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Peculiarities of the volume magnetostriction in $La_{1-x}Sr_xMnO_3$ in the Curie point region

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The parallel $\lambda_{\|}$ and perpendicular $\lambda_{\perp}$ magnetostriction with respect to the applied magnetic field and the thermal expansion $\Delta l/l$ are studied on $La_{1-x}Sr_xMnO_3$ single crystals with $x = 0.1$, 0.15, and 0.3. For the conducting sample with $x = 0.3$ and the semiconducting sample with $x = 0.15$ the volume magnetostriction ($\omega = \lambda_{\|} + 2\lambda_{\perp}$) is negative and the $|\omega|(T)$ curves go through a maximum at the Curie point T_C. At $T > T_C$ its $\Delta l/l$ temperature dependence is stronger than the linear one. For the semiconducting sample with $x = 0.1$ ω is negative at $T < T_C$ and $|\omega| \to 0$ at $T \sim T_C$. Its $\Delta l/l$ is linear at $T \geq T_C$. The behavior of ω and $\Delta l/l$ are explained by a magnetic two-phase state, due to strong s–d exchange.

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Introduction

At present the perovskite Mn oxides $R_{1-x}A_xMnO_3$ (R = La, Pr, Y, Nd, Sm and other rare-earth elements; A = Ca, Sr and Ba) are intensively studied. These investigations are described in a great number of papers and reviews [1–4]. The interest in these materials is associated with a colossal magnetoresistance near room temperature which has been observed at certain doping levels. Unfortunately, there is no common point of view on the physical processes leading to colossal magnetoresistance in manganites. Attempts have been made to relate this observed colossal magnetoresistance to the Zener double exchange, to the polaron effect caused by a very strong electron–phonon coupling stemming from a Jahn–Teller splitting of the Mn^{3+} ions, and to the charge ordering. However, the calculations performed in Refs. 5, 6 have shown that double exchange alone cannot account for the very large resistivity of the $T > T_C$ phase or for the sharp drop in resistivity just below T_C. In addition, the calculated resistivity has a too weak doping dependence and incorrect behavior for $T > T_C$ or in a field. Millis and co-workers [6,7] proposed to combine the physics of dynamic Jahn–Teller and double-exchange effects to explain the anomalies of the electrical resistivity ρ and colossal magnetoresistance in these compounds. However, this hypothesis cannot explain the fact that the temperatures of the metal–semiconductor transition and of the region of maximum colossal magnetoresistance are focused in the immediate vicinity of the Curie point.

In this paper we propose another mechanism for the explanation of anomalies of the electrical resistivity, colossal magnetoresistance, volume magnetostriction, and thermal expansion of $La_{1-x}Sr_xMnO_3$ compounds in the T_C region. Namely, we believe that the magnetic phase separation that is characteristic for magnetic semiconductors [8] is responsible for these features.

Experimental procedure

We studied the parallel $\lambda_{\|}$ and perpendicular $\lambda_{\perp}$ magnetostriction with respect to the applied magnetic field, the thermal expansion $\Delta l/l$, the magnetization, and the paramagnetic susceptibility of $La_{1-x}Sr_xMnO_3$ single crystals.

Single crystals were grown by the method of floating-zone method by Balbashov and have a rhombohedral structure (the sample with $x = 0.3$) or an orthorhombic structure (the samples with $x = 0.1$ and 0.15). The magnetization measurements, carried out with the aid of a vibrating magnetometer, showed that the magnetization reaches saturation at a magnetic field $H < 0.2$ T. The Curie points were determined by the Belov–Arrot method and practically coincide with the published data [9]. The temperature dependence of the paramagnetic susceptibility, measured by the Faraday balance method, is described by the Curie–Weiss law. The strain gauge technique was used for study of the magnetostriction and thermal expansion. The magnetostriction was measured in a dc magnetic field up to $H \le 1$ T and for the sample with $x = 0.15$ up to $H = 12$ T in the laboratory of M. R. Ibarra (University of Zaragoza, Spain). The accuracy of the $\Delta l/l$ measurements was better than $4 \cdot 10^{-6}$.

