

## Structural phase transition in $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$ perovskite: Elastic, magnetic, and lattice anomalies and microscopic mechanism

E. Fertman,<sup>1</sup> E. Syrkin,<sup>1,2</sup> V. Lykah,<sup>2</sup> V. Desnenko,<sup>1</sup> A. Beznosov,<sup>1</sup> P. Pal-Val,<sup>1</sup> L. Pal-Val,<sup>1</sup> A. Fedorchenko,<sup>1</sup> D. Khalyavin,<sup>3</sup> and A. Feher<sup>4</sup>  
<sup>1</sup>*B. I. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, 47 Lenin Ave., 61103 Kharkov, Ukraine*  
<sup>2</sup>*National Technical University "Kharkov Polytechnic Institute", 21 Frunze str., 61002 Kharkov, Ukraine*  
<sup>3</sup>*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, UK, OX110QX*  
<sup>4</sup>*P. J. Šafárik University in Košice, Faculty of Science, Park Angelinum 9, 04154 Košice, Slovakia*

(Received 5 June 2015; accepted 25 July 2015; published online 31 July 2015)

The temperature dependences of the elastic and magnetic properties of polycrystalline perovskite manganite  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  were studied using ultrasonic and SQUID magnetometer techniques. The minimum of the temperature-dependent sound velocity  $v(T)$  and corresponding maximum of the decrement  $\delta(T)$  were found in the vicinity of the structural phase transition  $R\bar{3}c \leftrightarrow Imma$  at  $T_s \sim 200$  K. Large alterations of  $v$  and  $\delta$  indicate a structural phase transition of the soft mode type. A high sensitivity of  $dc$  magnetization to a low uniaxial pressure caused by the softening was found in the  $T_s$  region. A negative value of the linear thermal expansion coefficient along one of the crystallographic axis was found in the  $Imma$  phase near  $T_s$ . The proposed microscopic mechanism explains the appearance of the soft mode in the vicinity of the structural phase transition temperature associated with the displacement of the manganese atom from the center of the oxygen octahedron. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4928075>]

### I. INTRODUCTION

Interest in mixed valence manganites with the general formula  $R_{1-x}A_x\text{MnO}_3$  ( $R$  = rare-earth cation,  $A$  = Ca, Ba, Sr) is caused by the colossal magnetoresistance effect they exhibit.<sup>1–3</sup> The strong interaction between charge carriers, localized spins, and the lattice is a characteristic feature of these materials, which results in the great variety and complexity of physical phenomena and phase transitions observed. Special attention has focused on phase-separation phenomena, which play a key role in the physics of this class of materials.<sup>2,4–7</sup> In particular, the coexistence of metallic and insulating phases leads to a percolative metal-insulator transition and unusually high magnetoresistance.<sup>2,4,5,8</sup>

Phase separation in manganites may have two origins: 1) electronic (microscopic) phase separation between phases with different charge carrier densities, which result in nanometer scale coexisting clusters, and 2) disorder-induced phase separation with percolative characteristics between equal-density phases, driven by disorder near first-order phase transitions.<sup>2,9–15</sup> The latter leads to coexisting clusters as large as a micrometer in size. It has become clear by now that first-order phase transformations, which result in the coexistence of two crystalline phases in a wide temperature range (so-called martensitic transformations), play an important role in the physics of manganites. Strong electron correlations and interactions between the coexisting crystalline phases lead to unique properties of a number of manganites.<sup>9,11,12,16</sup> The physical properties of martensitic systems are governed by long-range deformations of the crystal lattice, i.e. accommodation strain, which are induced as a result of the nucleation of martensitic particles within the parent high temperature phase.<sup>17</sup>



Considerable attention has been given to the martensitic character known as charge ordering (CO) transition, as the transport properties of this class of manganites are governed in many respects by the charge-disordered insulating phase stabilized at low temperature by virtue of martensitic accommodation strain.<sup>8</sup> The martensitic nature of a magnetic field-induced CO insulating anti-ferromagnetic to ferromagnetic phase transition has been reported to lead to unusual relaxation phenomena in these compounds, such as magnetic-field-induced ultrasharp magnetization steps.<sup>11,12</sup>

First order structural transformations are still little studied for wide band manganites which do not exhibit charge ordering, although experiments on  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ <sup>18-21</sup> and  $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$  ( $x = 0.15 - 0.33$ )<sup>14,22-25</sup> have revealed many interesting peculiarities of their behavior, such as the strong dependence of the structural transition temperature  $T_s$  on the magnetic field and hydrostatic pressure and the wide temperature range of phase coexistence.

