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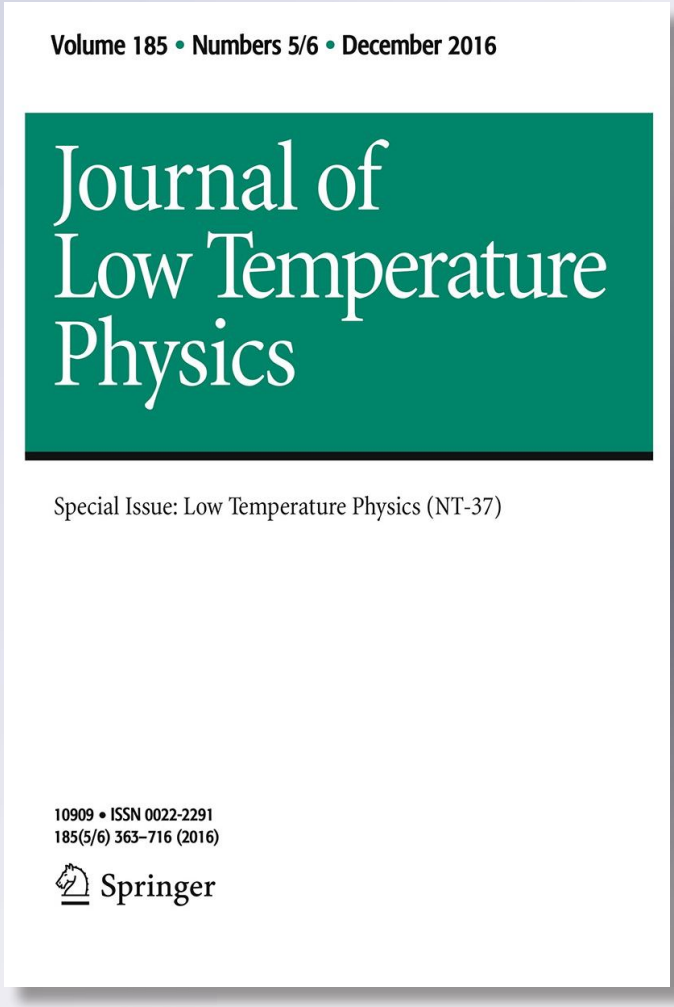

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Interplay Between Structural, Jahn–Teller, and Magnetic States of Slightly Doped Lanthanum Manganites

V. A. Golenishchev-Kutuzov[1] · **A. V. Golenishchev-Kutuzov**[1] · **R. I. Kalimullin**[1] · **A. V. Semennikov**[1]

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Abstract By combining the results of elastic moduli, electrical resistivity, and magnetization measurements for $La_{1-x}Sr_xMnO_3$ ($x = 0.125$, $x = 0.15$, and $x = 0.175$), we have constructed a phase diagram that describes the structural, magnetic, transport properties and the relationships among them as a function of the composition and temperature (140–340 K). The local, intermediate, and cooperative Jahn–Teller distortions of the octahedral structural units MnO_6 have been studied. It is common for these distortions to be observed using probes of intermediate structures (domains or super-cells), but they are absent in the averaged crystallographic structure. In the cooperative Jahn–Teller distorted phase, the macroscopic sample length is temperature dependent. We presume that the structural transitions from the cooperative Jahn–Teller phase to the charge ordering phase at low temperatures (150 and 180 K at $x = 0.125$ and $x = 0.15$) are due to the increase in the spontaneous magnetization with the conservation of the local deformations of separate octahedra. The agreement between the types of the orbital ordering and the local, intermediate, and Jahn–Teller cooperative distortions of octahedra was established.

