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ABSTRACT

of the dissertation for the degree of doctor of philosophy

CRYSTAL AND MAGNETIC STRUCTURE OF SOLID SOLUTIONS $La_xBa_{1-x}MnO_3$ AT LOW TEMPERATURES

Speciality: 2220.01-Semiconductor Physics

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GENERAL DESCRIPTION OF WORK

Relevance and development of the work. In the presented thesis, changes in the crystal structure and magnetic properties of the $La_xBa_{1-x}MnO_3$ system at low temperatures were studied. It is known that the areas of application of complex oxides in modern electronics and spintronics have recently expanded. The main reason for this is the change in physical properties over a period of time due to oxidation in non-oxidized materials. Therefore, the study of various physical properties of complex oxides further expands the possibilities of their application.

Many interesting physical properties have been discovered in complex oxides with a perovskite structure. These materials have semiconducting properties. They may exhibit ferroelectric or antiferroelectric properties. Ferromagnetic or antiferromagnetic properties can also be observed when magnetic ions are included in these compounds. More important are multiferroics, in which both ferroelectric and ferromagnetic properties are observed. With cation-cation substitution, the physical properties of these materials can be controlled. Therefore, the study of the fundamental physical properties of perovskite compounds and solid solutions synthesized on their basis is one of the main areas of condensed matter physics. In this work, the crystal structures and magnetic properties of $La_xBa_{1-x}MnO_3$ compounds (x = 0.50, 0.63 and 0.78) at low temperatures were studied. It is known that manganites exhibit magnetic properties mainly at low temperatures. One of the main requirements for expanding their applications is that they must be magnetic at room temperature. As a result of comprehensive studies carried out by X-ray and neutron diffraction methods, it was established that these compounds have a highly symmetrical crystal structure at room temperature and, therefore, have long-range magnetic order. It is known that crystals have magnetic properties mainly at low temperatures. Due to the increase in the amplitude of thermal vibrations, the magnetic properties also weaken. Therefore, the magnetic properties of $La_xBa_{1-x}MnO_3$ compounds were studied at low temperatures. For each composition, the magnetic moments of

Mn atoms are determined and the mechanism for changing the value of the magnetic moment under the influence of temperature is determined. It has been established that these compositions have cubic symmetry with a fairly high symmetry of the Pm-3m space group and ferromagnetic properties. The magnetic properties of these compositions are explained by structural features.

The object and subject of the research:

Semiconductor manganites $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.78}Ba_{0.22}MnO_3$ were chosen as objects of study. These compounds were synthesized by the method of partial cation-cation replacement of Ba atoms with La atoms in the $BaMnO_3$ compound. It is known that Mn atoms create magnetic properties in these compositions. However, changes in magnetic properties occur depending on the concentration of La and Ba cations. Therefore, the study of both the crystal structure and magnetic properties of these compounds opens up new possibilities for the use of these materials.

The purpose and objectives of the study:

The main goal of the dissertation work is to obtain perovskites $La_{0.5}La_{0.5}MnO_3$, $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.78}Ba_{0.22}MnO_3$ by partially replacing lanthanum atoms with barium atoms, studying their crystal structure, thermal and magnetic properties at low temperatures and the magnetic moments of Mn atoms at low temperatures, which consists in determining the Curie temperature of these compounds based on temperature dependence.

In order to ensure a successful solution to the issues posed in the objectives of the dissertation topic, the following specific issues are addressed:

- Synthesis of $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.78}Ba_{0.22}MnO_3$,
- Study of the thermal stability and physicochemical properties of $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.78}Ba_{0.22}MnO_3$ solid solutions,
- Study of crystal structures of $La_xBa_{1-x}MnO_3$ compounds (x = 0.50, 0.63 and 0.78),

- Study of the influence of low temperatures (T = 5-295 K) on the crystal structures of these compounds,
- Determination of the magnetic properties of $La_xBa_{1-x}MnO_3$ compounds (x = 0.50, 0.63 and 0.78),
- Determination of the mechanism for changing the magnetic moments of Mn atoms in the compounds $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.78}Ba_{0.22}MnO_3$ at low temperatures.

Research methods:

The research objects were obtained in polycrystalline form and ground into powder. Structural-phase analysis and crystal structures of the synthesized compounds were studied by X-ray diffraction. As a result of the analysis of X-ray diffraction spectra, lattice parameters, crystal lattice symmetry, space group and atomic coordinates were determined. The thermal stability of these compositions and the physicochemical processes occurring under the influence of temperature were studied using the method of differential thermal analysis. Structural studies in the low temperature region were carried out using the neutron diffraction method operating in a pulsed mode.

X-ray and neutron diffraction spectra were analyzed using the "VMRIA" and "FullProf" programs using the Rietveld method. To construct the resulting model of crystal structures, "DIAMOND 3.2" was used, "Origin 9" programs were used to construct and analyze lattice parameters and temperature dependences of magnetic moments. The use of modern software increased the accuracy of the results obtained.

