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Influence of Jahn–Teller Ordering on the Structural and Magnetic Phase Transitions in Lightly Doped Manganites

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Abstract—Processes of the mutual influence of Jahn–Teller and magnetic orderings in lightly doped lanthanum–strontium manganites of the composition $La_{1-x}Sr_xMnO_3$ ($0.12 < x < 0.18$) are considered. A correspondence between the local (or cooperative) distortion of the oxygen octahedra MnO_6 and the types of the orbital ordering of electron orbitals is established, based on a comprehensive study of the temperature behavior of the elastic moduli, magnetization, and electrical conductivity.

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The uncommon physical properties of lightly doped manganites (e.g., colossal magnetoresistance (CMR) and variety of structural, magnetic, and electronic states) have long been the objects of numerous experiments [1]. In addition to CMR, features of diverse phase transitions and nanosized inhomogeneities became the objects of investigations and, as was assumed in [1–3], were mainly associated with manifestations of the Jahn–Teller (J–T) effect. It is known [3] that the J–T orbital degeneracy of *d* levels of Mn^{3+} ions disappears because of distortions in the MnO_6 octahedra, which at high concentrations of Mn^{3+} ions ($x \le 0.16$) produce macroscopic deformations of the crystal lattice (the cooperative J–T effect). To date, the structural and magnetic defects and phase transitions induced by the J–T effect have mainly been investigated by means of X-ray and neutron diffraction only for undoped manganites $LaMnO_3$, for $La_{1-x}CaMnO_3$ [4–8], and for a sample of $La_{1-x}Sr_xMnO_3$ ($x = 0.125$) [2, 5, 6]. Lanthanum–strontium manganites with other concentrations of Sr have been investigated only poorly.

Since some distortions of the crystal lattice appear in all processes associated with the J–T effect, apart from structural methods we have used original high-frequency (700–1000 MHz) magnetoacoustic techniques [9, 10] to study the dynamics of electron–lattice and spin–lattice interactions.

Along with magnetic and resistive measurements, studying changes in the values of the elastic moduli C_{ij}, depending on the temperature and concentration of the doping centers and external magnetic fields, enables us to obtain additional information on the specific features of the phase states and transitions between them, on different inhomogeneities, and on their dependence on J–T orderings, both local and cooperative; and to estimate the energy of the J–T transition.

As a result of our measurements of the temperature and magnetic characteristics of elastic moduli, a number of new structural transitions were revealed for the lanthanum–strontium manganites in the interval of $0.12 < x < 0.18$. Figures 1 and 2 show the most characteristic behavior of C_{ij} for $x = 0.125$ and 0.175 (between these values of x, similar dependences were observed). Sharp transitions, both low-temperature (near 150 K for $x = 0.25$ and near 110 K for $x = 0.175$ K) and high-temperature (at 270 K for $x = 0.125$ and at 290 K for $x = 0.175$) were revealed. In both samples, the low-temperature and high-temperature changes in C_{ij} were of a sharply pronounced hysteresis nature, indicating that the transitions were first-order. It follows from the inserts in Figs. 1 and 2 that the temperature characteristics of magnetization and resistivity were affected by these transitions to a lesser extent.

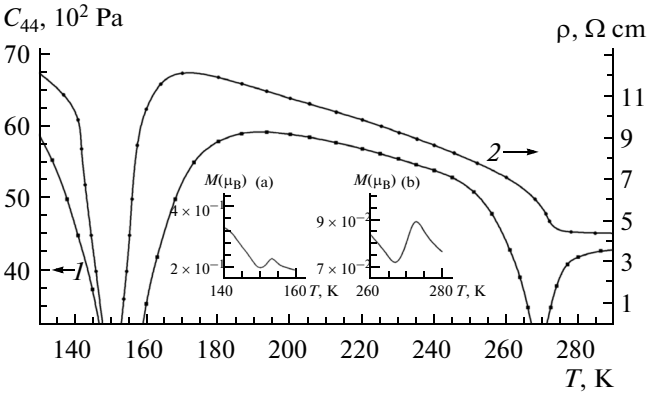

Fig. 1. Temperature dependences of (*1*) the shear modulus of elasticity C_{44} and (*2*) electrical resistivity ρ for $La_{1-x}Sr_xMnO_3$ ($x = 0.125$). The inserts show the $M(\mu_B)$ dependences at (a) T = 140–160 K and (b) T = 260–280 K.

The J–T distortions of the structure, and thus of the energy near the phase transitions, diminished considerably with an increase in the concentration of dopants (Sr ions).

The application of an external magnetic field, which increases spontaneous magnetization, led to a temperature shift of the J–T phase transitions: downward for the transition at 280 K, and upward for the transition at 150 K. In both cases, the magnetic field partially or completely suppressed the cooperative J–T ordering in the samples with $x \le 0.15$.

