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Critical behavior of $La_{0.87}K_{0.13}MnO_3$ manganite

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ABSTRACT

The heat capacity of $La_{0.87}K_{0.13}MnO_3$ manganite is measured in temperature intervals from 80 to 350 K. A nature of the ferromagnetic phase transition and critical properties of the heat capacity near Curie temperature are studied. The principles of change in universal critical parameters near a phase transition point are determined. The critical exponents and heat capacity amplitude are calculated with account of correction to the scaling $\alpha = -0.13$, $A^+/A^- = 1.178$, and correspond to the critical behavior of 3*D* Heisenberg model. It is found a critical exponent of the correlation radius $\upsilon = 0.71$, which is also conform to the Heisenberg universality class.

1. Introduction

A research on a nature of the phase transitions in magnetic materials has been and still remains one of the actual directions in the condensed state physics. Study of phase transitions in perovskite manganites is of special interest, since a competition between the electric, lattice, and magnetic degrees of freedom in these materials leads to the effect of colossal magnetoresistance (CMR) near a phase transition temperature. The models of double exchange, phase layering, and Jahn–Teller distortion are used for explanation of the CMR effect and metal–insulator transition in manganites. The manganites are complex materials for exploration that is why the researchers meet with difficulties in estimation of a phase transition type, apropos of what there are many opinions in the literature. It is connected with that a majority of works on manganites is dedicated to the CMR effect. The exploration of a nature of the phase transitions on basis of different thermophysical parameters (magnetization, susceptibility, heat capacity, etc.) with calculation of values of the universal critical parameters is beyond of deserved attention. Though a critical behavior of the magnetization and susceptibility with calculation of the critical exponents β and γ [1–8 and References in them] is researched to some extent, a plight with study of critical behavior of the heat capacity is far worse. Lack of investigations on a critical behavior of the heat capacity could be explained by the difficulties arousing at preparation and realization of precision experiments for the heat capacity measuring in the neighborhood of critical point.

The known works [9–16] on a critical behavior of the manganites heat capacity near the phase transition temperature show rather contradictory results. So work [9], where a critical behavior of the heat capacity and thermodiffusion of $La_{1-x}Sr_xMnO_3$ manganites was explored, demonstrates that critical exponent α corresponds to 3*D* Heisenberg model at $x < 0.1$, when the system is antiferromagnetic, and it coincide with 3*D* Ising model at $x > 0.28$, when the ordering is ferromagnetic, the system is hard to describe within any universality class in the range of $0.1 \leq x < 0.28$. While the universality class of $La_{1-x}Ag_xMnO_3$ critical behavior does not depend on Ag concentration and corresponds to 3*D* Heisenberg model for $x = 0.1$; 0.15 and 0.2 [10]. A majority of parent compositions $LnMnO_3$ (Ln = La, Y, Pr, Nd, Ca) also satisfy to Heisenberg 3*D* universality class of the critical behavior [11–13]. Such spread in critical exponents can be explained both by a variety of approaches and different temperature intervals for analysis of the heat capacity critical behavior.

In presented work we try to give a quantitative estimation of a critical behavior of $La_{0.87}K_{0.13}MnO_3$ heat capacity near the Curie temperature. It should be noted that manganites substituted by univalent ions have been started to research not long ago, particularly, only $La_{1-x}Ag_xMnO_3$ system is studied in detail [8,10,17,18], there are merely a few works devoted to the heat capacity of $La_{1-x}K_xMnO_3$ [19,20], and the researches on critical properties