Results and discussion

By way of example, Fig. 1 shows the isotherms of the parallel and perpendicular magnetostriction with respect to the applied magnetic field at some selected temperatures for the sample with $x = 0.3$. From the experimental $\lambda_{\parallel}(H)$ and $\lambda_{\perp}(H)$ curves the isotherms of the anisotropic magnetostriction $\lambda_t = \lambda_{\parallel} - \lambda_{\perp}$ and volume magnetostriction $\omega = \lambda_{\parallel} + 2\lambda_{\perp}$ were constructed. Their temperature dependence for the sample with $x = 0.3$ at $H = 0.9$ T is shown in Fig. 2. On increase in temperature the anisotropic magnetostriction decreases continuously to zero in the T_C region, as can be seen in Fig. 2. The $\lambda_t(T)$ curves, measured in magnetic fields above 0.2 T, practically coincide with the $\lambda_t(T)$ curve shown in Fig. 2. It should be pointed out that the λ_t value is large in the low-temperature region, e.g., $\lambda_t \cong 10^{-4}$ at 90 K ($H = 1$ T) and $\lambda_t \cong 10^{-3}$ at 4.2 K ($H = 3$ T). As illustrated in Fig. 2, the volume magnetostriction is positive at $T < 280$ K; however, it becomes negative at $T > 280$ K and its magnitude reaches a maximum in the vicinity of $T_C = 371$ K. On further heating $|\omega|$ vanishes rapidly. The $\omega(T)$ dependence in some selected magnetic field is shown in the insert in Fig. 2. As will be seen from Fig. 3, the behavior of ω for the sample with $x = 0.15$ is rather like the one for the sample with $x = 0.3$. For the sample with $x = 0.15$ the anisotropic magnetostriction λ_t is positive and its value decreases continuously to zero in the Curie point region, too ($T_C = 268$ K). The temperature dependence of the thermal expansion $\Delta l/l$ in the T_C region is stronger than linear for the samples with $x = 0.15$ and 0.3. This is apparent from Fig. 4, which shows the $\Delta l/l(T)$ dependence for the sample with $x = 0.3$. It is well known that this dependence is nearly linear for dia- and paramagnetic systems.

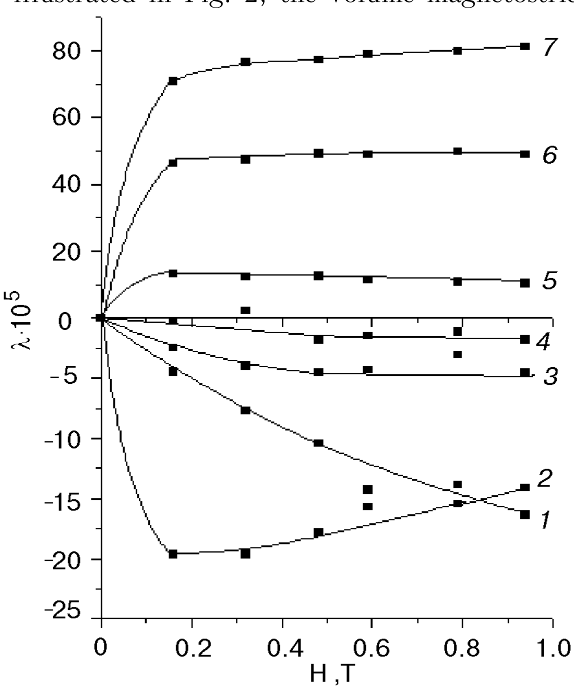

Fig. 1. The isotherms of the perpendicular (curves *1–4*) and parallel (curves *5–7*) magnetostriction λ at different temperatures T, K: 361 (*1*), 97 (*2*), 349 (*3*), 375 (*4*), 300 (*5*), 188 (*6*), and 96 (*7*) for the single crystal $La_{0.7}Sr_{0.3}MnO_3$.

