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Structural transitions in $La_{0.82}Ca_{0.18}MnO_3$ single crystal

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The influence of structural transitions from high-temperature pseudocubic O^* to the Jahn–Teller O' phase and the reverse transition from O' to a low-temperature O^* phase on the elastic, magnetic, and transport properties of a $La_{0.82}Ca_{0.18}MnO_3$ single crystal at the temperature decrease from 400 K is studied. Significant anomalies are observed in the temperature dependences of the velocity of longitudinal sound waves and the internal friction. The sound velocity and the internal friction in the Jahn–Teller O' phase are significantly lower than those in the pseudocubic O^* phase. The structural transitions take place in the temperature range 30 – 50 K. The majority carriers in the low-temperature O^* phase are electrons, whereas the majority carriers in the O' and high-temperature O^* phases are holes. Electronic states are characterized by substantially stronger spin-orbital interaction than hole states. The positive magnetoresistance is observed in low magnetic fields in the low-temperature O^* phase. At a certain field value, the magnetoresistance changes its sign. Such magnetoresistance has not been observed in the La-Sr and La-Ba manganites. Positive magnetoresistance indicates significant anisotropy of the transport properties of the low-temperature O^* phase in the $La_{0.82}Ca_{0.18}MnO_3$ single crystal. It is established that the magnetic and transport properties of the low-temperature ferromagnetic O^* phase differ markedly from those of the ferromagnetic Jahn–Teller O' phase.

Keywords: structural transition, manganite, crystal.

УДК: 537.6; 534.16; 537.31

Структурные переходы в монокристалле $La_{0.82}Ca_{0.18}MnO_3$

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Изучено влияние структурного перехода от высокотемпературной псевдокубической O^*-фазы к ян–теллеровской O'-фазе и обратного перехода от O'-фазы к низкотемпературной псевдокубической O^*-фазе при понижении температуры от 400 К на упругие, магнитные и транспортные свойства монокристалла $La_{0.82}Ca_{0.18}MnO_3$. Значительные аномалии наблюдаются на температурных зависимостях скорости продольных звуковых волн и внутреннего трения. Скорость звука и внутреннее трение в ян–теллеровской O'-фазе значительно меньше, чем в псевдокубической O^*-фазе. Структурные переходы в ферромагнитном и парамагнитном состояниях монокристалла происходят в температурном интервале шириной 30 – 50 К. Установлено, что в низкотемпературной O^*-фазе основными носителями являются электроны, в то время как в ян–теллеровской O'-фазе и высокотемпературной O^*-фазе основными носителями являются дырки. Электронные состояния характеризуются более сильным спин-орбитальным взаимодействием, чем дырочные состояния. Положительное магнитосопротивление наблюдается в слабых магнитных полях в низкотемпературной псевдокубической O^*-фазе и при определенном значении магнитного поля меняет знак на отрицательный. Такое поведение магнитосопротивления не наблюдается в других La-Sr и La-Ba манганитах. Положительное магнитосопротивление указывает на значительную анизотропию транспортных свойств в низкотемпературной O^*-фазе монокристалла $La_{0.82}Ca_{0.18}MnO_3$. Установлено, что магнитные и транспортные свойства низкотемпературной ферромагнитной O^*-фазы отличаются заметно от свойств ферромагнитной ян–теллеровской O'-фазы.

Ключевые слова: структурный переход, манганит, кристалл.

1. Introduction

Lanthanum manganites $La_{1-x}D_xMnO_3$ (D = Ca, Sr, Ba) are characterized by strong coupling between the electronic, magnetic, and lattice subsystems, which results in rich diversity of the physical properties of these complex oxides [1].

