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Hirschfeld surface analysis and short-range ferromagnetic ordering in La$_{0.5}$Ca$_{0.4}$Ag$_{0.1}$MnO$_3$ based on critical behavior study

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Abstract

We investigated the Hirschfeld surface analysis and critical behaviour in La$_{0.5}$Ca$_{0.4}$Ag$_{0.1}$MnO$_3$ near the second-order ferromagnetic phase transition at Curie temperature $T_C$. We determined the critical exponents, $\beta$, $\gamma$ and $\delta$ corresponding to the temperature dependence of spontaneous magnetization, initial susceptibility and isothermal magnetization, respectively. The study of Hirshfeld surface reflects that both the electrostatic and intermolecular interactions are short range. The values for critical exponents obtained from magnetic measurements are very close to those predicted by the mean field tri-critical model. The critical-exponent values deduced here were in a good conform to those obtained using the modified Arrott plot and Widom scaling relation.

Keywords: Perovskite manganite; Hirshfeld surface; Critical behavior; Critical exponents; Magnetic phase transition.

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INTRODUCTION

Various interesting phenomena observed in half-doped perovskite structure manganites with the generic formula Ln$_{0.5}$A$_{0.5}$MnO$_3$ (where Ln is the trivalent rare earth and A is the divalent alkaline-earth ions). These phenomena are attributed to the coexistence of competing phases and their extreme susceptibility to the internal or external parameters; which, causes colossal...
changes [1,2]. Generally, half-doped manganites are in an antiferromagnetic (AFM) state at low temperatures with a competing but slightly higher energy ferromagnetic (FM) state in the vicinity [3]. These phenomena have traditionally been explained through the double-exchange (DE) theory based on the exchange of electrons between Mn$^{3+}$ and Mn$^{4+}$ ions [4]. However, it is suggested that DE alone is not sufficient to explain all the physical characteristics of these mixed-valence compounds. The importance of lattice distortion due to strong electron–phonon coupling in addition to DE has intensively been investigated and discussed [5, 6]. This coupling is ascribed to the fact that the Mn$^{3+}$ ion is of a Jahn–Teller (JT) type. Localization of the charge carriers with JT distortion is very likely to be a key factor determining the physical properties. The La$_{0.5}$Ca$_{0.5}$MnO$_3$ system is widely studied in the literature of manganite materials [7]. Upon cooling, the “conventional” compound changes to a ferromagnetic metallic (FM) phase at $T_C$$\approx$220 K and, subsequently, to a charge-ordered antiferromagnetic (CO-AFM) phase at $T_{CO}$$\approx$150K (180K upon warming) [7]. However, it has been established that this system is better described as magnetically phase-segregated over a wide range of temperatures [8]. The partial orbital disordering is claimed to lead to the incommensurate CO physical properties, in spite of complete CO [9]. It should be noted that oxide studies during the 1970s and 1980s will remain relatively episodic until the advent of "high temperature" superconductivity in 1986. This event has rekindled enormously the enthusiasm of researchers in systematic exploration of transition metal oxides and, thus, generating a pantagruelic literature. In this paper, we focus on the structural, Hirschfeld surface analysis and critical behaviour La$_{0.5}$Ca$_{0.4}$Ag$_{0.1}$MnO$_3$ (LCAMO). Thus, to understand the nature of the magnetic transition in LCAMO, we have performed a critical exponent analysis in the vicinity of the ferromagnetic–paramagnetic region. The LCAMO sample shows ferromagnetic to paramagnetic transition at TC. It is noteworthy to mention that even 10% of Ag substitution at the A-site destroys the low temperature CO phase and transforms it into an FM phase. The absence of CO is due to the dominating influence of ferromagnetic interactions over the antiferromagnetic contributions.