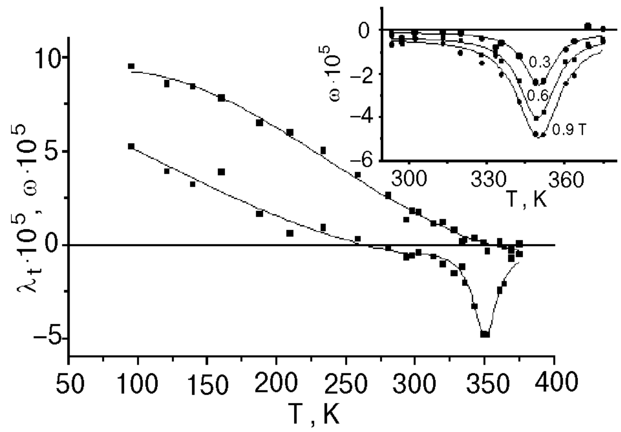

Fig. 2. Temperature dependence of the anisotropic magnetostriction λ_t and volume magnetostriction ω in the magnetic field of 0.9 T for the single crystal $La_{0.7}Sr_{0.3}MnO_3$. Insert: temperature dependence of ω in the T_C region in some selected magnetic fields for this sample.

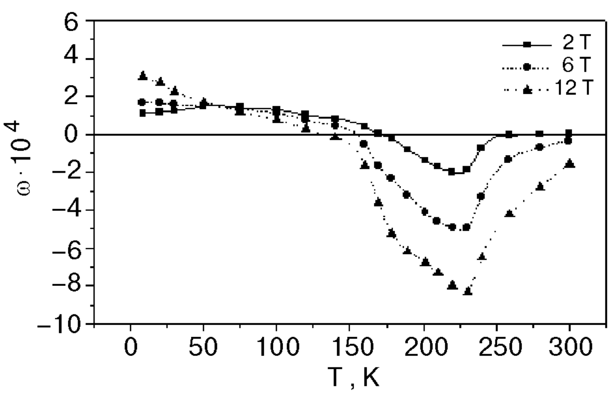

Fig. 3. Temperature dependence of the volume magnetostriction ω in some selected magnetic fields for the single crystal $La_{0.85}Sr_{0.15}MnO_3$.

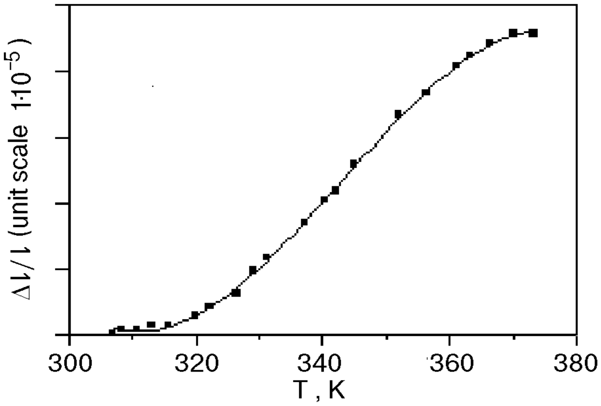

Fig. 4. Temperature dependence of the thermal expansion $\Delta l/l$ for the single crystal $La_{0.7}Sr_{0.3}MnO_3$.

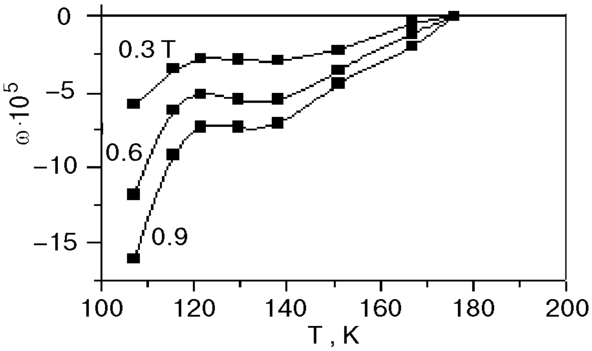

Fig. 5. Temperature dependence of the volume magnetostriction in some selected magnetic fields for the single crystal $La_{0.9}Sr_{0.1}MnO_3$.