The  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  compound experiences a structural phase transition at  $T_s \sim 200$  K.<sup>14,26,27</sup> This transition possesses certain features of a martensitic transformation and causes a crystal phase separation in the compound: below room temperature, the compound represents a mixture of the high temperature rhombohedral phase  $R\bar{3}c$  (austenite) and the low temperature orthorhombic phase  $Imma$  (martensite).

Ultrasonic testing is one of the most widely used techniques for the characterization of perovskites over a wide temperature range. In the present study, we performed an ultrasonic and magnetic study of the  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  manganite. The ultrasound anomalies found were associated with the appearance of a soft mode in the vicinity of the structural phase transition, which was confirmed by magnetic measurements. On the basis of the structural data,<sup>14</sup> a negative coefficient of linear thermal expansion was found. A microscopic mechanism for the phase transition is offered.

## II. EXPERIMENTAL DETAILS

Samples for the experiments were made from polycrystalline pellets of the  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  compound which were prepared using a standard solid-state reaction with stoichiometric amounts of  $\text{La}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{Mn}_2\text{O}_3$  powders; the details have been published.<sup>14</sup> Sample quality was confirmed by x-ray and neutron diffraction studies.

The acoustic properties were investigated by the two-component oscillator technique.<sup>28</sup> The longitudinal standing ultrasonic waves with a frequency of about 70 kHz and ultrasound strain amplitude of  $1 \cdot 10^{-7}$  were excited in the samples by means of a quartz transducer. The logarithmic decrement  $\delta$  and resonant frequency  $f$  of the forced vibrations were measured. The longitudinal sound velocity  $v$  was determined as  $v = 2lf$  where  $l$  is the sample length. The measurements were carried out in gaseous  $^4\text{He}$  under a pressure of 100 Pa in the temperature range of 5-340 K with a mean rate of thermocycling of 1 K/min.

The effect of uniaxial pressure  $P$  of 0.05 kbar on dc magnetization was measured in the temperature range of 50-250 K in an external magnetic field  $H = 20$  Oe by means of SQUID magnetometry.

## III. ELASTIC AND MAGNETIC PROPERTIES

Ultrasonic measurements can give direct information on structural phase transitions in solids, in particular in manganites.<sup>29-31</sup>

The study of the elastic properties of the  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  compound performed in the present work brought out a number of features (Fig. 1) which are characteristic for martensitic transformations.<sup>32</sup> Upon decreasing the temperature from 340 K to 190 K the ultrasound velocity  $v$  strongly decreased from 3433 m/s to 2746 m/s. Such a strong decrease in the velocity was attributed to the appearance of a soft mode.<sup>33</sup> A deep minimum of  $v(T)$  was observed at 190 K on cooling and at 202 K on heating (Fig. 1, upper panel). The temperature dependences of the decrement  $\delta(T)$  on cooling and heating show the corresponding maxima (Fig. 1, lower panel). Further cooling below 190 K resulted in an increase in sound velocity  $v$  up to about 4000 m/s. At the same time, the decrement  $\delta$  decreased from 0.02 to 0.005.