Keywords Jahn–Teller effect · Distortion · Elastic moduli · Transition · Magnetic properties

1 Introduction

The interest in perovskite manganites was initiated primarily by the discovery of colossal magnetoresistance (CMR). It became clear soon that CMR in these materials is

✉ A. V. Semennikov
campoce6e@gmail.com

[1] Department of Industrial Electronics, Kazan State Power Engineering University, 420066 Kazan, Republic of Tatarstan, Russian Federation

accompanied by specific features not only in the electric and magnetic but also in the structural properties. This stimulated the investigation of CMR and other intriguing phenomena using various experimental techniques. It was found that manganites exhibit a complex interplay and competition among orbital, charge, lattice, and spin degrees of freedom [1–3]. A recent concept that may be relevant for many of these systems is the observation of intrinsic nanoscale inhomogeneities. When the scale of the fine structure is small enough that the interface energy becomes an appreciable fraction of the total free energy, then the fine structure itself can be important in determining the temperature and magnetic field dependences of physical properties of such materials [4,5]. In manganites, the microscopic driving force for such intrinsic texturing is the strong spin-charge-lattice coupling. In particular, CMR can be driven by the local and cooperative Jahn–Teller (J–T) distortion of the manganite unit cell MnO_6 rather than that of the sample as a whole. Our approach for establishing a correlation between inhomogeneities and electron properties is to study the complete phase diagram of systems of interest.

We constructed a phase diagram that describes the structural, transport, magnetic, and J–T properties as a function of the composition (x) and temperature (T).

Single crystals $La_{1-x}Sr_xMnO_3$ with $x = 0.125$, 0.15 and 0.175 for investigations were grown by the team headed by A. M. Balbashov at the Moscow Power Institute. The samples had the shape of a parallelepiped with sizes of $3\times4\times3$ mm^3. The velocities of longitudinal and transverse ultrasonic waves at frequencies of 700–1000 MHz were measured with an accuracy of 0.1 % as a function of temperature in the range of 140–340 K and magnetic field (0–1.5 T) on an apparatus based on the phase comparison method.

We performed a complete study of the features of the J–T ordering, spontaneous magnetization, resistance, and the effect of applied magnetic fields. Our main experimental method was to measure the parameters of elastic moduli C_{ij}, which correlate with the bond angles O–Mn–O of the MnO_6 (C_{44}) and bond lengths Mn–O $(C_{11}-C_{12})/2$ [6]. Recently, it was found from neutron diffraction experiments that the local distortion of oxygen octahedra was observed only in $LaSrMnO_3$ in the rhombohedral phase [7–9]. The value of the local distortion is characterized by the variation of the Mn–O bond length and remains constant over the temperature range up to T_C of the magnetic phase transition from the isolated paramagnetic state to the conducting ferromagnetic state.

2 Results and Discussion

All investigated samples exhibited a sharp decrease in some elastic moduli in certain temperature intervals. Figures 1a and 2a show the most intense variations of C_{ij} moduli, while other moduli exhibit a less intense variation in the same temperature intervals. It was established earlier [5] that the structural phase transitions (T_{str1}) from the rhombohedral to the weakly distorted orthorhombic phase occur upon cooling to 450 K for the sample with $x = 0.125$ and 340 K ($x = 0.15$) as a result of the distortion of MnO_6 octahedra. We assumed that the continuous reduction of the moduli C_{11}–C_{12} for $x = 0.125$ (Fig. 1) and C_{44} for $x = 0.15$ (Fig. 2) upon cooling from 340 to

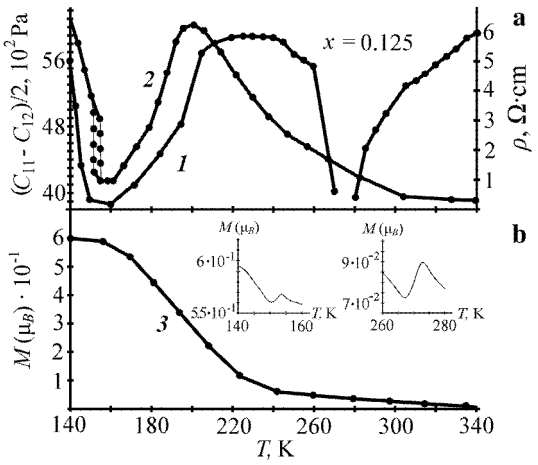

Fig. 1 Temperature dependence of the transverse elastic moduli $(C_{11} - C_{12})/2$—*1*; resistivity ρ—*2* (**a**) and magnetization $M(\mu_B)$—*3* (**b**) of $La_{1-x}Sr_xMnO_3$ with $x = 0.125$; the *insets* show the magnetization dependence at J–T transitions (150 and 270 K)