**EXPERIMENTAL DETAILS**

LCAMO is prepared according to the sol–gel method. This method is chosen because it minimizes possible Ag evaporation from the system owing to the low melting point (961, 8°C) and high vapor pressure of Ag$_2$O and it is known to give a high degree of homogeneity. Magnetization measurements of the samples were made as a function of temperature and
applied field using a Quantum Design® Vibrating Sample Magnetometer: operated in PPMS systems capable of fields up to 9 T and 14 T.

SCALING ANALYSIS

According to the scaling hypothesis, for second order phase transitions, the spontaneous magnetization $M_s(T)$ below $T_c$, inverse initial susceptibility $\chi^{-1}_0(T)$ above $T_c$, and magnetization $M$ at $T_c$, show the following power-law dependencies: \[10\]

$$M_s(T) = M_0 (-\varepsilon)^\beta; \quad \varepsilon < 0, \quad T < T_c$$ \hspace{1cm} (1)

$$\chi^{-1}_0(T) = \left(\frac{\hbar_0}{M_0}\right) \varepsilon^\gamma; \quad \varepsilon > 0, \quad T > T_c$$ \hspace{1cm} (2)

$$M = DH^{\delta/\beta}; \quad \varepsilon = 0, \quad T = T_c$$ \hspace{1cm} (3)

where $M_0$, $\hbar_0$, and $D$ are the critical amplitudes; $\beta$, $\gamma$ and $\delta$ are the critical exponents; and $\varepsilon = (T - T_c)/T_c$ is the reduced temperature. The magnetic equation of state is a relationship among the variables $M(H, \varepsilon)$, $H$, and $T$. Using the scaling hypothesis, this can be expressed as:

$$M(H, \varepsilon) = \varepsilon^\beta f_+ (H / \varepsilon^{\beta+\gamma})$$ \hspace{1cm} (4)

where $f_+$ for $T > T_c$ and $f_-$ for $T < T_c$ are regular analytic functions. Eq. (4) implies that for true scaling relations and right choice of $\beta$, $\gamma$ and $\delta$ values, the scaled $M / |\varepsilon|^\beta$ plotted as a function of $H / |\varepsilon|^{\beta+\gamma}$ should reveal that the magnetic isotherms in the vicinity of $T_c$ falls on two individual branches, one for $T < T_c$ and the other for $T > T_c$.

Exponents in the asymptotic regime ($\varepsilon \to 0$) usually exhibit universal properties. Besides, they are independent of microscopic details on the sample. However, exponents often evince various systematic trends or crossover phenomenon as one approaches $T_c$ \[11, 12\]. This occurs because of the presence of various competing couplings and/or disorder. For this
reason, it is useful to introduce temperature-dependent effective exponents for $\epsilon \neq 0$. It can be mentioned that effective exponents are non-universal properties, and they are defined as:

$$
\beta_{\text{eff}}(\epsilon) = \frac{d\left[\ln(M_{\epsilon}(\epsilon))\right]}{d(\ln(\epsilon))}, \quad \gamma_{\text{eff}}(\epsilon) = \frac{d\left[\ln(\chi_{\epsilon}^{-1}(\epsilon))\right]}{d(\ln(\epsilon))}
$$

In the asymptotic limit, effective exponents approach universal exponents.

## RESULTS AND DISCUSSIONS

### A. Structural properties

X-ray diffraction (Fig. 1) of the sample confirmed the single phase nature of the entire prepared sample. X-ray diffraction patterns have been indexed in the orthorhombic system with space group Pnma (No. 62). In order to obtain the structural parameters, the diffraction data in Fig.1 were analyzed, using the Rietveld powder diffraction profile fitting technique. The refinement results for our sample are listed in Table 1.