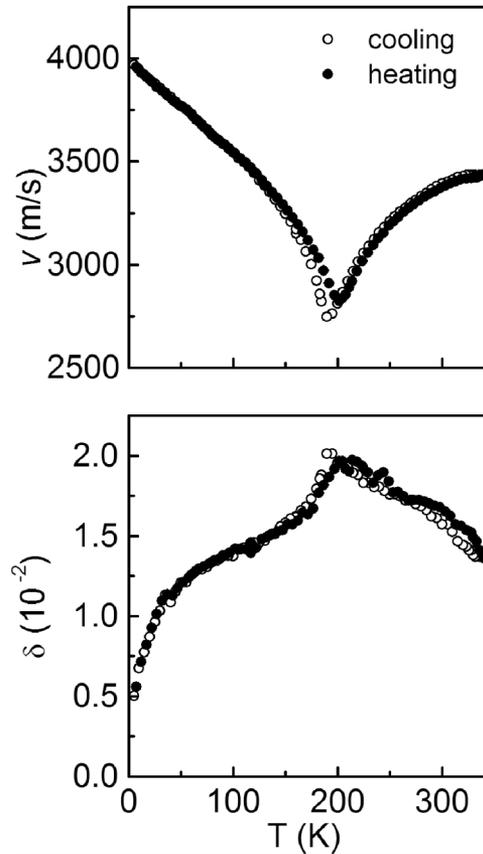


FIG. 1. Temperature dependences of the sound velocity  $v$  (upper panel) and logarithmic decrement  $\delta$  (lower panel) of the  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  compound on cooling ( $\circ$ ) and heating ( $\bullet$ ).

These clear anomalies of the temperature dependences of the elastic characteristics are associated with the structural phase transition from the  $R\bar{3}c$  to the  $Imma$  space symmetry lattice. The temperature hysteresis of ultrasound properties reflects the first order character of the transition.

The specific anomalies of the elastic properties, together with the neutron diffraction and ESR data,<sup>14,26,27</sup> are evident of the martensitic character of the observed structural phase transition, which results in the coexistence of two phases with different crystal structures stabilized by the induced inner strain. The coexisting phases form a microstructure in the substance, which probably represents a sort of “red cabbage” structure.<sup>34</sup> Marked dips in the temperature dependences of the sound velocity on heating and cooling (Fig. 1, upper panel) define a difference in the transition temperatures for the direct and reverse martensitic transformations. The lowest value of sound velocity and the corresponding highest value of sound damping correspond to the equal coexisting phase fraction, i.e. to the region of the maximal rate of the interchange of crystal phases.

The hysteresis loops of  $v(T)$  and  $\delta(T)$  (Fig. 1) are asymmetrical: they extend much further toward higher temperatures (about 150 K) compared with low temperatures (about 55 K). They do not “converge” at 340 K, so the low temperature residual phase exists up to this temperature. Thus the reverse martensitic transformation completes at higher temperature (about 370 K<sup>14</sup>).

The character of the obtained dependences is typical for martensitic compounds and alloys.<sup>32,35</sup> For example, temperature dependences of ultrasound velocity for  $\text{Ni}_{2.18}\text{Mn}_{0.82}\text{Ga}$ <sup>35</sup> in the temperature region of the direct and reverse martensitic transitions are similar to those presented in Fig. 1 (upper panel). In this regard, it should be noted that the dependences found have much in common with those for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x = 0.15-0.20$ ) manganites, which experience structural phase transition.<sup>19,20</sup> This implies that the transition in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  has a martensitic nature as well, and so the martensitic transition in  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  is not something unique for the perovskite manganites.

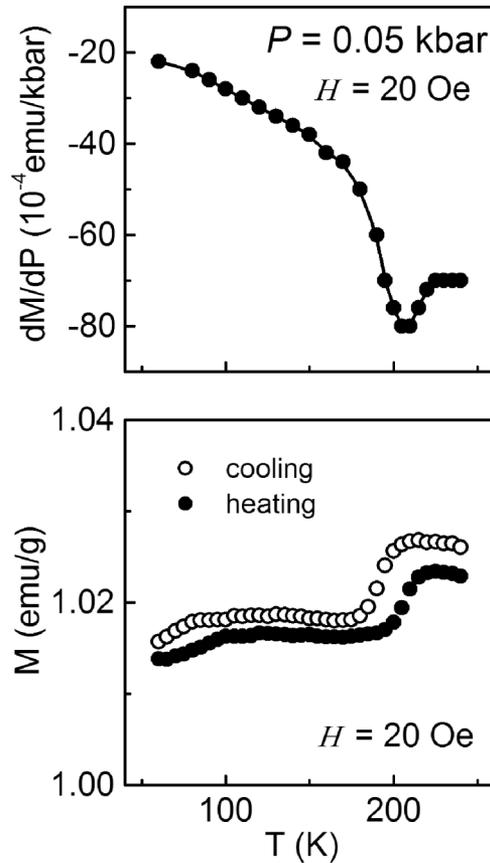


FIG. 2. Change in the static magnetization of the  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  compound under uniaxial pressure  $P = 0.05$  kbar as a function of temperature measured in the magnetic field  $H = 20$  Oe on heating (upper panel); temperature dependence of the static magnetization on cooling and heating (lower panel).

