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МАТЕРИАЛЫ ЭЛЕКТРОНИКИ

Electronic Structure of Bismuth Ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$

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Abstract—Multiferroics based on complex oxides of transition metals, particularly ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$, are promising functional materials for use in various electrical devices. However, in scientific publications there is no information about systematic studies of the $BiFe_{0.5}Mn_{0.5}O_3$ solid solution. In this work, a model structure of rhombohedral $BiFe_{0.5}Mn_{0.5}O_3$ is studied using ab initio methods. Theoretical estimations of the effective magnetic moments of iron and manganese ions, the degree of localization of the 3*d* states of these ions, and the energy gap for different spin configurations of Fe and Mn ions are carried out. The nature of the exchange interactions between the transition-metal ions is clarified. It is established that in the antiferromagnetic ordering, the magnetic moments of the iron and manganese ions are very close and have values of 4.16 and 4.23 цB, respectively; moreover, the 3*d* states of the Fe ions are localized, while the 3*d* states of the Mn ions, on the contrary, are delocalized and asymmetric. The presence of a small resulting magnetic moment of 0.012 цB per unit cell is shown. The nonequivalence of the positions of the Fe and Mn ions leading to the formation of an energy gap of 1.28 and 1.48 eV for spin-down and spin-up channels, respectively, is substantiated. The results obtained for the model structure make it possible to qualitatively describe the electronic structure of orthorhombic $BiFe_{0.5}Mn_{0.5}O_3$ using a fourfold reduced number of ions as compared to its real structure, and significantly broaden the scope of information obtained by experimental methods on the structure and physical properties of $BiFeO_3$-$BiMnO_3$ solid solutions.

Keywords: ferromanganites, multiferroics, density-functional theory, pseudopotential theory, density of states, population of atomic orbitals
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INTRODUCTION

Multiferroics combine ferroelectric and ferromagnetic ordering and have a wide range of physical properties, which makes them promising materials for use in various electrical devices, such as electromagnetic- field sensors, piezoelectric actuators, and devices and instruments based on magnetoelectric interaction [1—8]. The most studied chemical compounds are those based on bismuth oxides and transition-element oxides, in particular bismuth manganite $BiMnO_3$ and bismuth ferrite $BiFeO_3$. The single-phase multiferroic $BiFeO_3$ is characterized by a high temperature of both the magnetic (N6el point of 650 K) and ferroelectric (Curie point of 1100 K) transitions, as well as antiferromagnetic ordering of the *G* type [1, 4, 9]. This ordering, observed under normal conditions, can be violated by the action of an applied magnetic field and chemical modification (replacement of iron ions with other magnetic or nonmagnetic ions) or their combined effect [9—13]. $BiMnO_3$ multiferroic is characterized by ferromagnetic ordering (Curie point of 475 K), which is caused by the orbital order of Mn^{3+} ions and is dependent on the bond length and bond angle in the Mn-O-Mn chains. Manganese ions play a key role in the formation of magnetic order through the superexchange mechanism; the disruption of ferroelectric ordering occurs at a temperature of 770 K and is accompanied by a structural transition from monoclinic to orthorhombic syngony [14-16].

In [17], thermally induced structural and magnetic transitions in the $BiFe_{1-x}Mn_xO_3$ system were investigated and a preliminary phase diagram of this system was constructed. It is also shown that the ratio of iron and manganese is a determining factor in the formation of magnetic ordering in this solid-solution system over a wide temperature range. In this regard, the electronic and magnetic properties of a $BiFeO_3$-$BiMnO_3$ solid solution with equal concentrations of iron and manganese (bismuth ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$) are of particular interest. $BiFe_{0.5}Mn_{0.5}O_3$ solid solution is the most representative composition of the $BiFeO_3$-$BiMnO_3$ system, as it is characterized by an equal content of iron and manganese ions, which determine its magnetic properties, as well as bismuth ions, which are responsible for the formation of an electric dipole moment. Thus, the $BiFe_{0.5}Mn_{0.5}O_3$ solid solution corresponds to the optimal chemical composition of the $BiFeO_3$—$BiMnO_3$ solid-solution system, which belongs to the class of magnetoelectrics. To date, there is no information in scientific publications on a systematic study of bismuth ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$. Thus, there is practically no data on the magnetic moments of iron and manganese ions, and little information on the nature of the localization of their 3*d* states and the width of the energy gap for ferroman- ganites with different spin orientations of transitionmetal ions.