The positive anisotropic magnetostriction λ_t of the sample with $x = 0.1$ decreases continuously to zero in the T_C region ($T_C = 162$ K), as in the samples with $x = 0.15$ and 0.3. However the behavior of volume magnetostrictriction ω of the sample with $x = 0.1$ differs from that of the samples with $x = 0.15$ and 0.3. Figure 5 shows the temperature dependence of ω at some selected magnetic fields for a $La_{0.9}Sr_{0.1}MnO_3$ single crystal. Notice that the volume magnetostriction of the sample with $x = 0.1$ is negative. With increasing temperature the values of $|\omega|$ decrease continuously to zero in the T_C region, as can be seen in Fig. 5. As mentioned above, the $\omega(T)$ curves have a minimum in the T_C region for the single crystals $La_{0.7}Sr_{0.3}MnO_3$ (Fig. 2) and $La_{0.85}Sr_{0.15}MnO_3$ (Fig. 3). Figure 5 shows that the $\omega(T)$ curves have no such minimum for the sample with $x = 0.1$. Their temperature dependence of the thermal expansion $\Delta l/l$ is nearly linear at $T \geq T_C$ as well as at $T \leq T_C$, and no surplus thermal expansion occurs at $T \geq T_C$ for this sample.

According to data [9,10] for these compositions, the electrical resistivity ρ of the metallic type is observed at $T < T_C$, and ρ increases abruptly in the T_C region for the sample with $x = 0.3$; for the samples with $x = 0.1$ and 0.15 a semiconducting type of conductivity is observed. The transition from the semiconducting to the metallic type of conductivity takes place at $x \sim 0.17$ in the $La_{1-x}Sr_xMnO_3$ system.

Ibarra et al. [11] observed a similar behavior of the volume magnetostriction and thermal expansion of a $La_{0.4}Y_{0.07}Ca_{0.33}MnO_3$ ceramic sample. In their opinion, the anomalies of the thermal expansion and the volume magnetostriction are due to the formation of a small polaron at $T \geq T_C$. As discussed in the Introduction, this hypothesis fails to explain the fact that the polaron formation occurs only in the vicinity of the Curie point.

Anomalies of the volume magnetostriction, thermal expansion, and electrical resistivity, listed above, may be attributed to the existence of a magnetic two-phase state (MTPS) in this crystal [8]. As is well known, in magnetic semiconductors the charge carrier energy is minimal when the total ordering in the crystal is ferromagnetic. However, in nongenerate antiferromagnetic semiconductors the carrier concentration is small, so they are not able to modify the state of the entire crystal. Nonetheless, these electrons may cause local changes in the magnetic ordering, creating ferromagnetic microregions, which provide a gain in the s–d exchange energy, and stabilize them by autolocalization inside them. At a not-too-high density of the charge carriers an insulating MTPS is realized in the crystal: ferromagnetic small droplets, in which the charge carriers are localized, are embedded in the insulating host. On increase in the carrier density, ferromagnetic droplets begin to make contact with each other. Thus, percolation of the electron liquid occurs and another MTPS is formed: the insulating antiferromagnetic microregions are embedded in a conducting ferromagnetic host. This is a conducting MTPS. Yanase and Kasuya showed [12] that inside a ferromagnetic part of crystal the lattice constants are reduced. The reason is that in a ferromagnetic part of crystal the spacing between an impurity ion and its nearest magnetic ion is shortened to screen the new charge distribution and to lower the energy of the ferromagnetic part of crystal by increasing the overlap between the valence electron shells of the impurity and the d shells of the nearest magnetic ions.

