical \( M^2 \) vs. \( \mu_0 H/M \) plots, for the \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \) sample.](image)

The Modified Arrott Plot (MAP) is a conventional method to estimate the critical exponents and critical temperature.\(^{19} \) According to this method, isotherms plotted in the form of \( M^2 \) as a function of \( \mu_0 H/M \) constitute a set of parallel straight lines around \( T_C \). The line at \( T = T_C \) should pass through the origin. It is worth mentioning that the Arrott plot assumes the critical exponents following the Mean-Field theory. In the present case, the lines in the Arrott plot are non-linear and concave as shown in Fig. 1. For this reason, we tried to analyze our data according to the MAP method, based on the Arrott–Noakes equation. This method is based on the equation of state:\(^{21}\)

\[ (\mu_0 H/M)^{1/\gamma} = a \frac{(T - T_C)}{T} + b(M)^{1/\delta} \]

where \( a \) and \( b \) are constants. The RS as function of the temperature curve for all models is shown in Fig. 3. From this
It can be seen that the Tricritical Mean-Field model is the best to describe our system.

The high field straight line portions of the isotherms in Fig. 2(b) can be linearly extrapolated to obtain the spontaneous magnetization $M_S(T, 0)$ and the inverse susceptibility ($\chi_0^{-1}(T)$). The temperature dependence of $M_S(T, 0)$ and $\chi_0^{-1}(T)$ for our sample are shown in Fig. 4. The continuous curves in Fig. 4 denote the power law fitting of $M_S(T, 0)$ and $\chi_0^{-1}(T)$ as a function of temperature according to eqn (1) and (2), respectively. This gives the values of $\beta = 0.24 \pm 0.004$ with $T_C = 299.48 \pm 0.12$ K and $\gamma = 0.98 \pm 0.065$, with $T_C = 299 \pm 0.66$ K. Moreover, $\beta$, $\gamma$ and $T_C$ can be also determined from the Kouvel–Fisher (KF) method based on the following expressions:

$$\left[ \frac{M_S}{dM_S/dT} \right] = \frac{T - T_C}{\beta}$$

### Table 1

| Samples | Technique | $T_C$ (K) | $\beta$ | $\gamma$ | $\delta$ | Ref. |
|---------|-----------|-----------|---------|---------|----------|-----|
| La$_{0.75}$Ca$_{0.05}$Na$_{0.20}$MnO$_3$ | MAP | 299.48 ± 0.12K | 0.24 ± 0.004 | 0.98 ± 0.065 | 5.08 | This work |
| | KF | 299.04 ± 0.03 | 0.22 ± 0.006 | 1.034 ± 0.063 | 5.70 | This work |
| | CI (exp) | 300 | — | — | 4.86 ± 0.004 | This work |
| Mean Field model | Theory | — | 0.5 | 1 | 3 | 18 |
| 3D-Heisenberg model | Theory | — | 0.365 | 1.336 | 4.8 | 18 |
| 3D Ising model | Theory | — | 0.325 | 1.24 | 4.82 | 18 |
| Tricritical Mean Field model | Theory | — | 0.25 | 1 | 5 | 19 |
| La$_{0.4}$Nd$_{0.6}$Sr$_{0.3}$MnO$_3$ | 249.36 ± 0.04 | 0.248 ± 0.006 | 1.066 ± 0.002 | 5.298 | 25 |
| Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ | 238 | 0.279 ± 0.006 | 0.929 ± 0.016 | 4.5 | 26 |
| La$_{0.4}$Ca$_{0.6}$MnO$_3$ | 311.2 | 0.54 ± 0.02 | 1.04 ± 0.04 | 3.08 ± 0.04 | 27 |
| La$_{0.4}$Ca$_{0.6}$Mn$_{0.91}$Ni$_{0.09}$O$_3$ | 199.5 ± 0.1 | 0.171 ± 0.006 | 0.976 ± 0.012 | 6.7 | 28 |
| La$_{0.4}$Pb$_{0.6}$Mn$_{0.97}$Co$_{0.03}$O$_3$ | 345 | 0.233 ± 0.002 | 1.06 ± 0.06 | 5.52 ± 0.04 | 29 |
| La$_{0.4}$Ca$_{0.6}$MnO$_3$ | 265.5 | 0.25 | 1.03 | 5 | 30 |
| La$_{0.8}$Sr$_{0.2}$MnO$_3$ | 354 | 0.37 ± 0.04 | 1.22 ± 0.03 | 4.25 ± 0.2 | 2 |

Fig. 2 Modified Arrott plots: ($M^{1/\beta}$ vs. $\mu_0 H/M$) for the La$_{0.75}$Ca$_{0.05}$Na$_{0.20}$MnO$_3$ sample.
According to eqn (6) and (7), we plotted \( M_s(T) \) vs. \( T \) and \( \chi_0^{-1}(T) \) vs. \( T \) from the obtained \( M_s(T) \) and \( \chi_0^{-1}(T) \) curves, which should yield straight lines with slopes \( 1/\beta \) and \( 1/\gamma \) respectively. The \( T_C \) values are obtained from the intercepts on the \( T \) axis. The \( T_C \) values are obtained from the intercepts on the \( T \) axis. The KF curve for our sample is shown in Fig. 5. Furthermore, the relationship between critical exponents can also be verified by plotting \( M(\mu H) \) as a function of \( \mu H \) for our sample. From this figure,

\[
\delta = 1 + \gamma / \beta
\]