Defensive provisions:

1. Crystal structure and magnetic properties of the $Ba_{0.5}La_{0.5}MnO_3$ compound at low temperatures. Ferromagnetic structure of this compound. The mechanism for reducing the magnitude of the magnetic moment in this regard under the influence of temperature..
2. Ferromagnetic – paramagnetic phase transition in the $La_{0.63}Ba_{0.37}MnO_3$ compound. Temperature dependences of the magnetic moments of Mn atoms.

3. The mechanism of changes in the crystallographic parameters of the $La_{0.63}Ba_{0.37}MnO_3$ compound at low temperatures. Thermal expansion coefficients.

4. Crystal and magnetic structure of the $Ba_{0.78}La_{0.22}MnO_3$ composition. Crystallographic parameters of cubic and rhombohedral two-phase systems.

5. Ferromagnetic – paramagnetic phase transition in $Ba_{0.78}La_{0.22}MnO_3$. The mechanism for reducing the magnitude of the magnetic moment in this regard under the influence of temperature.

Scientific novelty of the research:

1. The crystal structure and crystallographic parameters of the $La_{0.5}Ba_{0.5}MnO_3$ compound were determined. It was established that the crystal structure of this compound at room temperature corresponds to a crystal structure of cubic symmetry with space group Fm-3m.

2. The crystal structure and magnetic properties of the $La_{0.5}Ba_{0.5}MnO_3$ compound were determined in the temperature range T = 5-295 K. It was established that the structure of cubic symmetry with the space group Fm-3m is maintained in the specified temperature range. The magnetic moments of Mn atoms have been determined and the mechanism for changing the magnetic moment depending on temperature has been established.

3. The crystal structure and lattice parameters of the $La_{0.63}Ba_{0.37}MnO_3$ compound were determined. It was established that the crystal structure of this compound corresponds to a crystal structure of cubic symmetry with space group Fm-3m and lattice parameters: $a = b = c = 3.9070$ Å.

4. The crystal structure and magnetic properties of the $La_{0.63}Ba_{0.37}MnO_3$ compound were determined in the temperature range T = 5-295 K. It was established that in the specified temperature range a cubic structure with high symmetry is preserved. The magnetic moments of Mn atoms were determined and it was found that with increasing temperature the value of the magnetic moment decreases from $\mu = 3.53$ μ_B to $\mu = 1.47$ μ_B.

5. The crystal structure of the composition $La_{0.78}Ba_{0.22}MnO_3$ was determined. It has been established that the crystal structure of this

composition consists of two phases. The crystallographic parameters of each phase were determined. It was established that the crystal structure of the first phase corresponds to the crystal structure of cubic symmetry of the space group Pm-3m, and the crystal structure of the second phase corresponds to the crystal structure of rhombohedral symmetry of the space group R-3c.

6. The crystal structure and magnetic properties of the $La_{0.78}Ba_{0.22}MnO_3$ compound at low temperatures were determined. It has been established that the magnetic moments of Mn atoms are determined in the temperature range T = 5-295 K and it has been established that with increasing temperature the value of the magnetic moment decreases from μ = 3.58 μ_B to μ = 1.49 μ_B.

Theoretical and practical significance of the research:

Since perovskite manganites are functional materials with a wide range of applications, they are considered materials of great theoretical and practical importance. It is known that materials with semiconductor properties are widely used in modern electronics. In addition, they also have magnetic properties, which creates the basis for their use in spintronics. Depending on the ionic radii of metals A and B, different crystal structures can be observed in perovskites of the general type ABO_3. An ideal cubic structure was observed in $La_xBa_{1-x}MnO_3$ compounds (x = 0.50, 0.63 and 0.78). Therefore, the results obtained during these studies can be used as a model object when studying other physical properties of these materials. The ferromagnetic structure discovered in these compounds can be used to study the magnetic properties of newly synthesized perovskites with ferromagnetic properties.

Approbation and application of the research:

The results obtained in the dissertation were discussed at subsequent conferences:

- ✓ "Step into the future" 1st republican scientific conference, April 12-14, 2017, Azerbaijan State Pedagogical University, Baku, Azerbaijan.
- ✓ International Conference Condensed Matter Research at IBR-2, Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, October 9-12, 2017, Dubna, Russia.

- ✓ LII PNPI School and Youth Conference on Condensed Matter Physics FKS-2018, St. Petersburg Institute of Nuclear Physics named after B. P. Konstantinov, March 12-17, 2018, St. Petersburg, Russia.
- ✓ International Conference "Condensed Matter Research at the IBR-2", Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, April 25-29, 2022, Dubna, Russia.

The main results of the dissertation were published in 12 publications (articles and theses). Of these, 9 are articles (including 3 on the WOS platform) and 4 are conference abstracts (including 3 abroad). The results were published in the annual scientific research reports of the Institute of Physics of the Ministry of Science and Education.

Author participation level:

The topic and main scientific direction of the presented dissertation were chosen by the author and his supervisor, and the main issues raised were determined with the direct participation of the author. He was directly involved in the synthesis of research samples and research experience. He played a leading role in the preparation of articles and conference proceedings and was the first author on all of them. The main results obtained were reported by the author at conferences at international and national levels.

Name of the organization where the dissertation work was completed:

The dissertation work was carried out in the laboratory of "Nuclear Physics and High Energy" of the Institute of Physics of the Ministry of Science and Education.