$La_{1-x}Ca_xMnO_3$ (La-Ca) compounds considerably differ in properties from $La_{1-x}Sr_xMnO_3$ (La-Sr) and $La_{1-x}Ba_xMnO_3$ (La-Ba) compounds. Their transition from a ferromagnetic state to a paramagnetic state in contrast to the two latter compounds can be either first-order or second-order, depending on the calcium concentration [2]. The La-Ca manganites ($x<0.2$), in which the magnetic transition is of the second order, undergo a series of structural phase transitions between different modifications of the orthorhombic *Pnma* structure when the temperature is varied [3]. The O' phase with lattice parameters $b/\sqrt{2}<c<a<b$ is characterized by strong Jahn–Teller distortions of the oxygen octahedra. The O^* phase is called pseudocubic. In this phase, the octahedron distortions are weaker and $b/\sqrt{2}\sim c\sim a$. However, the Mn-O-Mn bond angles noticeably differ from 180°, similar to those in the O' phase [3]. The $La_{1-x}Ca_xMnO_3$ phase diagram is shown in Fig. 1.

Upon cooling from ~400 K, a sample (where $x<0.2$) undergoes the transition from the O^* phase to Jahn–Teller O' phase, then, the magnetic transition from the paramagnetic state to the ferromagnetic one, and the reverse structural transition from the O' to O^* phase at the temperature lower than 100 K. Charge ordering is observed in the low-temperature O^* phase.

The purpose of this work is to study and analyze the influence of the structural transitions on the elastic, magnetic, and kinetic properties of a $La_{0.82}Ca_{0.18}MnO_3$ single crystal. In our analysis, we use some experimental data published earlier [4, 5].

Elastic properties are known to be sensitive indicators of structural transitions and structural heterogeneities [6]. The transition between the high- temperature O^* and O' phases and the reverse transition from O' to the low-temperature

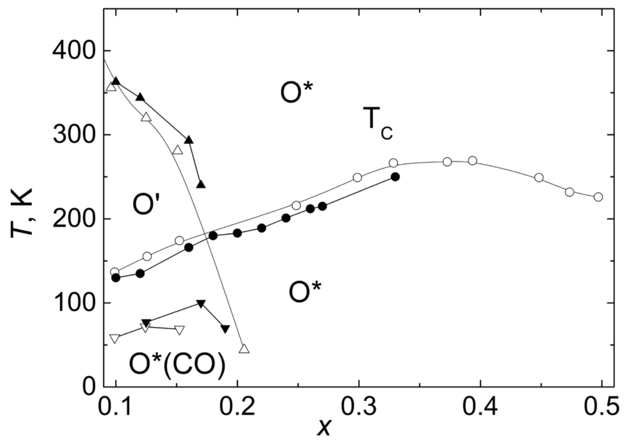

Fig. 1. $La_{1-x}Ca_xMnO_3$ phase diagram. Open symbols — data for polycrystals. Dark symbols — data for single crystals [3].

O^* phase are accompanied by much more significant changes in the elastic characteristics than the transition between orthorhombic and rhombohedral phases in La-Sr and La-Ba manganites. The high-temperature structural O^*-O' phase transition is clearly seen on the curve of the temperature dependence of the local activation energy $E_a = dln\rho/d(T^{-1})$. Positive magnetoresistance is observed in the low-temperature pseudocubic O^* phase. Notice that the positive magnetoresistance is not found in the La-Sr and La-Ba manganites.

2. Experiment

A single crystal with a nominal $La_{0.8}Ca_{0.2}MnO_3$ composition in the shape of a rod ~4 mm in diameter and ~40 mm in length was grown by the floating-zone method with radiation heating [7]. The growth direction of the crystal was closed to the [110] cubic axis. Sound velocity V and internal friction Q^{-1} were measured by the composite vibrator method [8]. X-cut quartz vibrators were the transducers exciting longitudinal vibrations. We used a vibrator with the resonant frequency of ~70 kHz. The temperature dependences of the elastic properties were measured in the helium atmosphere in the range 77 – 400 K at a mean rate of temperature change of 20 K/h. Magnetization M was measured using a vibrating sample magnetometer. Resistivity ρ and magnetoresistance $\Delta\rho/\rho$ were measured using a plate-shaped sample with the dimensions of $5.5\times1.8\times0.6$ mm, whose long side was parallel to the crystal growth axis. The Curie temperature of the plate was found to be 181 K. The sample composition, which was identified to be $La_{0.82}Ca_{0.18}MnO_3$, was determined using a JEOL scanning electron microanalyzer.