320 K is associated with the increase in the local ordering of J–T distorted MnO_6 octahedra.

The sharp changes in the moduli at 280 K ($x = 0.125$) and at 240 K ($x = 0.15$) are characterized by a hysteresis that makes it possible to attribute them to the first-order structural phase transitions. It was established that octahedra undergo a tension deformation on the order of 10^{-3} along their a, b axes, and a compression deformation of $\sim 2 \cdot 10^{-2}$ along the c axis of a hypothetical cubic lattice. These deformation values were in good agreement with the changes in octahedra parameters obtained from neutron and X-ray measurements [2]. Here we present the results of the observation of the abrupt jump in the values of the elastic moduli in the low-temperature region (140–340 K). We refer the high-temperature transitions ($T_{S1} = 280$ and 240 K for samples with $x = 0.125$ and $x = 0.15$) to the formation of the ordering among the distorted MnO_6 octahedra of disorder-order type, since only randomly located distortions exist above T_{S1}. Upon cooling the samples with $x = 0.125$ and $x = 0.15$ below $T_{S2} = 150$ K ($x = 0.125$) and $T_{S2} = 160$ K ($x = 0.15$), we observed sharp changes in the elastic moduli values corresponding to a step in magnetization and conductivity (Figs. 1b, 2b). The insets in Fig. 1b show step-like changes of the spontaneous magnetization at $T_{J-T} = 270$ and 150 K, which are characteristic for the competition between the magnetization and J–T distortion. It was unusual that these steps were of the hysteresis nature, since they occur under the conditions of structural J–T rearrangement. The narrowness in the temperature interval of these transitions corresponds to the narrow interval of changes in elastic moduli.

On the basis of our data and literature results [2] for the sample with $x = 0.125$, we presume that there is a gradual competitive substitution of one phase state for another upon cooling in the interval of 160–140 K. The gradual suppression of the cooperative J–T ordering occurs first due to the increase in the spontaneous magnetization that is terminated stepwise at 150 K with the conservation of the local deformations of separate octahedra. As we showed in [2], a reverse stepwise transition in a similar manner at 280 K is due to the competitive suppression of the initial magnetization via

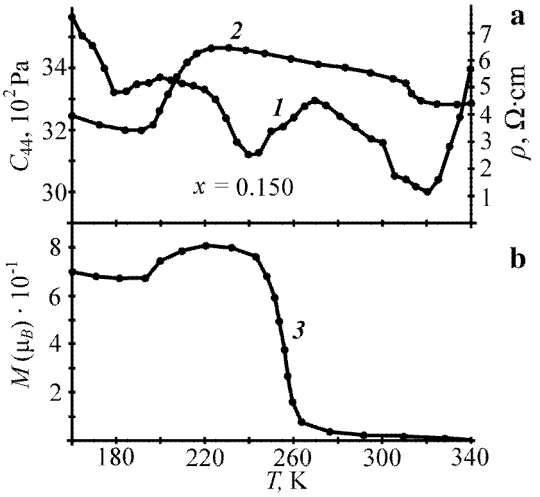

Fig. 2 Temperature dependence of the transverse elastic moduli C_{44}—*1*; resistivity ρ—*2* (**a**) and magnetization $M(\mu_B)$—*3* (**b**) of $La_{1-x}Sr_xMnO_3$ with $x = 0.15$

the increase in the cooperative ordering. For the sample with $x = 0.15$ on cooling below 180 K, an additional structural transition of the J–T type takes place, but in the ferromagnetic phase. The temperature range of the variation of moduli values correlates very well with the resistive and magnetic anomalies, which can be clearly identified with the structural J–T transition to the cooperative ordering of distorted octahedra. On cooling below 160 K, we observed sharp changes of C_{ij} moduli, electric, and magnetic parameters, which were associated with the suppression of the cooperative J–T ordering under the increase the magnetization and the transition to the ferromagnetic phase. These T_{S2} transitions for $x = 0.125$ and $x = 0.15$ can be readily attributed to structural J–T changes due to the reduction in the J–T ordering of the distorted octahedra.

