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Tricritical point and magnetocaloric effect of $Nd_{1-x}Sr_xMnO_3$

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A tricritical point is observed in the $Nd_{1-x}Sr_xMnO_3$ (NSMO) (x=0.3, 0.33, and 0.4) manganites at x=0.33 which separates the first-order transition in NSMO-0.3 and second order transition in NSMO-0.4. The ferromagnetic transition of these compounds is further investigated by measuring magnetocaloric effect (MCE) and by applying a theoretical model based on Landau theory of phase transitions. Results indicate that the contributions to the free energy from the presence of correlated clusters are strongly influencing the MCE by coupling with the order parameter around the Curie temperature. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2832412]

INTRODUCTION

Ferromagnetic perovskite manganites with a general formula of $R_{1-x}A_xMnO_3$, where R=La and Nd and A=Ca and Sr, have been actively studied due to their colossal magnetoresistance and exotic physics.[1] Recently, magnetocaloric effect (MCE) studies have revealed their potential in magnetic refrigeration.[2] Apart from applications, MCE also helps for understanding some of the rich magnetic properties exhibited by manganites. For example, combining critical exponent analysis with MCE data, we have recently reported the existence of a complex ferromagnetic state in single crystalline $Nd_{0.7}Sr_{0.3}MnO_3$ (NSMO-0.3) with a first-order-like transition at low fields.[3] Intrigued by this, we extended this study to NSMO with x=0.33 and 0.4 to investigate the doping dependence of the paramagnetic (PM) to ferromagnetic (FM) phase transition.

EXPERIMENTAL DETAILS

Polycrystalline samples of NSMO-0.33 and 0.4 were prepared by conventional solid state reaction. The phase purity and crystal structure of the powder samples were checked by powder x-ray diffraction (XRD) pattern using Cu $K\alpha$ radiation by PAN analytical X'pert PRO powder diffractometer, as shown in Fig. 1. Critical exponent analysis was carried out using dc magnetization measurements performed in a superconducting quantum interference device magnetometer (MPMS 5XL, Quantum Design, USA) up to 5 T.

RESULTS AND ANALYSIS

The critical exponent analysis is first described. In an attempt to analyze the nature of ferromagnetism in NSMO-0.3 quantitatively, H/M vs M^2 plot is made using the dc magnetization (M) data around the critical temperature (203 K). According to the criterion proposed by Banerjee,[4] a magnetic transition is of first-order transition if the slopes of the Arrott plot between H/M and M^2 are negative and is of second order if the slopes are positive. In the case of NSMO-0.3, a few isotherms above T_C have negative slope indicating a complex first-order-like transition as in Fig. 2 and is discussed in Ref. 3. In the case of NSMO-0.33, the Arrott isotherms were positive indicating a continuous phase transition and allowing us to determine the critical exponents associated with the transition.

A continuous FM-PM transition is characterized by a set of critical exponents in the critical region: β [associated with the spontaneous magnetization (M_s)], γ [associated with the initial susceptibility (χ_0)], and δ [which describes the magnetization dependence on the magnetic field (H) at T_C]. They are defined as

$$M_s = m_0|t|^{\beta}, \quad t \geqslant 0, \tag{1}$$

$$\chi_s^{-1} = h_0/m_0|t|^{\gamma}, \quad t \leqslant 0, \tag{2}$$

$$H = DM^{\delta}, \quad t = 0, \tag{3}$$

where t is the reduced temperature $(1-T/T_C)$ and m_0, h_0, and D are critical amplitudes.

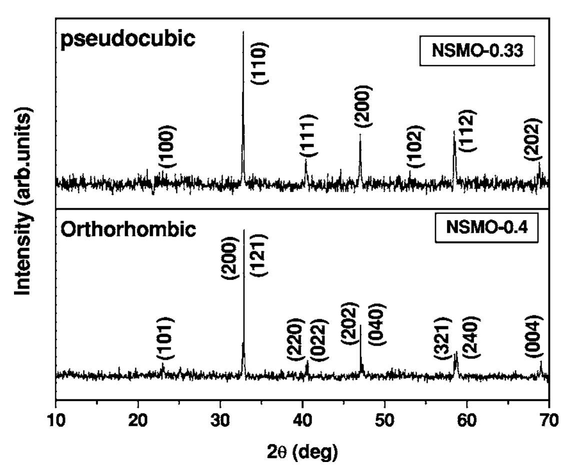

FIG. 1. Powder XRD patterns for NSMO-0.33 [a=3.88(2) Å] and NSMO-0.4 [a=5.47(5) Å, b=7.70(1) Å, and c=5.40(2) Å].

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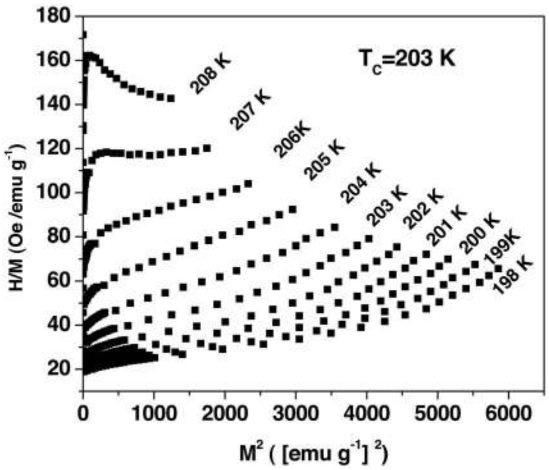

FIG. 2. H/M vs M^2 plot for NSMO-0.3 with negative slope as indicative of being a first-order transition.