$La_{0.7}Sr_{0.3}MnO_3$ is a heavily doped antiferromagnetic semiconductor $LaMnO_3$, in which a conducting MTPS is realized. The MTPS is destroyed at $T \geq T_C$ and so an extra contribution in $\Delta l/l$ arises. An applied magnetic field induces magnetization near impurities at $T > T_C$, since its action is enhanced by the $s-d$ exchange. One produces MTPS and the lattice compression inherent in it. The sharp increase in the negative volume magnetostriction at the T_C region (Fig. 2) can be explained by this effect. However, the above-mentioned process of MTPS restoration by a field takes place only in a limited temperature interval at $T \geq T_C$. Because of this the $\omega(T)$ curves have a sharp minimum in the T_C region, and $|\omega|$ quickly falls upon further increase in temperature. The MTPS in the sample with $x = 0.3$ is confirmed by the fact that the value of its spontaneous magnetization at 4.2 K is less than the value expected in the case of a total ferromagnetic ordering. Namely, the former is equal to 95% of the latter (our data agree with those found in Refs. 9, 10) and a value of 84% is obtained by neutron experiments [13]. This indicates that the ratio between the volumes of the ferromagnetic and antiferromagnetic portions of the crystal is $\sim 90/10$. In this case the T_C value is determined by the ferromagnetic portion of the crystal only. It is well known that the paramagnetic Curie point Θ is determined by the sum of the exchange interactions realized in the crystal. The contribution from the antiferromagnetic microregions to the total exchange lowers the Θ value and, therefore, $T_C = 371$ K exceeds $\Theta = 364$ K in the sample with $x = 0.3$ (in ferromagnetic ordering $T_C \leq \Theta$ is normally observed).

It should be remarked that the volume magnetostriction of the sample with $x = 0.1$ is negative (Fig. 5). By this we mean that the sample shrinks in an applied magnetic field. It is known [9] that this sample is a p-type semiconductor. There is a small maximum of the electrical resistivity ρ and a negative colossal magnetoresistance in the T_C region for this crystal [9,10]. Thus ρ and the magnetoresistance anomalies are attributable to an insulating MTPS [8]. If an insulating MTPS is present in this sample, the negative ω denotes that the radii of the ferromagnetic droplets are increased by a magnetic field. This is characteristic of an insulating MTPS [8]. At the same time, the ferromagnetic phase in an insulating MTPS sample occupies as little as a few per cent of the sample volume [8]. Therefore the volume of the ferromagnetic part is small in the sample with $x = 0.1$, and the anomalies of ω and $\Delta l/l$ are not detected at the T_C region. In the conducting MTPS sample with $x = 0.3$ the ferromagnetic phase occupies $\sim 90\%$ of the sample volume, and the destruction of MTPS in the T_C region may have a marked effect on ω and $\Delta l/l$. The sample with $x = 0.15$ is situated on the boundary between the semiconducting and metallic states [9]. Therefore the volume of its ferromagnetic phase is larger than in the sample with $x = 0.1$, and the anomalies of ω and $\Delta l/l$ at $T \sim T_C$ are observed in this sample.

In connection with the aforesaid we may be make the following supposition. It is well known that the crystal volume per manganese ion is higher in the orthorhombic than in the rhombohedral structure of this system. Recently it has been found that in the semiconducting compound with $x = 0.17$ of the system considered, a transition from the orthorhombic to the rhombohedral phase occurs in an applied magnetic field at $T \leq T_C$ [14,15]. This can be explained by the increase of the volume of the ferromagnetic phase in an applied magnetic field, accompanied by the lattice compression.

It is known that the compounds of this system with $x \leq 0.17$ have the orthorhombic structure and the semiconductive type of conductivity, while the compounds with $0.175 \leq x \leq 0.6$ have the rhombohedral structure and the metallic type of conductivity [9,10]. On this basis it is reasonable to expect that the transition from the semiconductive orthorhombic phase to the metallic rhombohedral phase in this system is caused by the transition from the insulating MTPS to the conducting MTPS, which is accompanied by lattice compression of the ferromagnetic phase, occupied the nearly all volume of crystal.