### B. Hirschfeld Surface Analysis

The Hirschfeld Surface analysis can provide information on all existing interactions in the structure so as to understand the overall packaging of the crystal. The normalized contact distance ($d_{\text{norm}}$) based on both $de$ and $di$ (where $de$ is distance from a point on the surface to the nearest nucleus outside the surface and $di$ is distance from a point on the surface to the nearest nucleus inside the surface) and the Van Der Waals radii of the atom, as given by Eq. (6) enables identification of the regions of particular importance to intermolecular interactions.

$$
d_{\text{norm}} = \frac{d_i - r_i^{\text{vdw}}}{r_i^{\text{vdw}}} + \frac{d_e - r_e^{\text{vdw}}}{r_e^{\text{vdw}}}
$$

The curvedness mapped from (-1) to (-0.5) on the Hirshfeld surfaces of Mn (4b) and O (4c) obtained from the structure of the LCAMO phase is shown in Figure 2. The curvedness varies from blue (large curvature) to red (flat), where the latter identifies flat regions that reflect closer contacts between adjacent atoms. The value of $d_{\text{norm}}$ was negative (Table 1) or
positive depending on intermolecular contacts, being shorter or longer than the van der Waals separations. The parameter \( d_{\text{norm}} \) displayed a surface with a red-white-blue color scheme, where bright red spots highlighted shorter contacts [13].

C. Critical exponent analysis

To understand the order of magnetic phase transition and critical behavior by using scaling hypothesis, we have taken M(H) isotherms at each 2K difference from 245 K to 265K for LCAMO, (see Fig. 3(a)). The slope of \( M^2 \) versus \( m_0H/M \) curves (Arrot plots) can determine the order of phase transition. The positive slope indicates a second-order transition while a negative slope corresponds to first-order transition [14]. The positive slope of \( M^2 \) versus \( m_0H/M \) curves above and below \( T_c \) confirms that the high temperature PM-FM transition is of second order in nature. According to the scaling hypothesis, the critical behavior of magnetic systems showing a second-order magnetic phase transition near the Curie temperature can be characterized by a set of critical exponents which are interrelated [15].

The critical exponents associated with the spontaneous magnetization \( (M_s) \), inverse susceptibility \( (\chi_0^{-1}) \), and magnetization isotherms at \( T_c \) were fitted by Eq. (1) and (2). In the mean field model, the Arrott plot drawn as \( M^2 \) vs \( (H/M) \) curves should be a series of parallel straight lines in the high field region. However, the curves in the Arrott plot illustrated in Fig. 3(b) are nonlinear which indicates that the critical exponents \((\beta = 0.5, \gamma = 1)\) based on the Landau mean-field theory alone cannot explain the critical behavior of these compounds. The modified Arrott plot with Ising critical exponents \( \beta = 0.25, \gamma = 1 \) was tried out and it resulted in parallel straight lines as depicted in Fig. 3(c) for LCAMO. The inverse of susceptibility, \( \chi_0^{-1}(T,0) \) vs \( T \) and spontaneous magnetization \( M_s(T,0) \) vs \( T \) are plotted in Fig. 3(d). According to Eq. (1) and (2), the experimental data can be fitted to two continuous curves (solid line). The obtained values of \( \beta \) and \( \gamma \) were then used to construct new modified Arrott plot and this process was repeated several times until the iterations converge, leading to optimum fitting values. It gives two new values of \( \beta = 0.248 \pm 0.002 \) with \( T_c = 256.765 \pm 0.02 \) K and \( \gamma = 1.058 \pm 0.005 \) with \( T_c = 255.662 \pm 0.06 \) K. These results are close to the theoretical ones for the tri-critical mean-field model. Thus, new values of the critical exponents for the sample were determined and reported in Table 2.
The effective exponents $\beta_{\text{eff}}$ and $\gamma_{\text{eff}}$ for LCAMO are obtained from Eq. (5). The effective exponents $\beta_{\text{eff}}$ and $\gamma_{\text{eff}}$ as a function of reduced temperature $E$ are plotted in Fig. 4. It can be seen that $\gamma_{\text{eff}}(e)$ and $\beta_{\text{eff}}(e)$ change almost monotonically with $E$, which indicates that the effective exponents are in agreement with the theoretical prediction of tri-critical mean-field model. According to Eq. (3), the value of the critical exponent $\delta$ can be determined directly from the critical isotherm $M(T_c, H)$ as seen in Fig. 5. Hence, new value of the critical exponent for the concentration is determined and presented in Table 2. Based on the scaling equation (Eq. (4)), the isothermal magnetization around the critical temperatures are plotted in Fig. 5, where all experimental data collapse onto two universal curves. Fig. 6 gives the log-log scale for LCAMO, which reveals that all experimental data fall into two independent branches even in low field region. The adherence to the scaling equation over the entire range of the normalized variables further confirms the reliability of the obtained critical exponents. Therefore, one can note that Rushbrooke scaling relation $\alpha + 2\beta + \gamma = 2$ (theory), [16] which gives the specific heat critical exponents $\alpha = 0.513$ for LCAMO sample. This value is the one which agrees well with that obtained using Tri-critical mean-field model [17].