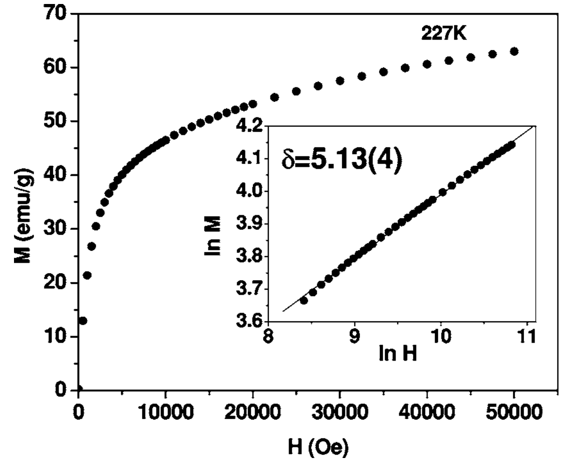

FIG. 4. M vs H isotherm measured at T_C=227 K. The inset shows the ln-ln plot for determining the critical exponent δ.

In order to determine the Curie temperature as well as the critical exponents β, γ, and δ accurately, a modified Arrott plot with a scaling equation of state $(H/M)^{1/\gamma}=at+bM^{1/\beta}$ is used. This causes isothermal curves of $M(H)$ data to fall into a set of parallel straight lines in a plot between $M^{1/\beta}$ vs $(H/M)^{1/\gamma}$, if the correct values of β and γ are chosen.[5] The intercepts of the isotherms on the x and y axes are $(1/\chi)^{1/\gamma}$ for $t>0$ and $M_s^{1/\beta}$ for $t<0$, respectively. The isothermal line that passes through the origin is the critical isotherm at $T=T_C$. A value of β is obtained from a $\ln(M_s)$ vs $\ln(t)$ plot and fitting the data to a straight line, the slope of which gives β. Similarly, a new value of γ is obtained from $\ln(1/\chi)$ vs $\ln(t)$ plot. These new values of β and γ are then used to make new modified Arrott plots. This procedure is continued until they converge to stable values. The final modified Arrott plot for NSMO-0.33 is shown in Fig. 3. The critical exponent δ is obtained from the $M(H)$ curve at T_C, as shown in Fig. 4, and from the ln-ln plot, as shown in the inset of Fig. 4. The values of critical exponent obtained for NSMO-0.33 are $\beta=0.23(2)$, $\gamma=1.05(3)$, and $\delta=5.13(4)$, which are strikingly close to theoretically predicted values for tricritical point exponents ($\beta=0.25$, $\gamma=1$, and $\delta=5$). A tricritical point separates a phase line of first and second

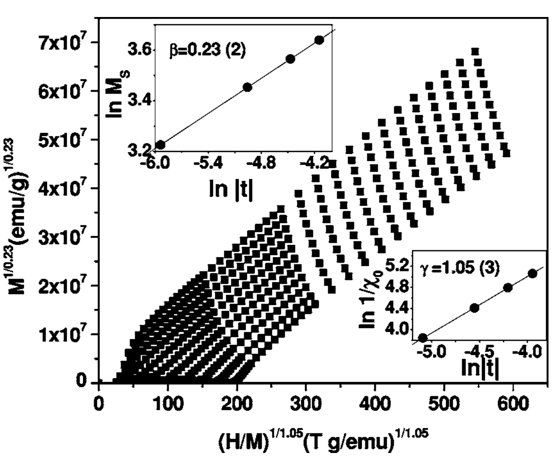

FIG. 3. Modified Arrott plot for NSMO-0.33 with insets showing the ln-ln plot for determining the critical exponent β and γ.

order transitions. The transition is continuous at the tricritical point and the associated critical exponents are universal.[6]

A similar analysis in NSMO-0.4 yields critical exponents of $\beta=0.51(2)$, $\gamma=1.01(3)$, and $\delta=3.13(2)$, which are close to those predicted for mean field approximation ($\beta=0.5$, $\gamma=1$, and $\delta=3$). Thus, our results show that NSMO with $x=0.33$ represents a tricritical point which separates a first-order transition for $x<0.33$ and a second order transition for $x>0.33$. The existence of such a tricritical point is an evidence for a transition driven by coupled order parameters[7] and confirms a similar proposal by Park *et al.*[8] based on a study of dc and ac magnetic susceptibilities of $Pr_{0.63}Sr_{0.37}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$ crystals. A tricritical point has earlier been observed at $x=0.4$ for $La_{1-x}Ca_xMnO_3$.[9]

The nature of these coupled order parameters was further studied using the magnetocaloric response [entropy change (ΔS)]. The magnetocaloric effect is calculated indirectly with Maxwell's relation from the magnetization data in various applied magnetic field[10] from 0 to H_{max} as

$$\Delta S_H = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH, \tag{4}$$

where $(\partial M/\partial T)_{H_i}$ is the experimental value obtained from M-T curve in a magnetic field H_i.