The Structure and the total volume of the dissertation:

The dissertation consists of an introduction, 4 chapters, a conclusion and a bibliography consisting of 131 items. The volume of work consists of 45 figures, 4 tables and a total of 216267 characters.

CONTENT OF THE WORK

The **introduction** indicates the relevance of the dissertation topic, the purpose of the dissertation, scientific innovations, the scientific and practical significance of the work, the stated goal and protected provisions, approval of the work, research methods in detail.

The **first chapter** of the thesis is devoted to a literature review of the results obtained in previous studies of the crystal structure and magnetic properties of compounds with a perovskite crystal structure. The electronic structure and semiconductor properties of these compounds are outlined, and the possibilities of application in modern electronics are shown. In perovskite manganites, the crystal structures and structural phase transitions obtained depending on the metal A included in the $AMnO_3$ compounds were analyzed. It has been established that, depending on the ionic radius of metal A in these compositions, different structures can be observed in the resulting crystals. It is known that the magnetic properties of crystals arise as a result of the ordered arrangement of metal atoms with magnetic properties included in this structure. Although the metal atom A does not have magnetic property, it has a serious effect on the crystal structure and partially disrupts the regular arrangement of Mn atoms or enhances the regularity. A literature review of the results obtained from studying the magnetic properties of $AMnO_3$ compounds in previous studies was analyzed. From studies carried out using vibrational magnetometry and neutron diffraction methods, it is known that the magnetic properties of these compounds are observed mainly in the low temperature region. With increasing temperature, as a result of an increase in the amplitude of thermal vibrations of the atoms forming the crystal structure, the long-range magnetic pattern is broken and a ferromagnetic (antiferromagnetic) - paramagnetic phase transition occurs. These analyzes were based mainly on the results obtained from studying the structural and magnetic properties of perovskite manganites $BaMnO_3$ and $LaMnO_3$. The structural characteristics and magnetic properties of the A'_1-

$_xA''_xMnO_3$ compounds obtained by cation-cation substitution in these compositions are analyzed, and the changes that occur depending on the ionic radii of the metal atoms A′ and A″ are also analyzed.

At the end of the chapter, the importance of studying the structure and magnetic properties of the $La_xBa_{1-x}MnO_3$ compounds, the future theoretical and practical possibilities of the results obtained in the course of their research, the relevance and scientific significance of the topic, as well as the importance of the research that will be carried out in this direction are explained.

The **second chapter** is devoted to the experimental methods, instruments and installations used during the research. The latest generation devices were used during the study. The objects of study were synthesized in the solid phase using a standard method suitable for the synthesis of complex oxides. The resulting substances in the form of polycrystals were crushed in a mortar, turned into powder, and samples were prepared for research. Structural-phase analysis of perovskite compositions and crystal structures at room temperature was carried out by the traditional X-ray method on a German D8 Advance diffractometer (Bruker) with parameters 40 kV, 40 mA, CuKα radiation, $\lambda = 1.5406$ Å. The spectra obtained during the structural phase analysis were compared with the original data and preliminary data were obtained. To determine the crystallographic parameters of perovskite structures, the spectra were analyzed by the Rietveld method in the "Fullprof" program.

The thermal characteristics of the samples were determined in the high-temperature zone using differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG). These methods are ideal for studying many temperature phenomena in crystals. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) studies were carried out on a German-made "STA 449 F3 Jupiter®" device. This calorimeter has an operating range from room temperature to 1000 °C, a thermal operating speed of 0.001-50 °C/min, and a "Julabo F25" cooling system. Kinetic parameters were determined using the "Proteus Analysis" program. The resulting thermal spectra were analyzed in the "Origin 9"

program and the values of thermodynamic parameters for each system were calculated.

Neutron diffraction experiments at low temperatures were carried out on a DN-2 neutron diffractometer (I.M. Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia), located in the 6th channel of the IBR-2 pulsed reactor. The DN-2 diffractometer allows you to study the structure and magnetic properties of crystals at low temperatures (in a specially designed He-chamber). Unlike X-ray diffraction spectra, neutron diffraction spectra provide information about the crystal structure as well as the magnetic structure of the crystals. Consequently, from the intensities of the maxima corresponding to the magnetic structure, it is possible to determine the magnetic moments of metal atoms with magnetic properties.

The resulting X-ray diffraction spectra were analyzed in the "FullProf" and "Origin 9" programs, neutron diffraction spectra were analyzed by the Rietveld method using the "FullProf", "MRIA" and "VMRIA" programs.

The **third chapter** is devoted to the study of the structure and thermal properties of the $La_xBa_{1-x}MnO_3$ system, studied in the dissertation work. The crystal structure of the studied samples, obtained in powder form, was studied at room temperature and under normal conditions. The studies were carried out using the traditional X-ray diffraction method; the resulting diffraction patterns were analyzed by the Rietveld method in the Fullprof program. It was established that the crystal structure of the $La_{0.5}Ba_{0.5}MnO_3$ compound corresponds to cubic symmetry with the space group Fm-3m (Fig. 1). In the compound $La_{0.5}Ba_{0.5}MnO_3$, the atoms of tetravalent Mn are located at the origin of coordinates - at the nodes of the elementary nucleus. These atoms form covalent bonds with O atoms and form MnO_6 octahedra. Mn atoms are located at the center of these octahedra. Therefore, there is a high probability of the formation of magnetic properties in this compound at room temperature. High symmetry of the structure is considered one of the important conditions for the formation of long-range magnetic order in compositions. Neutron diffraction studies are necessary to

determine the magnetic moments of Mn atoms. As can be seen from the crystal structure of the $La_{0.5}Ba_{0.5}MnO_3$ compound, Ba and La atoms alternate in the center of the unit lattice and form covalent bonds with O atoms.