The  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  is ferromagnetic below  $T_C \sim 340$  K,<sup>26</sup> so the structural phase transition  $R\bar{3}c \leftrightarrow Imma$  takes place while the compound is in the ferromagnetic state. It is known that martensitic transitions are very sensitive to different external factors (pressure, applied magnetic fields) and the history of the experiment. The effect of low uniaxial pressure ( $P = 0.05$  kbar) on low field magnetization appeared to be very strong: a strong temperature dependence of the change in magnetization under uniaxial pressure  $\frac{dM}{dP}(T)$  was found (Fig. 2). A pronounced minimum of  $\frac{dM}{dP}(T)$  was seen in the vicinity of the  $T_s$  temperature, which implies high sensitivity of magnetization to applied pressure, which confirms a softening of the crystal lattice in the vicinity of the phase transition temperature.

A significant decrease in the elastic modulus found in the martensitic phase transition means that slow acoustic waves may propagate in such systems. Slow acoustic waves are important from the standpoint of their practical use (ultrasonic filters, delay lines, amplifiers).<sup>36</sup> This suggests the possibility of practical applications of manganites in acoustic electronic devices. It is important that the martensitic transformation temperature can be varied within a wide temperature range by varying the composition.

#### IV. MICROSCOPIC MECHANISM OF THE STRUCTURAL TRANSFORMATION

As mentioned above, when cooling below the room temperature,  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  experiences a structural transition from the rhombohedral  $R\bar{3}c$  to the orthorhombic  $Imma$  space symmetry. A difference between these crystal structures is seen in Fig. 3, where the positions of the Mn and O

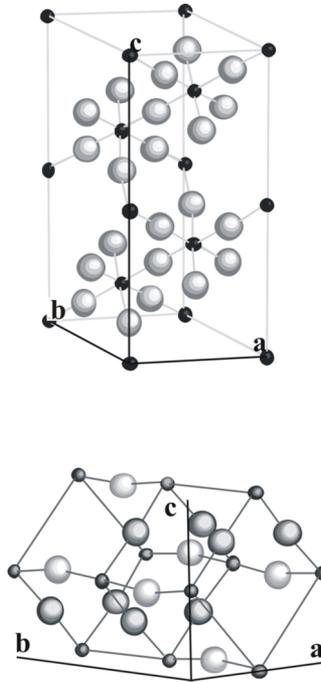


FIG. 3. Positions of Mn (small circles) and O (large circles) ions in the rhombohedral  $R\bar{3}c$  (upper panel) and orthorhombic  $Imma$  (lower panel) crystal structures of the  $La_{2/3}Ba_{1/3}MnO_3$  compound. In the orthorhombic structure (lower panel), the large light circles represent oxygen ions at the O1 positions (six of eight ions are shown), while the large dark circles represent those at the O2 positions (eight of twelve ions are shown). La and Ba ions are not shown.

ions are presented. The transition between such symmetries is the 1st order one as based on group theory,<sup>37</sup> our previous studies<sup>14,27,26</sup> and the present ultrasonic and magnetic measurements.

The expansion of free-energy density in the powers of the order parameter components  $Q_i$  for the first order phase transition should be carried out to the terms of the sixth power:<sup>38-41</sup>

$$F_Q(Q_i; T) = F_0(T) + \frac{1}{2}\alpha(T - T_c)f_2(Q_i) + \frac{1}{4}a_4f_4(Q_i) + \frac{1}{6}a_6f_6(Q_i) + \frac{1}{2}b(\nabla Q)^2. \quad (1)$$

In this equation,  $f_n(Q_i)$  denoted the  $n^{\text{th}}$ -order invariants of the components of the order parameter, which are homogeneous functions of degree  $n$  in the  $Q_i$  components, and which remain unchanged under all possible symmetry operations. All the coefficients weakly depend on temperature except for  $a_2 = \alpha(T - T_c)$ , which goes through zero at  $T_c$ . If  $a_4 < 0$ , the first order phase transition is observed in the system.  $\nabla Q_i$  denotes space derivations of the order parameters  $Q_i$ . If a system is described by two order parameters (namely, displacement and elastic deformation), the free energy can be written as:

$$F(Q_i, e_k; T) = F_Q(Q_i; T) + F_m(e_k) + F_c(Q_i, e_k), \quad (2)$$

where  $F_m(e_k)$  corresponds to the elastic part of the energy only,  $F_c(Q_i, e_k)$  describes coupling of the order parameters (coupling term), and  $e_k$  is a strain tensor. For a longitudinal wave, elastic energy takes the form:  $F_m(e_k) = Ee_k^2/2$ . In the terms that describe the interaction, we take the minimal powers of the order parameters:

$$F_c(e, Q_i) = \beta_{ij}Q_i e_j + \gamma_{ijk}Q_i Q_j e_k + \delta_{ijk}Q_i e_j e_k \quad (3)$$