A different type of mechanism behind the emergence of J–T distortions was observed for the samples with $x > 0.15$. In this case, the distortion of some MnO_6 octahedra had already occurred in the rhombohedral phase. This was confirmed by major changes in the values of the C_{11}–C_{12} and C_{44} moduli, and by the nearly identical values of the C_{11} and C_B moduli, indicating the appearance of strong local lattice distortions of the J–T type near 310 K in the absence of cooperative ordering and J–T distortion of the octahedral, and thus in the absence of volume deformations of the crystal. This effect corresponds to a structural transition from the rhombohedral to the orthorhombic phase. The formation of the cooperative J–T ordering of the octahedra was apparently prevented by spontaneous magnetization of the FM-I type (a ferromagnetic insulator).

Our experimental findings allow us to suggest the following phenomenological model of the relationship between orbital ordering and the nature of the Jahn–Teller lattice distortions: The emergence of static J–T deformations of some MnO_6 octahedra is accompanied by a phase transition from the quasi-cubic to the rhombohedral state. For the samples with $x = 0$, this transition evidently occurs at 1050 K [5], and the value of the distortion characterized by a change in the Mn–O bond length then remains constant. However, it diminishes sharply with an increase in the concentration of doping ions. With a drop in temperature, cooperative macroscopic ordering of the axes of the already distorted MnO_6 octahedra was observed in the paramagnetic phase ($T > T_C$) at $x \le 0.15$ in the investigated samples; this was apparent in the sharp change in all elastic moduli (C_{11}, C_{11}–C_{12}, C_{44}) for the sample with $x = 0.125$–0.15. The transition to the orthorhombic phase at 270 K for the sample with $x = 0.125$ was accompanied by competition between an increase in the cooperative J–T ordering and spontaneous magnetization. As the temperature fell further to 150 K, there was suppression of the J–T cooperative ordering by large magnetization in the state of the ferromagnetic insulating phase (FM-I), but the J–T distortions of the MnO_6 octahedra continued. Under the conditions of the transition to the metallic phase (FM-M), the mutual arrangement of the MnO_6 octahedra was determined by the structure of the orbital ordering.

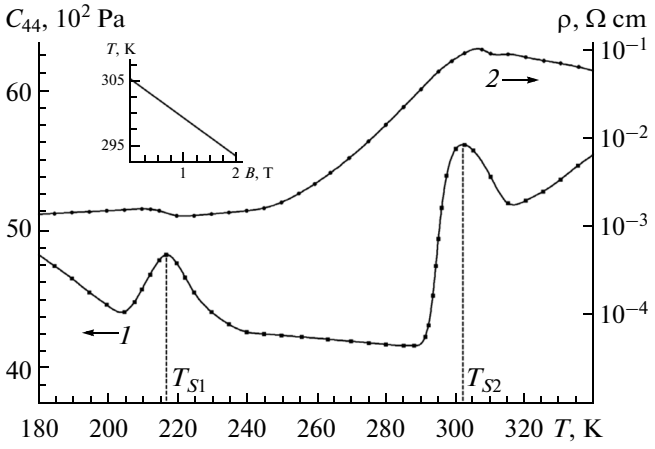

Fig. 2. Temperature dependences of (*1*) the shear modulus of elasticity C_{44} and (*2*) electrical resistivity ρ for $La_{1-x}Sr_xMnO_3$ ($x = 0.175$). The insert shows the dependence of the temperature of the Jahn–Teller transition T_{S1} on the applied magnetic field.

Our analysis of the sharp temperature changes in the elastic moduli revealed in the samples of $La_{1-x}Sr_xMnO_3$ with $x = 0.12$–0.18, and of the corresponding changes in the J–T energies, thus led to the conclusion that there was a deep relation between the magnetic and J–T orderings, and that they influence the CMR.

With a further drop in temperature (to $T < 300$ K) and as we approached T_C, new sharp and strong changes in all elastic moduli were observed in the interval of $285 < T < 295$ K. It should be emphasized that this effect was observed only in the samples with $x \ge 0.175$, and not for the samples with $x = 0.165$ [11]. We assume that a mixed magnetostructural transition occurs near T_C and T_S as a result of a change in the local structure of ordering of MnO_6 octahedra distorted due to the J–T effect. The dynamic ordering of the medium of octahedra is replaced by magnetic ordering associated with the formation of orbital ordering. This explanation was confirmed by the purely magnetic phase transitions having virtually no effect on the values of the elastic moduli.

As in the case of the samples with $x \le 0.15$, the application of a magnetic field in the range of $300 < T < 340$ K shifted the J–T transition toward lower temperatures in the more doped samples (see the insert in Fig. 2).

With a further drop in temperature, we also observed a change in the elastic moduli near 200 K; this was ascribed to the reconstruction of the local structure of the octahedral, and to their further suppression upon the transition from the magnetic FM-I phase to the FM-M phase. These low-temperature elastic effects were not confirmed by the behavior of the electrical conductivity; however, it was precisely at 200 K that the CMR was observed in [12], confirming our assumption that the nature of the CMR is related

to the process of the suppression of local structure of MnO_6 octahedra distorted due to the J–T effect by the magnetic field.

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