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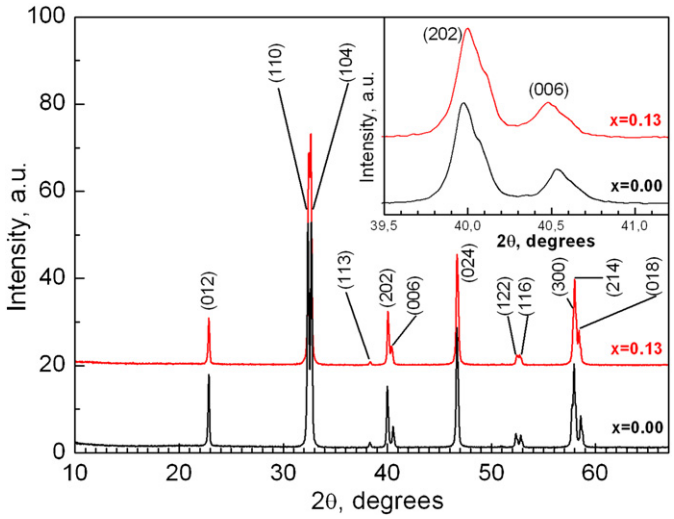

Fig. 1. Powder XRD patterns of $La_{1-x}K_xMnO_3$ solid solutions ($x = 0$; 0.13). The inset presents the enlarged region of powder XRD patterns of $La_{1-x}K_xMnO_3$ ($x = 0$ and 0.13) near (2 0 2) and (0 0 6) reflections.

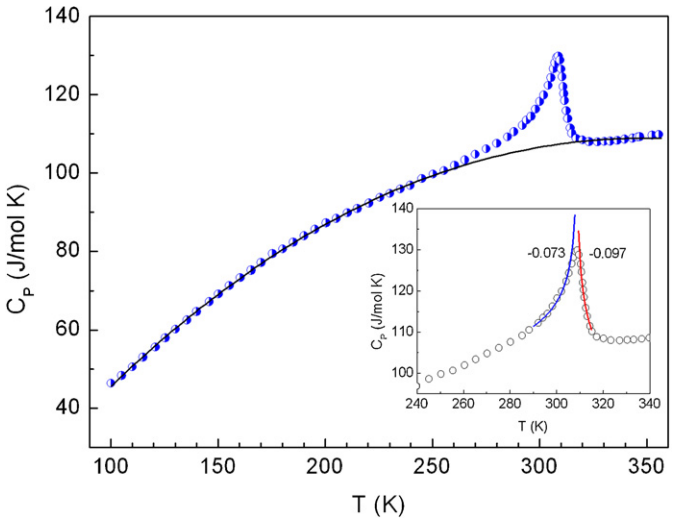

Fig. 2. Temperature dependence of $La_{0.87}K_{0.13}MnO_3$ heat capacity. The line corresponds to the regular part described by formula (1).

potassium-substituted manganites are absent at all. Manganites doped by monovalent cations (Na^+, K^+, Ag^+) have an advantage over the manganites doped by divalent cations (Sr^{2+}, Ca^{2+}, Ba^{2+}) owing to their high sensitivity to the magnetic field at room temperatures, what enables to explore the fundamental physical laws revealing in them in low available fields. The large values of the magnetocaloric effect are inherent to these manganites compositions together with CMR effect, what causes a high interest from a perspective of applied researches.

2. Results and discussion

A sample was synthesized from $Mn(NO_3)_2$, $La(NO_3)_3$, and K_2CO_3 by means of Peccini method. Stoichiometric amounts of K_2CO_3 were added to a nitrate solution of La and Mn together with citric acid and ethylene glycol. The obtained solution was evaporated at 60 °C until gel state, which in its turn was decomposed during 5 h at 600 °C in the air. Received powder was compacted into pellets, which were pressed into the powder of the same composition in order to avoid of potassium evaporation and annealed at 1000 °C in the air during 30 h.