Amaral *et al.*[11] has suggested a successful model based on Landau's theory of phase transition with a contribution from magnetoelastic and electron interaction in manganites. According to this model, change in entropy is obtained by differentiating the Gibbs free energy and is given as $\Delta S=-\frac{1}{2}A'(T)M^2-\frac{1}{4}B'(T)M^4$, where $A'(T)$ and $B'(T)$ are the temperature derivatives of the expansion coefficients. This model is used to analyze the experimentally observed ΔS vs T plot in NSMO compounds.

A set of H/M vs M^2 plot is constructed at different temperatures for NSMO-0.4. The parameter A in the above equation is determined by fitting a straight line and interpolating the linear portion in high fields to find the y intercept, and the slope of the straight line gives the parameter B of the equation. From the derived parameters A and B and using the above equation, we estimated the temperature dependence of

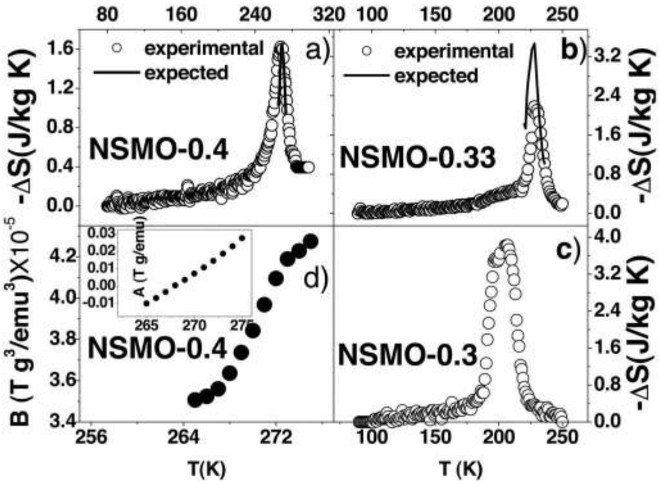

FIG. 5. Temperature dependence of observed and theoretically estimated ΔS for (a) NSMO-0.4, (b) NSMO-0.33, and (c) NSMO-0.3 taken from Ref. 3. (d) B parameter vs T with inset showing A parameter vs T.

ΔS using the model based on magnetoelastic coupling and electron interaction. The temperature dependence of the A parameter is linear, as shown in the inset of Fig. 5(d). It can be seen that the agreement between the experimentally and theoretically estimated data is satisfactory; the analysis clearly demonstrates the importance of magnetoelastic coupling and electron interaction in determining the magnetocaloric properties of NSMO-0.4 as in Fig. 5(a).

In the case of NSMO-0.33, it is seen that the theoretically estimated entropy exceeds the observed entropy, as shown in Fig. 5(b). This is in accordance with an analysis using heat capacity of NSMO-0.33 (Ref. 12) in which the magnetic entropy across T_C could not be accounted for without considering magnetic degrees of freedom.

For NSMO-0.3 which exhibits a first-order-like transition, the fit could not be performed and the observed ΔS is given in Fig. 5(c). This suggests that an additional order parameter together with the magnetoelastic contributions is necessary for the observed magnetocaloric data in case of NSMO-0.3, which deviate from the behavior of a second order mean field ferromagnet.

In order to understand these results, it is noted that "colossal magnetoresistance" (CMR) is maximum in $Nd_{1-x}Sr_xMnO_3$ compounds for $x \sim 0.3-0.33$,[13] in which short range correlations with charge/orbital order have been observed by synchrotron x-ray measurements above and below T_C.[14] It has recently been shown theoretically that such correlations are directly responsible for CMR.[15]

Contributions to the free energy from such correlated clusters as evidenced from the presence of tricritical point in NSMO-0.33 and first-order transition in NSMO-0.3 might couple with the magnetic order parameter resulting in a difference between measured ΔS and a Landau-theory-based computation. In the case of NSMO-0.3, its complex ferromagnetism and the presence of a first-order-like transition at low field due to the presence of correlated clusters at T_C prevent the application of a Landau-theory-based MCE computation. For NSMO-0.33, although the transition is continuous, it occurs at a tricritical point brought about by competing degrees of freedom, which are also responsible for the short range correlations. Such correlations may suppress the magnetic entropy resulting in a difference between computed and observed MCE.

Thus, using a critical exponent study combined with magnetocaloric data, we show that the para-ferromagnetic transition in $Nd_{1-x}Sr_xMnO_3$ is strongly influenced by competing order parameters resulting in a tricritical point for $x \sim 0.33$ with a first-order transition occurring for $x < 0.33$ and a second order transition for $x > 0.33$. The influence of such coupled order parameters on the magnetocaloric response could be determined from the agreement or lack thereof between entropy change across T_C obtained from magnetization data and a Landau-theory-based computation.

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