The interaction in (3) defines a type of the dependence of sound velocity on temperature.<sup>38</sup> The first and second terms in (3) give the dependence  $v(T)$  with a jump. The experimental dependence  $v(T)$  with a minimum at  $T_s$  (Fig. 1) corresponds to the third term in the equation (3). Therefore, to describe the interactions in the system, we can restrict ourselves this term. In the phase transition, this term,  $\delta_{ijk}Q_i e_j e_k$ , makes a significant contribution to the free energy and can change the relative

height of the potential minima. It may change the relative depth of the potential wells for  $Q$  and cause the displacement of atoms at ultrasound frequency. This mechanism gives a microscopic picture of the absorption and the appearance of the soft mode in the spectrum of the lattice vibrations. Therefore, the attenuation and the velocity behavior are connected with the dynamics of the order parameter.

It should be noted that the unit cell construction of  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  is typical for perovskites and is similar to the classical perovskite compound  $\text{BaTiO}_3$ , which exhibits a set of first order structural phase transitions, one of them between the orthorhombic and rhombohedral phases in the vicinity of 183 K. The last transition has been described in detail,<sup>39,40</sup> where it was shown that the order parameter of the transition has to be chosen as the displacement of the Ti atom from the center of the surrounding oxygen octahedron. Typical perovskites have a cubic paraphase, where a titanium or manganese atom is in the center of the oxygen octahedron and in the center of the cube formed by Ba or Ba/La atoms, in the case of  $\text{BaTiO}_3$  and  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$ , respectively (Fig. 4). The studied  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  compound is of the mixed-valence type:  $\text{Mn}^{3+}$  ions with an ionic radius  $r \approx 0.70 \text{ \AA}$  coexist with  $\text{Mn}^{4+}$  ions with an ionic radius  $r \approx 0.52 \text{ \AA}$ , which is close to the ionic radius of  $\text{Ti}^{4+}$  ( $r \approx 0.64 \text{ \AA}$ ). It is clear that the difference in the size of the ionic radii, as well as a chaotic arrangement of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ , as well as  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  ions, does not allow one to expect an exact match of temperatures and the sequence of phase transitions in  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  and  $\text{BaTiO}_3$  compounds.

The thermodynamic potential is a multiwell function on this order parameter; in the simplest case, it is a double-well potential.<sup>41</sup> It means that minima of free energies of the coexisting phases have the same value at the phase transition point (Fig. 5, upper panel). This model has been extensively used to describe different phase transitions, including martensitic ones.<sup>42</sup> Possible displacements of the central atom in the  $Imma$  phase in the vicinity of the structural transformation are shown in Fig. 4. There are twelve possible positions of equilibrium, two along each of the  $[110]$  type direction, that correspond to the minima of the multiwell potential. Below  $T_s$ , only the  $Imma$  phase is stable (Fig. 5, lower panel).

The main element of the perovskite structure is the oxygen octahedron surrounding a manganese (titanium) ion. The displacement of the central atom reduces the symmetry of the crystal lattice. When the central ion is displaced from the center of the oxygen octahedron, the initially-centered cubic structure becomes tetragonal, orthorhombic, or rhombohedral, depending on the direction of displacement.<sup>33,39,40</sup> The initially cubic lattice of the paraphase is elongated in the direction of displacement of the central ion. Typically, such transitions occur according to the mechanism of the soft mode. In this case, the potential barrier between the minima was greatly reduced. The central