The application of relatively low magnetic fields ($H \leq 2$ T) shifts the temperature T_S by approximately 5 K/T (inset in Fig. 1b) leading to the considerable variation of some parameters near T_S (elastic moduli, dielectric permittivity, magneto capacitance [10], and electric resistance). Due to the narrowness of the transition at T_S, these parameters change by 30 % or more making it possible to control elastic, electric, and dielectric characteristics.

On the basis of structural, electric, and magnetic data, the following structure properties relationships were determined for slightly doped lanthanum manganites. For samples with $0.125 < x < 0.15$, the structural transition characterized by the large cooperative orbital ordering of the J–T type takes place in the paramagnetic orthorhombic phase. On cooling during the ferromagnetic transition, the insulating orthorhombic O' phase transfers to the orthorhombic O phase characterized by the suppressed cooperative J–T ordering and large local J–T distortions (Fig. 3).

For $0.15 < x \leq 0.175$ on cooling during the ferromagnetic transition, the semiconducting R phase transfers to the metallic R phase with suppressed cooperative J–T distortions.

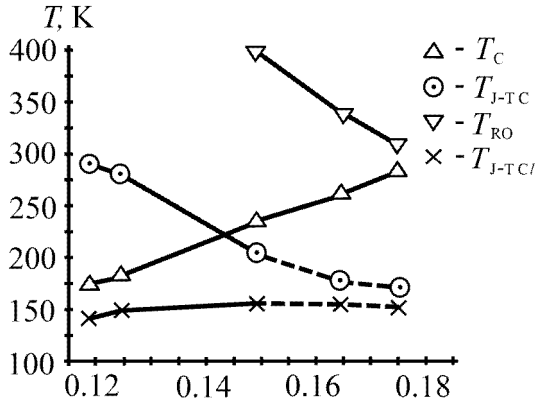

Fig. 3 Temperatures of magnetic ordering T_C, cooperative J–T ordering—T_{J-T}, structural transition from rhombohedral to weakly distorted orthorhombic phase—T_{RO}, structural J–T transition from cooperative J–T phase to local ordering J–T phase—T_{J-TCl}

3 Conclusions

Using complex measurements of the parameters of high-frequency acoustic waves and the magnetic and electric characteristics of single crystal $La_{1-x}Sr_xMnO_3$ with $x = 0.125$, 0.15, and 0.175 in the temperature range of 300–130 K, we observed abrupt first-order structural J–T transitions due to the suppression of the cooperative J–T ordering of MnO_6 octahedra under the increase in magnetization for the samples with $x = 0.125$ and 0.15. The intensity of J–T distortions of MnO_6 octahedra decreases with the increase in doping of manganites. The softening of some elastic moduli corresponds to the character of the orbital ordering. The application of the external magnetic field leads to the increase in the magnetization of the samples and shifts the phase transition temperature upward.

In spite of the previous conclusion that the J–T coupling suppresses the ferromagnetic state [1], our experimental results and those of other investigators [2] indicate that on the contrary the ferromagnetic state suppresses the J–T ordering. This contradiction can be explained by the interplay between the charge mobility and the cooperative J–T effect below the T_{J-T} transition. There is the energy gain due the enhanced charge mobility, while the continuous reduction of the structural distortion implies the loss of the J–T energy. When the external magnetic field increases, the r cooperative J–T distortion decrease additionally. Thus the slightly doped manganites significantly differ from those at higher doping, where no cooperative J–T distortion is present in the ferromagnetic phase.

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