3. Result and discussions

The calcium distribution is always inhomogeneous in the $La_{1-x}Ca_xMnO_3$ single crystals grown by the floating-zone method [7]. To estimate the degree of the inhomogeneity of the calcium distribution over the rod used in the work for the investigation of the elastic properties, we measured the temperature dependences of the magnetization of thin discs that were cut from the opposite ends of the rod. Fig. 2 shows the temperature dependences of magnetization $M(T)$ of the discs in the magnetic field $H=2$ kOe. Magnetization curves $M(T)$ are typical of ferromagnets. Inset (a) in Fig. 2 shows $M(H)$ curves taken at $T=78$ K for two samples. In sample 2, the domain wall displacement and magnetization rotation take place in the fields below 7 kOe, whereas these processes in sample 1 are only completed at $H>11$ kOe. Curie temperatures that were found from the extremum of dM/dT are $T_C=178$ and 184 K for samples 1 and 2, respectively (see Inset (b) in Fig. 2). $M(T)$ curves in different magnetic fields (0.1, 0.5, and 2 kOe) show that the position of the dM/dT minimum does not depend on the magnetic field which indicates the second-order transition. We may accept the mean Curie temperature T_C of the rod to be close to 181 K which corresponds to the calcium concentration of about $x\approx0.18$.

Fig. 3 shows the temperature dependences of the velocity of longitudinal sound V measured as follows. The sample was heated from the room temperature to 400 K and was kept at this temperature for about half an hour; then the measurements were performed upon cooling down to $T = 77$ K. As the temperature is reduced from 400 to 270 K, the sound velocity V decreases almost linearly from ~4.0 to ~3.4 km/s and it drops to ~2.7 km/s as the temperature is reduced from 270 to 220 K. In Inset (a) in Fig. 3, the curve of derivative dV/dT is presented. The maximum of dV/dT is observed at the temperature of ~245 K. In the temperature range 220 – 110 K, the temperature dependence of V is weak and the sound velocity is low. A strong increase of the velocity occurs upon cooling below 100 K. The dV/dT minimum is observed at ~80 K. The temperature dependence of V measured at heating nearly coincides with that measured at cooling. Keeping the sample at room temperature for 24 h and the liquid-nitrogen temperature did not reveal any time dependence. In Inset (b) in Fig. 3, the field dependences of the magnetoresistance $\Delta\rho/\rho = [\rho(H) - \rho(0)]/\rho(0)$ of the $La_{0.82}Ca_{0.18}MnO_3$ single crystal at $T = 90, 98, 106$ K are presented. In low magnetic fields, $\Delta\rho/\rho$ is positive. At a certain field the magnetoresistance changes sign. It should be noted that positive $\Delta\rho/\rho$ takes place in the low-temperature region, where a sharp increase of the sound velocity is observed upon cooling below 100 K.

Fig. 4 shows the temperature dependence of the internal friction Q^{-1}. The curves measured at heating and at cooling almost coincide, except for the range from 225 to 275 K. The curves exhibit two sharp peaks at the temperatures of 254 and 84 K. In the range of 100 – 190 K, the internal friction is very low and its temperature dependence is weak. The regions of low values of the sound velocity and the internal friction almost coincide.