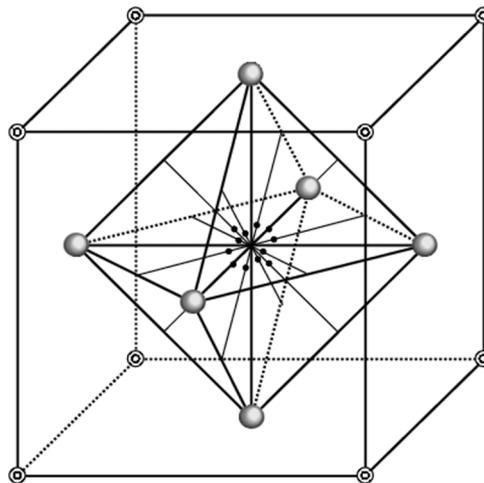


FIG. 4. The unit cell of the cubic perovskite paraphase. The La/Ba ions are at the vertices of the cube; in the center of the cube is a Mn ion surrounded by oxygen octahedra. Possible displacements of the central Mn atom that cause the structural transformation in the  $Imma$  phase are shown.

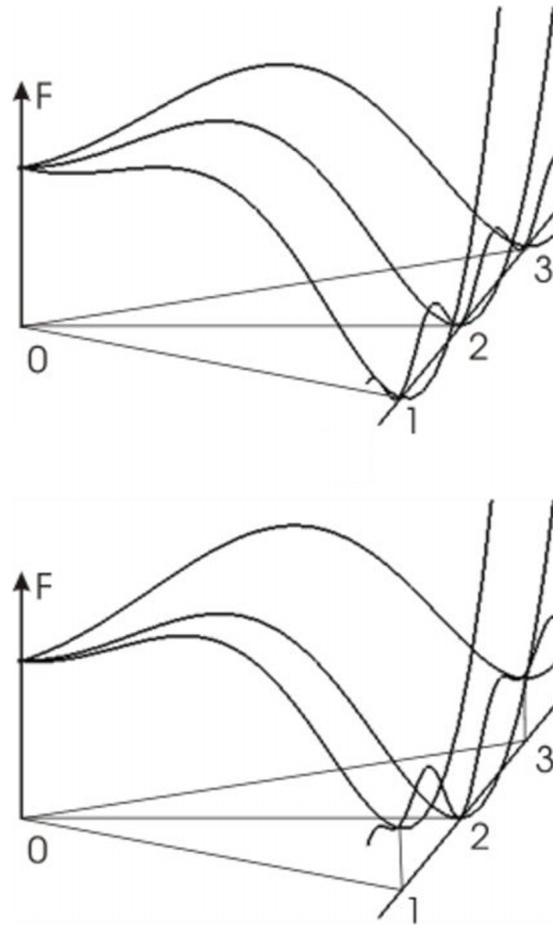


FIG. 5. Thermodynamic potential  $F(Q_i)$  (Eq. (1)) in the (110) plane. Points 1, 2, 3 correspond to equiprobable positions of Mn ion in  $T_s$  temperature (upper panel) and to the non equiprobable energy state of Mn ion in  $Imma$  phase below  $T_s$  (lower panel). The potential is soft in the phase transition point  $T_s$  and becomes rigid below this temperature.

ion moves nearly freely between all equilibrium sites with very low potential barriers (Fig. 5), which agrees well with the soft mode mechanism found in our ultrasound data (Fig. 1). Almost free movement of the central ion should lead to a highly symmetric (cubic) perovskite structure near the temperature of the structural phase transition. Therefore, the crystal lattice parameters should be close to each other near  $T_s$ . The temperature dependences of the  $Imma$  lattice constants reduced to the cubic paraphase lattice  $a' \equiv a/\sqrt{2}$ ,  $b' \equiv b/\sqrt{2}$  are shown in Fig. 6; where  $a, b$  and  $c$  are the  $Imma$  lattice constants.<sup>14</sup> The lattice parameters converge with increasing temperature. The parameters  $a'$  and  $b'$  converge with increasing temperature and become equal in the vicinity of the phase transition temperature  $T_s$ . The parameter  $c'$  shows the most interesting temperature behavior: it reaches its highest value in the vicinity of  $T_s$  and then begins to decrease with increasing temperature. That is, the coefficient of linear expansion  $\alpha$  along the  $c$ -axis becomes negative (Fig. 7). The nature of the negative thermal expansion was investigated both experimentally and theoretically in compounds of various types, such as strongly anisotropic structures,<sup>43,44</sup> high-temperature superconductors,<sup>45</sup> carbon structures,<sup>46,47</sup> and niobium diselenide.<sup>48</sup> In our case, the appearance of the negative linear coefficient of expansion can be attributed to the appearance of the soft mode in the structural phase transition region.