Using this scaling relation and the estimated values of \( \beta \) and \( \gamma \), we found that \( \delta \) value is close to the value directly determined from the critical isotherm at \( T_C \), implying that the obtained \( \beta \) and \( \gamma \) values are consistent. All the obtained critical exponents determined from the various methods are listed in Table 1 and compared with other works.\(^2,25-30\)

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Furthermore, the relationship between critical exponents can also be verified by plotting \( M(\mu H) \) as a function of \( \mu H \) for our sample. From this figure,
we observe that all the points fall into two curves, one below \( T_C \) and another one above \( T_C \). This suggests that the values of the exponents and that of the \( T_C \) are reasonably accurate. The inset of Fig. 7 displays the same plot on a log-log scale. One can see the same behavior is observed in Fig. 7. This confirms that our obtained critical exponents and \( T_C \) are in agreement with the scaling hypothesis.\(^{16}\) Besides, the reliability of the critical exponents can be tested by other rigorous methods. The first method is based on the \( m^2 \) vs. \( \mu_0 h/m \) curve.\(^{18}\) Here, \( m = M(\mu_0 H, \epsilon) e^{-\beta} \) and \( h = \mu_0 H e^{-(\beta+\gamma)} \) are the renormalized magnetization and field, respectively. The \( m^2 \) vs. \( \mu_0 h/m \) curve for our sample is shown in Fig. 8. We can see from this figure that all the data still fall on two separate curves. These results confirm that the critical exponents can generate the scaling equation of state for \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \).

The second method is shown in Fig. 9. According to the scaling equation of state:\(^{31}\)

\[
\left( \frac{\mu_0 H}{M^2} = \frac{\epsilon}{M^2} \right)
\]

where \( \epsilon \) is the scaling function. Based on this, we can confirm the reliability of the used \( T_C \) and the critical exponents. The hypothesis from the scaling eqn (9) is that all the experimental data points should collapse onto a universal curve.\(^{32}\) Fig. 9 displays \( M(\mu_0 H)^{1/\alpha} \) vs. \( \epsilon/(\mu_0 H)^{1/\beta+\gamma} \), using the critical exponents and the \( T_C \) determined from the KF method and the critical isotherm. It is clear that our curves collapse onto a universal curve, which confirms that the critical exponents are appropriate.

Moreover, the reliability of the critical exponents can be checked by an equation proposed by Franco et al.\(^{33}\) In fact, for magnetic systems, the scaling equation of state takes the form:

\[
-\Delta S_M(\mu_0 H, T) = (\mu_0 H)^{(1-a)/\alpha} \left( \frac{\epsilon}{(\mu_0 H)^{1/\alpha}} \right)
\]

Eqn (10) is based on the relationship between the critical exponents and the magnetic entropy change, where \( \alpha = \beta + \gamma \) and \( 2\beta + \gamma = 2 \) are the usual critical exponents. According to eqn (10) and using the critical exponents from MAP, Fig. 10 shows \( -\Delta S_M(\mu_0 H, T) \) vs. \( \epsilon/(\mu_0 H)^{1/\alpha} \) plot. We can see that all \( (-\Delta S_M) \) curves collapse on a single curve. This indicates

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**Fig. 7** Scaling plot below and above \( T_C \) for the \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \) sample. The inset shows the same plots on a ln-ln scale.

**Fig. 8** The renormalized magnetization \( m^2 \) versus \( \mu_0 h/m \) for the \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \) sample.

**Fig. 9** \( M(\mu_0 H)^{1/\alpha} \) as function of \( \epsilon/(\mu_0 H)^{1/\beta+\gamma} \) for the \( \text{La}_{0.75}\text{Ca}_{0.05}\text{Na}_{0.20}\text{MnO}_3 \) sample in the critical region, at different temperatures.

**Fig. 10** The variation of \( -\Delta S_M(\mu_0 H, T) \) vs. \( \epsilon/(\mu_0 H)^{1/\alpha} \).
excellent agreement between the critical exponents and the scaling hypothesis near the magnetic transition.

4. Conclusion

In the present study, we have comprehensively studied the critical phenomenon at the FM–PM phase transition in a polycrystalline manganite of La$_{0.75}$Ca$_{0.05}$Na$_{0.20}$MnO$_3$ via dc magnetization. The values of the critical exponents for our sample were extracted using the MAP method, KF method and critical isotherm analysis. Interestingly, the obtained exponent values are very close to the values expected for the universality class of the Tricritical Mean Field model. The validity of the obtained critical exponents using the various methods was confirmed by the Widom scaling relation and the universal scaling hypothesis.

Conflicts of interest

The authors declare no conflict of interest.

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