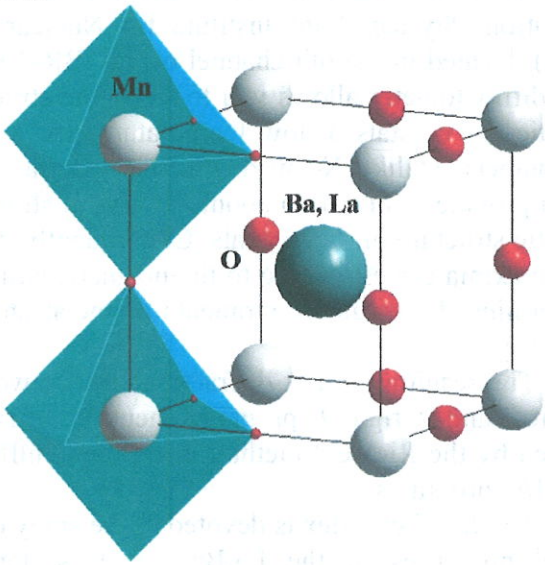

Fig. 1. Crystal structure of the $La_{0.5}Ba_{0.5}MnO_3$ compound.

Comprehensive DSC, DTA, TG and TGA analyzes were carried out to study the thermal properties of $La_{0.5}Ba_{0.5}MnO_3$ compound. During the analysis of the obtained spectra in the "Origin 9" program, it was found that this compound has a fairly stable structure at high temperatures.

Similarly, experiments were carried out to study the structure and thermal properties of the $La_{0.63}Ba_{0.37}MnO_3$ compound. It has been established that the compounds $La_{0.5}Ba_{0.5}MnO_3$ and $La_{0.63}Ba_{0.37}MnO_3$ correspond to cubic symmetry with the space group Fm-3m.

When studying the thermal properties, the results for the $La_{0.5}Ba_{0.5}MnO_3$ compound were obtained both on the DSC and DTA curves of the temperature dependence of the heat flow, and on the

TG and TGA curves. When studying the crystal structure of the $La_{0.78}Ba_{0.22}MnO_3$ compound, different results were obtained. By analyzing X-ray diffraction patterns taken at room temperature and under normal conditions, it was found that the crystal structure of this composition corresponds to two different phases. One of these phases corresponded to a cubic crystal structure, and the other to a rhombohedral crystal structure. The crystallographic parameters of these phases were determined: symmetry, space group, lattice parameters and atomic coordinates. These differences observed in the crystal structure were also observed in DSC, DTA, TG and TGA analyses.

The **fourth chapter** is devoted to the study of the crystalline and magnetic structure of the compounds $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.78}Ba_{0.22}MnO_3$ at low temperatures. When comparing neutron diffraction spectra obtained from room temperature to $T = 5$ K, it was found that the structures observed at room temperature are preserved even at low temperatures and a structural phase transition does not occur. In the neurogram of the compound $La_{0.5}Ba_{0.5}MnO_3$, obtained at room temperature and under normal conditions, maxima were observed at $d_{hkl} = 3.6$ Å and 4.9 Å, which does not correspond to the crystal structure. As a result of the analysis carried out by the Rietveld method in the Fullprof program, it was found that these maxima correspond to a ferromagnetic structure. As a result of their analysis, the values of the magnetic moments of Mn atoms were determined. As a result of analysis of neutron diffraction spectra, it was established that the values of magnetic moments are higher at low temperatures. This phenomenon is associated with a partial violation of the remote magnetic pattern as a result of an increase in the amplitude of thermal vibrations under the influence of temperature. The temperature dependences of the magnetic moments of Mn atoms in the $La_{0.5}Ba_{0.5}MnO_3$ compound are presented in Fig. 2. As can be seen from the dependence, the ferromagnetic-paramagnetic phase transition occurred at a temperature $T_C = 317$ K.

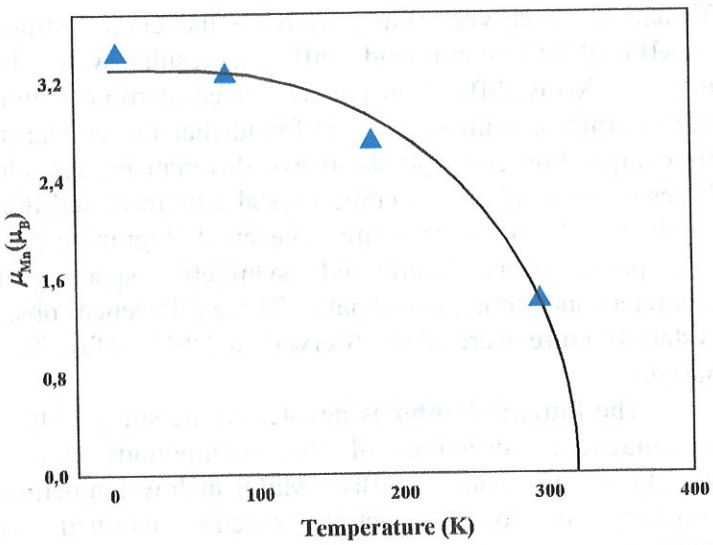

Fig. 2. Temperature dependences of magnetic moments in the $La_{0.5}Ba_{0.5}MnO_3$ compound.