The temperature dependences of the velocity of the longitudinal sound and internal friction of the $La_{0.82}Ca_{0.18}MnO_3$ single crystal have no marked peculiarities at $T_C \sim 181$ K (Figs. 3 and 4). We observed a weak sensitivity of the longitudinal sound to the second order magnetic transition when studying La-Sr and La-Ba single crystals [6]. On the contrary, the structural transitions are always well seen in $V(T)$ and $Q^{-1}(T)$ curves. According to the phase diagram (Fig. 1) the single crystal under consideration can undergo the structural transition from the O^* to the O' phase in the range 200 – 300 K and the reverse transition from the O' to the O^* phase at the temperature lower than 100 K. Since in the range 220 ÷ 270 K, the sound velocity sharply changes and the internal friction has maximum

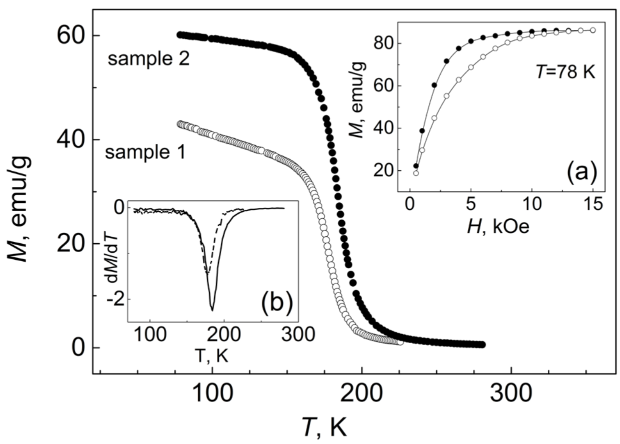

Fig. 2. Temperature dependence of magnetization in field $H = 2$ kOe of two samples excised from opposite ends of the rod. The inset: field dependence of magnetization of samples: 1 — open circles; 2 — dark circles (a), dM/dT of two samples (b).

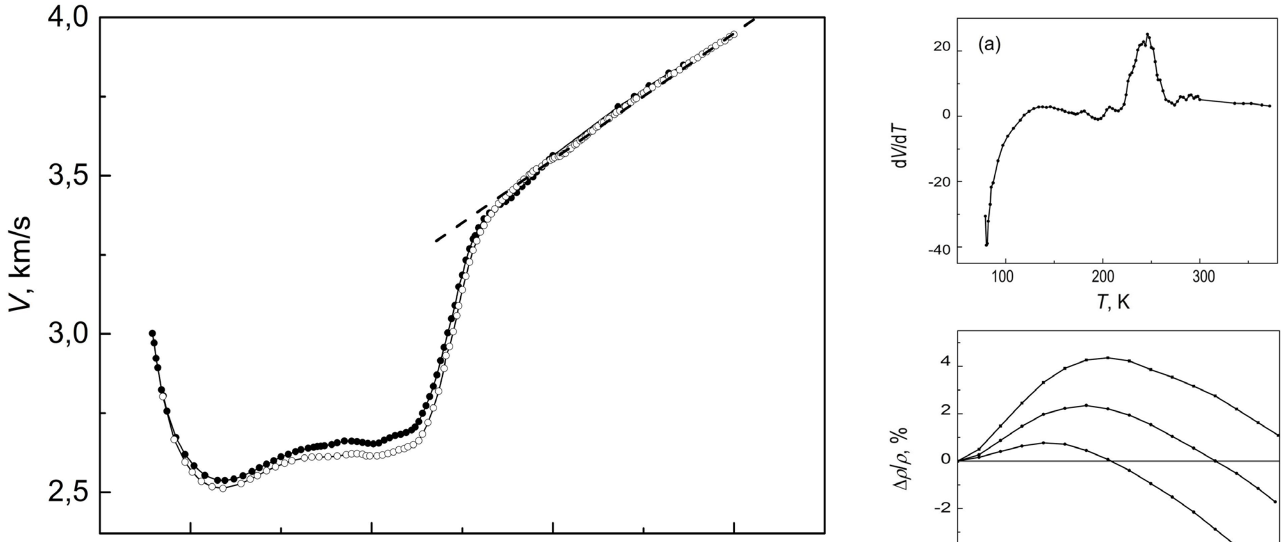

Fig. 3. Temperature dependence of the velocity of the longitudinal sound of the $La_{0.82}Ca_{0.18}MnO_3$ single crystal measured on cooling (dark circles) and heating (open circles). The inset: derivative dV/dT (a); field dependences of the longitudinal magnetoresistance, from top to bottom, at $T = 90, 98, 106$ K, respectively (b).