The powder XRD patterns were collected on Rigaku SmartLab X-ray diffractometer ($Cu_{K\alpha}$). No impurity phases were detected in samples. All solid solutions $La_{1-x}K_xMnO_3$ (LKMO) have rhombohedraly distorted perovskite-type structure. The powder XRD patterns of LKMO show that degree of such distortion decrease with increase in potassium concentration (x), which is apparent through decrease in splitting of the pseudocubic reflections (Fig. 1, pseudocubic reflections are groups of closely spaced reflections: (0 1 2); (1 1 0) + (1 0 4); (2 0 2) + (0 0 6); (0 2 4); (1 2 2) + (1 1 6), etc.). The XRD patterns were indexed in hexagonal unit cell (space group $R\bar{3}c$). Cell parameters of LKMO are $a = 5.5256(3)$ Å and $c = 13.3384(9)$ Å for $x = 0$ and $a = 5.5171(3)$ Å and $c = 13.3857(9)$ Å for $x = 0.13$. The inset in Fig. 1 presents the enlarged region of powder XRD patterns of $La_{1-x}K_xMnO_3$ ($x = 0$ and 0.13) near (2 0 2) and (0 0 6) reflections. The peaks shift indicates increasing of cell parameter c and decreasing of parameter a with addition of potassium. (2 0 2) and (0 0 6) peaks convergence indicates decreasing rhombohedral distortion of perovskite.

A cation composition of the sample is confirmed by the methods of atom-emission spectrometry and mass-spectrometry of inductively coupled plasma. The defined composition is practically identical within an error of the analysis to the composition specified at synthesizing. Minute results of structural researches of $La_{1-x}K_xMnO_3$ system are presented in work [21].

For measuring of the heat capacity were used an original version of modulation calorimetry [22]. The sample of $3 \times 2 \times 0.43$ mm^3 in sizes was heated by light impulses with the modulation frequency $\omega = 2$ Hz. The periodic oscillations of the sample temperature caused by heating were measured by the chromel–constantan thermocouple with wires of 0.025 mm in diameter. A thermojunction was flattered to 5 μm in order to improve a thermal contact with the sample. The rate of temperature change in the phase transition ranges did not exceed 0.05 K/min.

Fig. 2 presents the results on measuring the temperature dependence of $La_{0.87}K_{0.13}MnO_3$ heat capacity within temperature intervals from 100 to 350 K. As it is clear from figure the $La_{0.87}K_{0.13}MnO_3$ heat capacity obeys to Debye heat capacity of solids except the abnormal part, being in intervals of 260–315 K, bounded with ferromagnetic–paramagnetic phase transition. A continuous change in heat capacity in transition regions indicates the magnetic second order phase transition, and strongly pronounced λ-shaped peak of the heat capacity testifies to essential influence of the thermodynamic fluctuations on $La_{0.87}K_{0.13}MnO_3$ heat capacity in the phase transition region. A temperature of the phase transition (of the heat capacity maximum) proved to be equal to $T_{max} \approx 308$ K. A value of the heat capacity discontinuity in the phase transition region is $\Delta C_p(T_{max}) \approx 24$ J/mol K, a width of the transition in the center of peak is $\Delta T \approx 12$ K.

The insert in Fig. 2 represents an approximation of heat capacity critical behavior near the phase transition temperature by means of formula $C_P = (A/\alpha)|t|^{-\alpha}$. It is evident that the critical exponent values before $\alpha' = -0.073$ and $\alpha = -0.097$ after phase transition have some distinctions and are close to the Heisenberg universality class. For more extensive quantitative estimation of the critical behavior near the T_C was separated an abnormal part of the heat capacity ΔC_p (Fig. 3) by means of deduction of the regular heat capacity interpolated by third power algebraic polynomial using the least-squares method from measured heat capacity dependence:

$$C_B = A_0 + A_1 T + A_2 T^2 + A_3 T^3, \quad (1)$$

with coefficients $A_0 = -19.31973$ J/mol K, $A_1 = 0.7727$ J/mol K^2, $A_2 = -0.00127$ J/mol K^3, $A_3 = -3.1781 \times 10^{-7}$ J/mol K^4. Temperature dependence of change in entropy connected with ferromagnetic–paramagnetic phase transition was determined by formula $\Delta S(T) = \int \left(\frac{\Delta C_P}{T}\right) dT$ and is shown in insert of Fig. 3. A