The elastic properties of the lattice are characterized by the following relation between the stress  $\sigma$ , Young's modulus  $E$  and strain  $\varepsilon$ :

$$\sigma = E \cdot \varepsilon \quad (4)$$

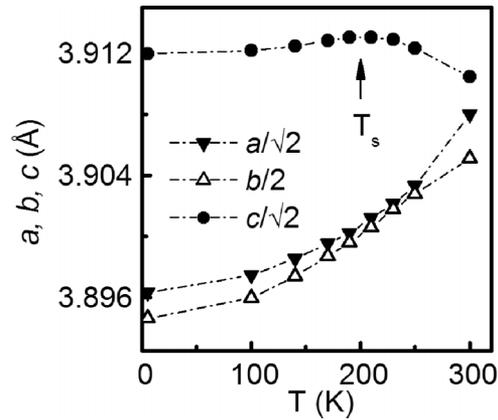


FIG. 6. Temperature dependences of the *Imma* lattice constants reduced to the cubic paraphase lattice.

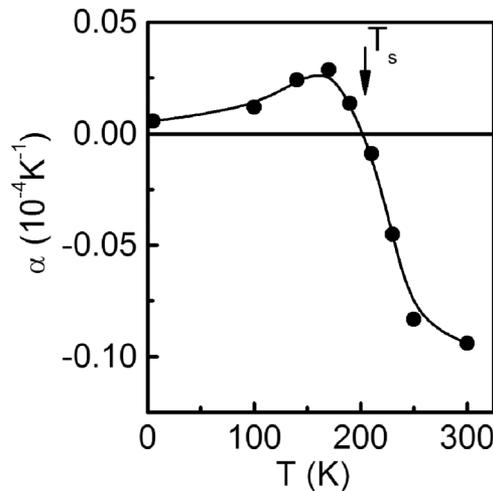


FIG. 7. Linear expansion coefficient  $\alpha$  along the *c*-axis (*Imma* phase) as a function of temperature.

The appearance of the soft mode indicates a presence of weak coupling (low stiffness) in the crystal lattice, i.e. a decrease in Young's modulus  $E$ . As follows from (4), a decrease in  $E$  at a fixed  $\sigma$  results in an increase in strain  $\epsilon$ . The crystal lattice becomes less stable, which ultimately leads to a structural phase transition. Since the magnetoelastic interaction is considerable in the studied compound, the appearance of the soft mode should be clearly seen in magnetic experiments. The acute minimum of  $v(T)$  was similar to the corresponding anomaly of the uniaxial pressure effect on magnetization  $M(T)$  (Fig. 2), which was associated with electronic transition.<sup>14,49</sup>

## V. SUMMARY

Structural phase transformation in the polycrystalline  $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$  compound was studied using an ultrasonic technique. The minimum of the temperature-dependent ultrasound velocity  $v(T)$  and the maximum of the decrement  $\delta(T)$  indicate a first order phase transition at  $T_s \sim 200$  K. The considerable change in both the sound velocity and the decrement indicate a structural phase transition of the soft mode type. The high sensitivity of *dc* magnetization to low uniaxial pressure confirms the appearance of the soft mode. A microscopic mechanism of this phenomenon associated with the displacement of the manganese atom from the center of the oxygen octahedron was proposed. The transformation  $Imma \rightarrow R\bar{3}c$  occurs via a structure similar to the cubic perovskite paraphase. A negative value of the linear thermal expansion coefficient along the crystallographic

$c$  axis in the *Imma* phase was found in the vicinity of  $T_s$ . It is of interest to conduct further studies of this compound for the possible detection of multiferroic properties. As the order parameter of this transition is the displacement of ions, a polarization is possible. So, we can expect anomalous temperature-dependent behavior of the dielectric constant.

## ACKNOWLEDGMENTS

The authors would like to thank Dr. C. Ritter (ILL, France) for his help and fruitful collaboration.

This work was supported by Research and Education at UPJŠ - Heading towards Excellent European Universities, ITMS project code: 26110230056, supported by the Operational Program Education funded by the European Social Fund (ESF) and the Slovak Grant Agency VEGA 1/0145/13.

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