The crystal structure of the $La_{0.5}Ba_{0.5}MnO_3$ compound was also studied at room temperature and in the region of low temperatures down to T = 5 K. When studying neutron diffraction spectra obtained in the range d = 1.6-5.1 Å, it was established that the diffraction maxima, corresponding to the crystal structure of this compound fall in the range d = 1.6-3.2 Å. As a result of the analysis, it was found that this neutron diffraction spectrum corresponds to the cubic highly symmetric perovskite structure with the space group Pm-3m. It is clear from low-temperature neutron diffraction patterns that as the temperature decreased, the reflections shifted along the abscissa axis towards smaller values of the distances between atomic planes. This is an indicator of the decrease in the value of interatomic bonds with decreasing temperature. The values of lattice parameters in the low temperature region were determined using the Fullprof, MRIA, and VMRIA spectra programs. It has been established that with decreasing temperature there is also a decrease in lattice

parameters, and the values of lattice parameters at a temperature T = 5 K are determined as: $a = b = c = 3.8945$ Å, $V = 59.068$ Å^3.

From the temperature dependences of the lattice parameters of the $La_{0.5}Ba_{0.5}MnO_3$ compound and the volume of the elementary lattice, it is clear that thermal expansion occurs with increasing temperature. Taking into account this dependence, the coefficients of linear and volumetric expansion were calculated and $\alpha_a = 1.16 \cdot 10^{-5}$ K^{-1}, $\alpha_V = 3.49 \cdot 10^{-5}$ K^{-1} were obtained. As can be seen, neutron diffraction studies carried out in the temperature range 5 K < T < 295 K showed that a structural phase transition does not occur in the $La_{0.5}Ba_{0.5}MnO_3$ compound at low temperatures. In the specified temperature range, this compound retained a highly symmetrical crystal structure.

Neutron diffraction studies were also carried out for the compositions $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.78}Ba_{0.22}MnO_3$. It has been established that in the diffraction spectra corresponding to these compounds, maxima corresponding to the ferromagnetic structure are also observed. The temperature dependences of the magnetic moment values for each composition were obtained and, as a result of interpreting these dependences using the Brillouin function, the values of the ferromagnetic-paramagnetic phase transitions were determined. The temperature dependences of the magnetic moments of Mn atoms in the $La_{0.63}Ba_{0.37}MnO_3$ compound are shown in Fig. 3.

As a result of the analysis, it was established that the values of the magnetic moments of Mn atoms in the $La_{0.63}Ba_{0.37}MnO_3$ compound are slightly higher. This effect was also found in Curie temperature values. From the dependence shown in Fig. 3, it is clear that the temperature of the ferromagnetic-paramagnetic phase transition in this compound corresponds to $T_C = 322$ K.

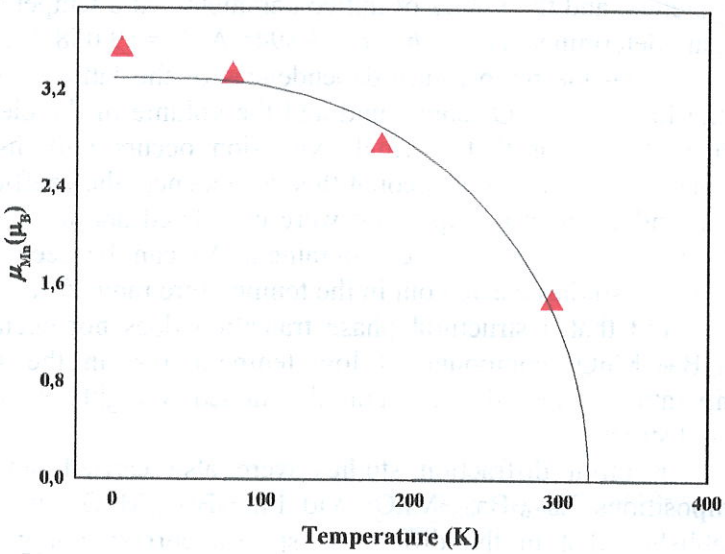

Fig. 3. Temperature dependences of magnetic moments in the $La_{0.63}Ba_{0.37}MnO_3$ compound.