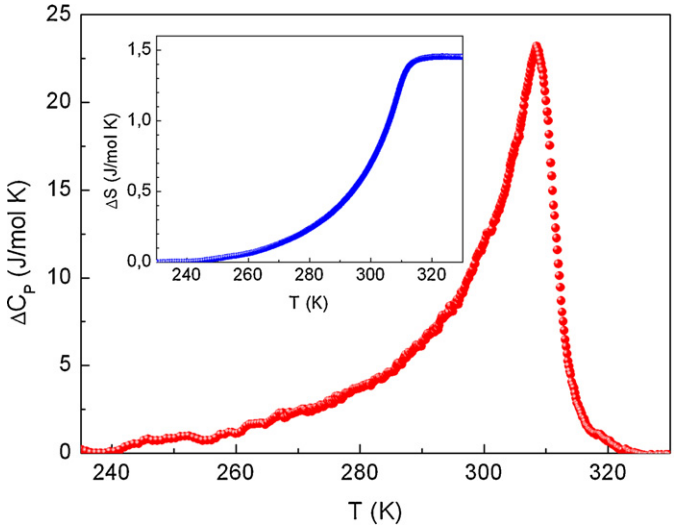

Fig. 3. An abnormal part of $La_{0.87}K_{0.13}MnO_3$ heat capacity. In the insert there is temperature dependence of change in entropy connected with phase transition.

value 1.47 J/mol K received for transition entropy is considerably lower than theoretical estimation $\Delta S = R\ln(2S+1) = 11.8$ J/mol K.

Evidently, the computed values of the transition entropy are much smaller than the theoretical estimates. It should be noted that a characteristic behavioral feature of the specific heat of manganites is the relatively low transition entropy, for which, as it was indicated in works [23–25], could be several reasons. First and foremost, such values could be an indication that a two-phase magnetic state exists in these materials and, correspondingly, only a part but not the entire sample transitions into a magnetically ordered state. Another possible reason is that a part of the "lost" entropy falls into the temperature range far above T_C because of the existence of the short-range correlations in this temperature range. In any case there is evidence that ferromagnetic clusters with characteristic size ~8 Å, incorporated in the dielectric matrix, have been observed in the paramagnetic phase of the manganites far from T_C [26]. Thus the question of the low values of ΔS in manganites requires further study.

Our earlier researches on critical behavior of the heat capacity of ceramic manganites [10,17,27] showed that more satisfactory values of the critical exponents (belonging to the one of universality classes) were derived when the critical behavior was approximated to the expression taking account of correction to the scaling, hence the critical behavior of abnormal heat capacity ΔC_p were described using the equation [17]:

$$\begin{aligned} \Delta C_P^+ &= \frac{A^+}{\alpha}|t|^{-\alpha}(1 + D^+|t|^\theta), \quad T > T_C \\ \Delta C_P^- &= \frac{A^-}{\alpha}|t|^{-\alpha'}(1 + D^-|t|^\theta), \quad T < T_C \end{aligned}, \tag{2}$$

where A^+ and A^- are the critical amplitudes of the specific heat above and below T_C, D^+ and D^- are the amplitudes of the correction to scaling, θ is the corresponding corrective exponent (in our instant $\theta = 0.55$, what corresponds to the Heisenberg model), α and α' are the critical exponents of the heat capacity above and below T_C, $t = (T - T_C)/T_C$ is reduced temperature.

A proper determination of the critical temperature is very important at studying of the critical properties. In a number of cases the critical temperature coincides neither with heat capacity maximum nor with susceptibility maximum. And it should be remembered that because of different reasons every separate sample has its own "critical" temperature. Thereby the calculation results of the critical parameters, where T_C is defined by the maximums of C and/or χ, often differ.

Table 1
The values of the critical parameters of the heat capacity for the $La_{0.87}K_{0.13}MnO_3$.