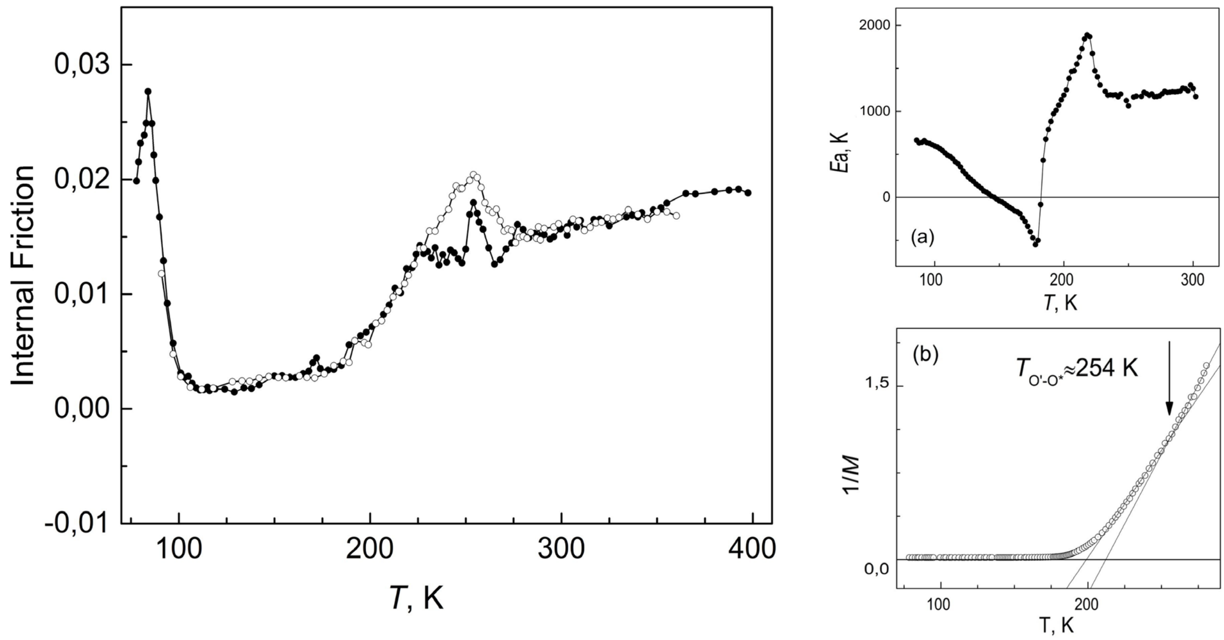

Fig. 4. Temperature dependence of the internal friction of the $La_{0.82}Ca_{0.18}MnO_3$ single crystal measured at cooling (dark circles) and heating (open circles). The inset: temperature dependence of the local activation energy (a); temperature dependence of the inverse magnetization at $H=2$ kOe (b).

at $T=254$ K, we assume that the features are due to the structural transition from the high-temperature O^* phase to the O' phase. It follows from our results that this transition occurs in a quite wide (~50 K) temperature range, not at any certain temperature. It is apparent that the spread of transition is due to the inhomogeneity of La-Ca manganite and strong concentration dependence of the O^*-O' transition temperature. The temperature $T=254$ K corresponding to the internal friction maximum can be taken as the mean transition temperature. It is to be noted that a weak peculiarity at this temperature is also observed on the curve of the temperature dependence of $1/M(T)$ (Inset (b) in Fig. 4).

At temperatures from ~100 to ~220 K, the crystal is in the O' phase with strong Jahn–Teller distortions. The phase is distinguished by low values of the sound velocity and the internal friction and their weak temperature dependences. As the temperature decreased below 100 K, the internal friction increased sharply and achieved the maximum at $T=84$ K. The increase of the internal friction is accompanied by a sharp increase in the sound velocity. It is apparent that such a behavior of $V(T)$ and $Q^{-1}(T)$ is due to the reverse structural transition from the O' to the low-temperature O^* phase. This transition is also smeared, and temperature $T\approx 84$ K can be taken as the mean temperature of this transition.