The neutron diffraction spectra of the compound $La_{0.63}Ba_{0.37}MnO_3$ at room temperature and in the region of low temperatures down to $T = 5$ K were analyzed and the crystallographic parameters were determined. When studying the spectra obtained in the range d = 1.6-5.1 Å of distances between atomic planes, it was found that the diffraction maxima corresponding to the crystal structure of this compound are located in the range d = 1.6-3.2 Å. As a result of the interpretation of the spectra obtained at room temperature, it was established that this neutron diffraction spectrum corresponds to the ideal perovskite structure with a highly symmetrical cubic system with space group Pm-3m. These results were consistent with those obtained from X-ray diffraction experiments carried out at room temperature and under normal conditions for the $La_{0.63}Ba_{0.37}MnO_3$ compound in our previous studies. The values of the parameters of the elementary nucleus were determined: $a = b = c = 3.9072$ Å, $V = 59.65$ Å^3. In the spectra of the

$La_{0.63}Ba_{0.37}MnO_3$ compound, as well as in the spectra of the $La_{0.5}Ba_{0.5}MnO_3$ compound, as the temperature decreased, the reflections shifted along the abscissa towards smaller distances between atomic planes. This is an indicator of the decrease in the value of interatomic bonds with decreasing temperature.

The spectra were analyzed using the Fullprof, MRIA, and VMRIA programs. As a result of comparing the theoretically generated curves with the experimental ones, the crystallographic parameters of the $La_{0.63}Ba_{0.37}MnO_3$ compound at low temperatures were determined: atomic coordinates, interatomic distances, angles between bonds, syngony and space group. It has been established that with decreasing temperature there is also a decrease in the lattice parameters, and at $T = 5$ K (helium temperature) the values of the lattice parameters are determined as: $a = b = c = 3.8963$ Å, $V = 59.15$ Å^3.

The temperature dependences of the lattice parameters of the $La_{0.63}Ba_{0.37}MnO_3$ compound in the low temperature region were obtained. From the dependencies it is determined that thermal expansion occurs with increasing temperature. Taking this dependence into account, the coefficients of linear and volumetric expansion were calculated. The values obtained were $\alpha_a = 0.96 \cdot 10^{-5}$ K^{-1} and $\alpha_V = 2.91 \cdot 10^{-5}$ K^{-1}.

From the results obtained when studying the crystal structure of the $La_{0.78}Ba_{0.22}MnO_3$ compound using neutron diffraction at low temperatures, it was established that the lattice parameters of this compound are related to the mechanism of changing the lattice parameters. The perovskite compounds $La_{0.5}Ba_{0.5}MnO_3$ and $La_{0.63}Ba_{0.37}MnO_3$ are varied accordingly, included in the $La_{1-x}Ba_xMnO_3$ system. However, slightly different values were obtained from the thermal coefficients of the compounds $La_{0.5}Ba_{0.5}MnO_3$ and $La_{0.63}Ba_{0.37}MnO_3$: coefficients of linear and volumetric thermal expansion, which is an indicator of the temperature stability of these systems. The results obtained from these studies confirmed the formation of a system of higher symmetry in the $La_{1-x}Ba_xMnO_3$ system with increasing concentration of La atoms. Therefore, according to preliminary indicators, the ferromagnetic properties of

the $La_{0.78}Ba_{0.22}MnO_3$ compound should be stronger, and the values of the magnetic moments of Mn atoms should be higher. However, to obtain more accurate data on the magnetic properties of this compound, it is necessary to analyze the reflections of neutron diffraction spectra, which are considered compatible with a ferromagnetic structure, and analyze the resulting data.

In order to study the magnetic properties of the perovskite compound $La_{0.78}Ba_{0.22}MnO_3$, the magnetic peaks observed in neutron diffraction patterns obtained during studies carried out at helium temperature (in the temperature range T = 5-295 K) were analyzed. Analyzes were performed analytically using the Rietveld method using the Fullprof program. It has been established that reflections corresponding to the magnetic structure of the $La_{0.78}Ba_{0.22}MnO_3$ compound are observed in the range d = 3.5-5.1 Å, and the center of the maxima falls on the points d = 3.65 Å and d = 4.96 Å. As a result of the analysis, it was established that the magnetic properties of the $La_{0.78}Ba_{0.22}MnO_3$ compound correspond to the magnetic properties of the $La_{0.5}Ba_{0.5}MnO_3$ and $La_{0.63}Ba_{0.37}MnO_3$ compounds. The compound $La_{0.78}Ba_{0.22}MnO_3$ at room temperature is also a compound with ferromagnetic properties. Although the intensity of the reflection observed at the point d = 3.65 Å is low, the intensity of the reflection observed at the point d = 4.96 Å is quite high. With a decrease in temperature in the low temperature region (up to T = 5 K), a slight increase in the intensity of both reflections was observed, which is associated with the damping of thermal vibrations (optical and acoustic) caused by the temperature in the crystal lattice of the compound and the appearance of a distant magnetic pattern and, accordingly, this is a sign increasing the values of the magnetic moments of Mn atoms.