	T_C (K)	α	A^+/A^-	D	t
$T > T_C$	308.4	−0.132	1.178	−8.39	5.6×10^{-4} to 1.2×10^{-2}
$T < T_C$		−0.126		−6.12	1.2×10^{-3} to 1.1×10^{-2}

To determine T_C we proceeded from static scaling prediction about the equality of the critical exponents $\alpha = \alpha'$ evaluated below and over T_C. In adjustable formula (2) the T_C is chosen near the heat capacity maximum so that values of α and α' coincide within the calculation error at minimum values of mean-square deviation of R at fixed values of temperature interval bounds t_{max} and t_{min}. The critical temperature value $T_C = 308.4 \pm 0.1$ K evaluated in this way we used as critical in further approximations. We attribute a determination accuracy of the critical temperature ±0.1 K with constancy of the critical exponent α at variation of T_C within this error.

The critical behavior of the heat capacity was approximated by means of nonlinear least squares method (Fig. 3). When the abnormal part of heat capacity was approximated by formula (2) $t_{max} = 1.2 \times 10^{-2}$ and $t_{min} = 5.6 \times 10^{-4}$ both at $T > T_C$ and $T < T_C$. Approximation parameters of the critical behavior at $T > T_C$ and $T < T_C$ by formula (2) are shown in Table 1. A choice of these parameters was caused by that a value of mean-square error R was minimal exactly at these parameters at approximation of our data by formula (2). Data approximation at these values of t_{max} and t_{min} gives a numerical value $\alpha = -0.13 \pm 0.003$, which is close to theoretically predicted estimation $\alpha = -0.115$ for isotropic Heisenberg magnets. Fig. 4 demonstrates a behavior of abnormal heat capacity for $La_{0.87}K_{0.13}MnO_3$ manganite near the critical temperature in log–log scale at $T > T_C$ and $T < T_C$. An approximation of ΔC_P by formula (2) at $\alpha = -0.13$ is shown in the same figure (solid line). The results of this approximation indicate that the critical behavior of $La_{0.87}K_{0.13}MnO_3$ heat capacity is similar to the critical behavior of classical Heisenberg ferromagnetic close to $t_{min} = 5.6 \times 10^{-4}$. Also the critical amplitudes of the heat capacity are calculated. A ratio of critical amplitudes before A^- and after A^+ transition was $A^+/A^- = 1.178$, what differs a little from a theoretically predicted value for isotropic Heisenberg magnetics.

A spatial dimension d of the magnetic order parameter and a number of its components n are estimated from derived values of the heat capacity critical exponents α and ratios of the critical

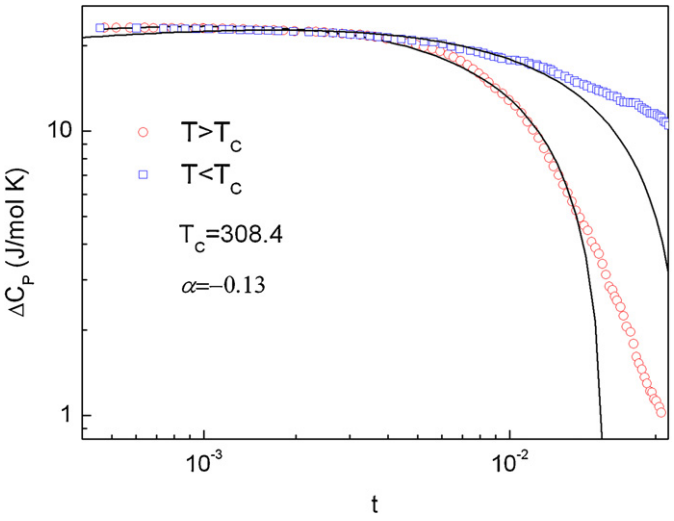

Fig. 4. Dependence of abnormal part of the heat capacity on reduced temperature both above T_C and below T_C. The line corresponds to the approximation of experimental results by formula (2).