Comparing the curves $V(T)$ for a $La_{0.82}Ca_{0.18}MnO_3$ single crystal with the available data for La-Sr and La-Ba single crystals [6], we can see that the change in the velocity of the longitudinal sound during the transitions between the O^* and O' phases is more significant than that during the transition between the orthorhombic (O) and rhombohedral (R) phases. The giant thermal hysteresis of the longitudinal sound velocity and internal friction is a specific feature of the O-R structural transition in La-Sr and La-Ba single crystals. It is to be noted that such a hysteresis is not observed at transitions between the O^* and O' phases in the $La_{0.82}Ca_{0.18}MnO_3$ single crystal. It is surprising that low values of the internal friction are observed for the crystal phase O' with significant Jahn-Teller distortions of the oxygen octahedra.

The study of the temperature dependence of the thermopower of the $La_{0.82}Ca_{0.18}MnO_3$ single crystal [5] suggests that the majority carriers in the low-temperature O^* crystal phase are electrons. In the O' and high-temperature O^* phases the majority carriers are holes. In the low- temperature O^* phase the magnetoresistance is determined by the competition of two mechanisms. In low magnetic fields, $\Delta\rho/\rho$ is positive and is caused by changes in the resistance with changing the magnetization direction with respect to the crystallographic axes. In strong fields, the suppression of spin fluctuations by the magnetic field plays a dominant role, thus $\Delta\rho/\rho<0$. Since the anisotropy originates essentially from the spin-orbit interaction, this implies that, in contrast to the holes states, the electrons states in the $La_{0.82}Ca_{0.18}MnO_3$ single crystal are characterized by a substantially stronger spin-orbit interaction. For the O' phase, the anisotropy is no longer a major factor.

From the results of the measurements of the temperature dependence of ac magnetic susceptibility [9] it follows that in the low-temperature O^* phase the real and imaginary ac susceptibilities are not temperature dependent, and the low temperature structural transition O^*-O' is accompanied by a sharp increase in these quantities.

The structural transition from the O' phase to the high-temperature O^* phase takes place in the paramagnetic state. The peculiarity due to the transition is distinctly seen on the curve of temperature dependence of the local activation energy E_a (Inset (a) in Fig. 4). A week peculiarity is also observed on the curve of temperature dependence of the inverse magnetization $1/M(T)$ at $H=2$ kOe (Inset (b) in Fig. 4).

The structural high-temperature O^*-O' and the low-temperature O'-O^* transitions occur in the temperature range 30 – 50 K, i.e., the transitions which take place in the ferromagnetic and paramagnetic states have close widths.

4. Conclusions

The structural transitions which are observed in the $La_{0.82}Ca_{0.18}MnO_3$ single crystal at $T<400$ K, have a strong influence on the elastic properties. The study of the elastic properties of the $La_{0.82}Ca_{0.18}MnO_3$ single crystal ($T_C \sim 181$ K) reveals that the structural O^*-O' phase transition which takes place at $T>T_C$, and the reverse O'-O^* phase transition which occurs at $T<T_C$, are accompanied by significant changes in the velocity of acoustic vibrations and internal friction. The sound velocity and internal friction in the Jahn–Teller O' phase are significantly lower than those in the pseudocubic O^* phase. The appearance of the Jahn–Teller distortions decreases the velocity of propagation of longitudinal acoustic vibrations in the rod and therefore decreases the corresponding elastic moduli. The influence of the structural transitions on the magnetic and transport properties depends on the magnetic state of the $La_{0.82}Ca_{0.18}MnO_3$ single crystal. Considerable changes of the properties take place in the ferromagnetic state at the structural transition from the low temperature O^* phase to the O' phase.

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