In the temperature range T = 5-295 K, the magnetic moments of tetravalent manganese atoms located in the exact center of the MnO_6 octahedra at the sites of the cubic perovskite lattice in the $La_{0.78}Ba_{0.22}MnO_3$ compound were determined. The temperature dependence of the magnetic moments in the $La_{0.78}Ba_{0.22}MnO_3$ compound is shown in Fig. 4. As a result of analyzing the spectra using the Rietveld method, it was established that the magnetic

moments of tetravalent manganese atoms (Mn^{4+}) at room temperature and under normal conditions have a relatively low value: $\mu = 1.49$ μ_B. As the temperature value decreased, an increase in the values of the magnetic moments was also observed (Fig. 4). At a temperature $T = 180$ K, the magnitude of the magnetic moments increased to: $\mu = 2.76$ μ_B, and at a temperature $T = 80$ K: $\mu = 3.36$ μ_B.

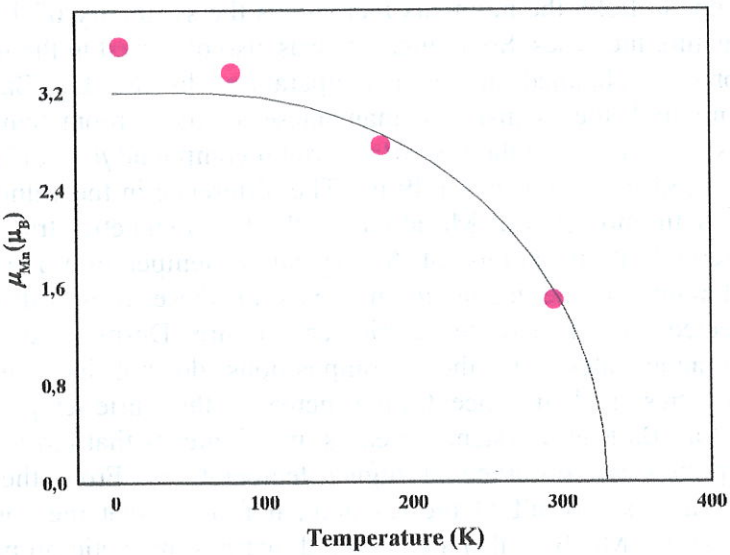

Fig. 4. Temperature dependences of magnetic moments in the $La_{0.78}Ba_{0.22}MnO_3$ compound.

At lower temperatures, an increase in the intensity of reflections corresponding to the ferromagnetic structure was observed in the neutron diffraction spectrum. As a result of the analysis, it was determined that $\mu = 3.58$ μ_B at a temperature $T = 5$ K. The graph of the dependence of manganese atoms on temperature in Fig. 4 is interpolated by the Brillouin function. Based on the temperature dependence of the magnetic moment, the value of the Curie temperature corresponding to the ferromagnetic-paramagnetic phase transition was determined. For the compound $La_{0.78}Ba_{0.22}MnO_3$, the point of intersection of the Brillouin function

with the abscissa axis was determined and the value T_C = 330 K for the Curie temperature was obtained.

In a comparative analysis of the ferromagnetic properties of the compounds $La_{0.78}Ba_{0.22}MnO_3$, $La_{0.63}Ba_{0.37}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$, it was found that with an increase in the concentration of metallic lanthanum atoms in the composition of the magnetic field, the moments increase as the symmetry of the crystal structure increases. Some increase was also observed in the magnetic moments obtained at room temperature. In the $La_{0.5}Ba_{0.5}MnO_3$ compound, the intensity of manganese atoms at room temperature was μ = 1.40 μ_B, in the $La_{0.63}Ba_{0.37}MnO_3$ compound μ = 1.47 μB, and in $La_{0.78}Ba_{0.22}MnO_3$ μ = 1.49 μ_B. The difference in the values of the magnetic moments of Mn atoms in the ferromagnetic structure was observed at all points of the specified temperature range. The difference in the magnetic moments of these compositions also affected the value of the Curie temperature. Despite the fact that lanthanum atoms in these compositions do not have magnetic properties, as their concentration increases, the Curie temperature in the $La_{1-x}Ba_xMnO_3$ system increases, which means that ferromagnetic properties are observed at higher temperatures. From the results obtained as a result of the research, it follows that the compound $La_{0.78}Ba_{0.22}MnO_3$ is also a compound that has magnetic properties at room temperature.

The crystal structure of the $La_{0.78}Ba_{0.22}MnO_3$ compound has been studied at low temperatures. When analyzing neutron diffraction spectra obtained at low temperatures up to T = 5 K, it was found that the diffraction maxima corresponding to the crystal structure of this compound are located in the range d = 1.6-3.2 Å. As a result of the interpretation of the spectra obtained at room temperature in the MRIA and VMRIA programs, it was established that this neutron diffraction spectrum corresponds to the ideal perovskite structure with a highly symmetrical cubic system with the space group Pm-3m. These results are consistent with those obtained from X-ray diffraction experiments performed at room temperature and under normal conditions for the compound $La_{0.63}Ba_{0.37}MnO_3$ in

our previous studies. The values of the parameters of the elementary nucleus were determined: $a = b = c = 3.9049$ Å, $V = 59.54$ Å^3.

It is clear from the neutron diffraction patterns that in the spectra of the perovskite compound $La_{0.78}Ba_{0.22}MnO_3$, as well as in the spectra of the compounds $La_{0.5}Ba_{0.5}MnO_3$ and $La_{0.63}Ba_{0.37}MnO_3$, as the temperature decreases, reflections appear shifted towards smaller distances between atomic planes along the abscissa axis. This is an indicator of a decrease in interatomic bonds and, accordingly, the values of lattice parameters with decreasing temperature.