Fisher et al. [18] have done a renormalisation group analysis for the critical exponents of systems with long-range exchange interactions of the form $J(r) \propto 1/(r^{\sigma+d})$ where $d$ is the dimension of the system and $\sigma$ is a measure of the range of the interaction. For $\sigma > 2$ (short-range interactions) the exponents are the ones of the nearest-neighbour model. For $\sigma > 0.5$ (long-range order), the mean field exponents describe the critical behaviour. In the case of $0.5 < \sigma < 2$, (mid-range order) the exponents depend on the parameter $\sigma$.

Indeed, Landau theory gives [19]: $\nu = 1/\sigma$ avec $\nu = (2 - \alpha)/d$ (theory of Josephson). Based on the previous two theories, we were able to calculate the value of the range of the interaction $\sigma$. In a notable order, $\sigma = 2.02$, this clearly shows that the magnetic interactions are short range.

The study Hirshfeld surface reflects that both the electrostatic and intermolecular interactions are short range. Furthermore, this study verified that the magnetic interactions are still at close range. The values of the critical exponents obtained from magnetic measurements are very close to those predicted by the mean field tri-critical model. This study displays a descriptive report of a correlation between structural and magnetic properties.
Conclusion

In summary, the critical exponents of manganite LCAMO around the PM-FM phase transition have been comprehensively studied by using the modified Arrott plot and critical isotherm analysis. Reliable critical exponents are obtained as $\beta$, $\gamma$ and $\delta = $, which coincide with the values in the tricritical mean-field model for LCAMO. The study Hirshfeld surface reflects that both the electrostatic and intermolecular interactions are short range. The value of the range of the interaction $\sigma = 2.02$. This clearly reveals that the magnetic interactions are short range.

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Tables captions

Table 1: Crystal data and structure refinement information for LCAMO.

Table 2: Comparison of critical exponents of LCAMO compound with earlier reports, and with the various theoretical models.

Figures captions

FIG. 1. XRD patterns for LCMO.

FIG. 2. Curvedness plotted on the atomic Hirshfeld surfaces of Mn (4b) and O (4c) mapped from -1 (flat; red) to -0.5 (sphere-like; blue).

FIG. 3. (a) M(H) isotherms around $T_c$; (b) Arrott plots ($M^2$ versus $H$) following mean field theory; (c) Modified Arrott plots; (d) Spontaneous magnetization $M_s(T)$ (left) and inverse initial susceptibility $\tilde{c}_0^{-1}(T)$ (right) were fitted by Eq. (1) and (2);

FIG. 4. Effective exponents $\beta_{\text{eff}}$ below TC and $\gamma_{\text{eff}}$ above $T_C$ are plotted as a function of reduced temperature $\varepsilon=(T-T_C)/T_C$ for LCAMO.

FIG. 5. Ln-Ln scale and the straight line are the linear fit following Eq. 3 for LCAMO. The critical exponent mentioned in the graph is obtained from the fitting of the data.

FIG. 6. Scaling plots around the critical temperatures for LCAMO.