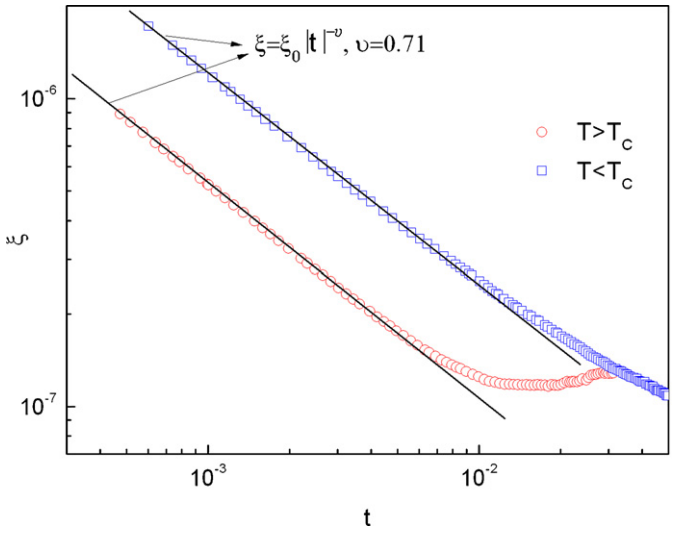

Fig. 5. Dependence of correlation radius on reduced temperature both above T_C and below T_C.

amplitudes A^+/A^-. A value of d agrees well with real physical spatial dimension of the studied manganites, which, as is known, has a cubic magnetic subsystem. The estimation of components number of magnetic order parameter by formula $A^+/A^- = n/2^{d/2}$ gives a value $n = 3$. These values $d = n = 3$ confirm the belonging of the heat capacity critical behavior of $La_{0.87}K_{0.13}MnO_3$ sample to the universality class of the classical 3*D* Heisenberg ferromagnetic [28].

A short length of correlations is one of the joining sign for strongly correlated electron systems (striking examples are perovskite manganites and HTSC). A temperature motion of the correlation length can be estimated using the Ginzburg criterion determining a temperature at which the fluctuations make a substantial contribution to the heat capacity:

$$\xi = \xi_0 |t|^{-\upsilon} = \left[\left(\frac{k_B}{\Delta C_P} \right) \left(\frac{1}{t_G 32\pi^2} \right)^{1/2} \right]^{1/3} |t|^{-\upsilon}, \quad (3)$$

where $\xi_0 = [(k_B/\Delta C_P)(1/t_G 32\pi^2)^{1/2}]^{1/3}$, $\upsilon = (2-\alpha)/d$, t_G is Ginzburg temperature with order $\sim 10^{-3}$. The estimations show that for $La_{0.87}K_{0.13}MnO_3$ $\xi_0 \approx 30$ Å what corresponds roughly to the sizes of two elementary cells. The similar estimations for a correlation length of the magnetic order parameter for $La_{0.9}Ag_{0.1}MnO_3$ represent a value $\xi_0 \approx 19$ Å in work [27]. A slightly overrated value of ξ_0 for $La_{0.87}K_{0.13}MnO_3$ indicates the vigorous influence of the thermodynamic fluctuations on the heat capacity near the phase transition temperature. By means of $\alpha = -0.13$ and $d = 3$ described above one can derive a critical exponent value of the correlation length $\upsilon = (2-\alpha)/d = 0.71$, which satisfies to Heisenberg universality class (0.705). In Fig. 5 is presented the dependence $\xi = f(t)$ at $T > T_C$ and $T < T_C$ in log–log scales, derived by means of formula (3), where the data from Fig. 4 are taken instead of ΔC_P. As it is evident from Fig. 5 the influence of thermodynamic fluctuations becomes considerable close by $t \approx 10^{-2}$ both above T_C and below T_C.

3. Conclusion

The critical behavior of the $La_{0.87}K_{0.13}MnO_3$ heat capacity is analyzed quantitatively with calculation of the heat capacity critical exponent α by means of the scaling theory of phase transitions near the Curie temperature. A temperature motion of the correlation length of the magnetic order parameter is estimated. A critical exponent υ of radius correlations is determined. The obtained values of the critical parameters show that critical behavior of $La_{0.87}K_{0.13}MnO_3$ manganite corresponds to the model of classical 3*D* Heisenberg ferromagnetic.

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