The spectra were analyzed using Fullprof, MRIA and VMRIA software and the values of the crystallographic parameters were determined. As a result of comparing theoretically plotted curves with experimental ones, the crystallographic parameters of the $La_{0.78}Ba_{0.22}MnO_3$ compound at low temperatures were determined: atomic coordinates, interatomic distances, angles between bonds, symmetry, gonium and space group. It has been established that with decreasing temperature there is also a decrease in lattice parameters, and at $T = 5$ K (helium temperature) the values of lattice parameters are determined as: $a = b = c = 3.8959$ Å, $V = 59.13$ Å^3.

The temperature dependences of the lattice parameters of the $La_{0.78}Ba_{0.22}MnO_3$ compound in the low temperature region were obtained and interpreted. The values obtained were $\alpha_a = 0.79 \cdot 10^{-5}$ K^{-1} for the coefficient of linear expansion of lattice parameters a, b and c, $\alpha_V = 2.37 \cdot 10^{-5}$ K^{-1} for the coefficient of thermal expansion of volume V of the elementary lattice.

As can be seen from the values of the thermal expansion coefficients, with an increase in lanthanum atoms, the crystal structure of compounds of the $La_{1-x}Ba_xMnO_3$ system becomes more stable, and the lattice parameters change less depending on temperature. It is known that the crystal structure of the $BaMnO_3$ compound has rhombohedral symmetry, and the crystal structure of the $LaMnO_3$ compound has cubic symmetry. According to it, with an increase in the concentration of the La metal in $La_{1-x}Ba_xMnO_3$ solid solutions, a more stable cubic crystal structure is formed.

At the end of the chapter, a comparison is made of the magnetic properties obtained for different compositions of the

$La_xBa_{1-x}MnO_3$ system. It has been established that with an increase in the concentration of La atoms in the compositions, the values of the magnetic moments of Mn atoms increase. This is due to the fact that as the concentration of La atoms with a large ionic radius increased, the symmetry of the crystal structure increased and, as a consequence, the remote order of Mn atoms increased. The results obtained are compared with the results obtained when studying the magnetic properties of perovskite manganites $A'_{1-x}A''_xMnO_3$.

RESULTS

1. It has been established that compounds of the $La_xBa_{1-x}MnO_3$ system (x = 0.5, 0.63, 0.78) have a highly symmetrical cubic perovskite structure with space group Fm-3m. As the concentration of lanthanum atoms in the composition increased, an increase in the values of the lattice parameters was observed, which was explained by the difference in the ionic radii of the divalent La^{2+} and Ba^{2+} atoms.

2. The values of the magnetic moments of Mn atoms in the $La_{0.5}Ba_{0.5}MnO_3$ compound were determined in the temperature range T = 5-395 K. It was shown that with increasing exposure to temperature, the value of the magnetic moment decreases (from μ_{5K} = 3.42 μB to μ_{295K} = 1.40 μB). This was explained by a violation of the long-range magnetic pattern due to thermal fluctuations.

3. The Curie temperature of the compound $La_{0.5}Ba_{0.5}MnO_3$ was determined. As a result of interpreting the temperature dependence of the magnetic moments of Mn atoms using the Brillouin function, it was established that the ferromagnetic-paramagnetic phase transition occurs at a temperature T = 317 K.

4. Based on the temperature dependences of the lattice parameters of the $La_{0.63}Ba_{0.37}MnO_3$ compound, the thermal expansion coefficients at low temperatures (T = 5-395 K) were calculated. For the coefficient of linear expansion in the specified temperature range: $\alpha_a = 0.96 \cdot 10^{-5}$ K^{-1}, and for volumetric expansion: $\alpha_V = 2.91 \cdot 10^{-5}$ K^{-1} the values are determined.

5. For the $La_{0.63}Ba_{0.37}MnO_3$ compound, the temperature dependence of the magnetic moments of Mn atoms in the low temperature region (T = 5-395 K) was obtained. It has been established that at a temperature T_C = 322 K the magnitude of the magnetic moments is $\mu = 0$ μ_B and a ferromagnetic-paramagnetic phase transition occurs.

6. The values of the magnetic moments of Mn atoms in the compound $La_{0.78}Ba_{0.22}MnO_3$ were determined in the temperature range T = 5-395 K. As the influence of temperature increased, the value of the magnetic moment decreased (from μ_{5K} = 3.58 μ_B to μ_{295K}

= 1.49 μ_B). The ferromagnetic-paramagnetic phase transition occurred at a temperature $T_C = 330$ K.

7. The values of the thermal expansion coefficients were calculated from the temperature dependences of the lattice parameters of the $La_{0.78}Ba_{0.22}MnO_3$ compound at low temperatures (T = 5-395 K). For the specified temperature range, the values of the linear expansion coefficient were determined: $\alpha_a = 0.79 \cdot 10^{-5}$ K^{-1} and the volumetric expansion coefficient: $\alpha_V = 2.37 \cdot 10^{-5}$ K^{-1}.

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