Summary

It has been found that for $La_{1-x}Sr_xMnO_3$ single crystals with $x = 0.15$ and 0.3 the volume magnetostriction ω is negative, the $|\omega|(T)$ curves go through a maximum at the Curie point T_C , and the temperature dependence of the thermal expansion $\Delta l/l(T)$ at $T > T_C$ is stronger than linear. For the sample with $x = 0.1$ ω is negative at $T < T_C$, $|\omega| \to 0$ at $T \sim T_C$, and $\Delta l/l(T)$ is linear at $T \geq T_C$. The behavior of ω, $\Delta l/l$, ρ, and the colossal magnetoresistance are explained by a magnetic two-phase state, due to strong $s-d$ exchange.

In antiferromagnetic semiconductors the charge carriers self-trap near impurities and produce ferromagnetic microregions because of energy gain in respect to the $s-d$ exchange [8]. At a not-too-high density of the charge carriers an insulating MTPS is realized in the crystal: ferromagnetic small droplets, in which the charge carriers are localized, are embedded in an insulating host. On increase in the carrier density, percolation of the electron liquid occurs and a conducting MTPS is formed: the insulating antiferromafnetic microregions are embedded in a conducting ferromagnetic host. Yanase and Kasuya showed [12] that inside a ferromagnetic part of the crystal the lattice constants are reduced.

$La_{1-x}Sr_xMnO_3$ is a doped antiferromagnetic semiconductor $LaMnO_3$. Let us suppose that a conducting MTPS is realized in the sample with $x = 0.3$. MTPS in this case is destroyed at $T \geq T_C$, and thus an extra contribution to $\Delta l/l$ arises. An applied magnetic field induces magnetization near impurities at $T > T_C$, since its action is enhanced by the s–d exchange. A field produces MTPS and the corresponding lattice compression. It follows that ω is negative in the T_C region and that a minimum on the $\omega(T)$ curves is observed at this region.

The sharp increase in the electrical resistivity in the T_C region is characteristic of a conducting MTPS [8]. There are two mechanisms through which the impurity–magnetic interaction influences the resistance: the scattering of charge carriers, which reduces their mobility; the formation of band tails, consisting of the localized states. The decrease of the mobility of the charge carriers and their partial localization in band tails are most prominent in the T_C region. Imposition of a magnetic field on the sample increases the charge carrier mobility and excites the charge carriers from the band tails; this is the cause of the colossal magnetoresistance.

If an insulating MTPS is present in the sample with $x = 0.1$, the negative ω indicates that the ferromagnetic droplet radii increase with applied magnetic field; this is typical for an insulating MTPS [8]. But the ferromagnetic phase in an insulating MTPS sample occupies only a few percent of the sample volume [8]. Therefore the volume of ferromagnetic part is small in the sample with $x =$ $= 0.1$, so that the anomalies of ω and $\Delta l/l$ are not detected near T_C. There is a small maximum of ρ and a colossal magnetoresistance in the T_C region for this semiconducting crystal [9,10]. Thus ρ and the magnetoresistance anomalies can be attributed to an insulating MTPS, too [8]. One can explain the colossal magnetoresistance by the increase of the ferromagnetic droplet radii in the magnetic field, which facilitates electron tunneling between ferromagnetic droplets. Moreover the magnetic moments of the ferromagnetic droplets are aligned along with the external field, and that also facilitates the tunneling. Ultimately the field tends to destroy the ferromagnetic droplets. Thus the magnetic field increases the electron energy inside the droplets and in doing so it facilitates their transition to a delocalized state.

The sample with $x = 0.15$ has conductivity of the semiconducting type, but it is situated near the boundary between the semiconducting and metallic states [9]. Therefore the volume of its ferromagnetic phase is larger than in the sample with $x = 0.1$, and the anomalies of ω and $\Delta l/l$ at $T \sim T_C$ are observed in this sample. The anomalies of ρ and the colossal magnetoresistance in the T_C region for the sample with $x = 0.15$ are explained as well as for the sample with $x = 0.1$.

Acknowledgments

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