The aim of this work is to study the electronic structure and analyze the orbital populations of bismuth ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$ by modeling using quantum-mechanical methods (ab initio methods).

EXPERIMENTAL

Bismuth ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$ is characterized by an orthorhombic structure, with the unit cell consisting of 80 ions [17, 18], which significantly complicates the quantitative study of its properties by quantum-mechanical modeling. One possible solution to this problem may be the use of so-called model systems, i.e., polymorphic phases of the compound under study, containing a smaller number of ions in the unit cell. In the case under consideration, the rhombohedral structure of bismuth ferromanganite $BiFe_x Mn_{1-x} O_3$, in which the unit cell contains only 10 ions, can act as a model system. The quantitative estimates obtained for such a structure can be qualitatively transferred to the case of the orthorhombic phase. The proximity of the ionic radii of Fe^{3+} and Mn^{3+} allows us to consider the $BiFe_{0.5}Mn_{0.5}O_3$ compound not only as isomorphic $BiFeO_3$, but also iso- structural to it; therefore, for modeling, the unit cell was constructed from experimental data for $BiFeO_3$ with the replacement of one iron ion by a manganese ion [17]. However, in this case, magnetic sublattices of iron and manganese with opposite directions of the spin magnetic moments are formed, and each of the sublattices is characterized by ferromagnetic ordering, whereas in the initial $BiFeO_3$, the sublattice of iron ions has antiferromagnetic ordering.

From a crystal-chemical point of view, it is necessary to construct a supercell in which the magnetic sublattices of iron and manganese will have antiferromagnetic ordering. The minimal supercell satisfying this condition is a doubled unit cell. Therefore, in order to correctly describe the system within the framework of the mathematical model, a supercell of size 2 x 1 x 1 was constructed, for which self-consistent calculation and subsequent analysis of the properties were carried out. The lattice parameters and ion positions in it were chosen in accordance with experimental data for $BiFeO_3$, since conducting structural optimization (relaxation) of the system under study can introduce additional uncertainty when extending the results of the study of the rhombohedral structure to the orthorhombic one. The effect of the substitution of iron by manganese on the structural parameters was not taken into account due to its expected insignificance.

Numerical modeling was carried out within the framework of the density-functional theory and pseudopotential implemented in the OpenMX software package [19—21]. The convergence criterion for calculating the self-consistent field was 10^{-9} eV/ion. Integration in the first Brillouin zone was performed over a Γ-centered regular grid of *k* points measuring 3 x 5 x 5. The grid for numerical integration was chosen such that the average value of the cutoff energy was 80 Hartree. The pseudopotentials included valence 5*d*-, 6*s*-, and 6*p* electrons for bismuth; 3*p*-, 3*d*-, and 4*s* electrons for iron; 3*s*-, 3*p*-, 3*d*-, and 4*s* electrons for manganese; and also 2*s*- and 2*p* electrons for oxygen. Numerical modeling was carried out within the framework of the generalized gradient approximation and the exchange-correlation functional *PBE*, which was proposed in the work [22]. To more accurately account for the Coulomb correlation of *d* electrons of iron and manganese, the Hubbard correction $U = 5.8$ eV for iron and $U = 5.2$ eV for manganese in a simplified rotationally invariant form, which corresponds to published data [23—25], was used. The density of electronic states was calculated using the tetrahedron method on a Γ-centered regular grid of *k* points measuring 3 x 6 x 6. Population analysis was carried out according to Mulliken and Voronoi.

RESULTS AND DISCUSSION

The model structure of bismuth ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$ is shown in Fig. 1. The magnetic moments of iron and manganese ions are antiparallel for antiferromagnetic ordering. The supercell lattice parameters are: $a = 10.992$ A, $b = c = 5.496$ A, and the interaxial angles are equal and amount to 62.01°. The simulation showed that the system under study has a small magnetic moment (~0.024 LIB per supercell), which is more than an order of magnitude greater than the calculation error. In fact, the obtained value of the magnetic moment can be interpreted as weak ferromagnetism, which is a consequence of the structural design of the supercell of rhombohedral $BiFe_{0.5}Mn_{0.5}O_3$. For the constructed configuration, the replacement of iron ions by manganese ions upon the transition from $BiFeO_3$ to $BiFe_{0.5}Mn_{0.5}O_3$ leads to violation of the original symmetry of the $BiFeO_3$ unit cell and nonconservation of the equality of the numbers of spin-up and spin-down states.

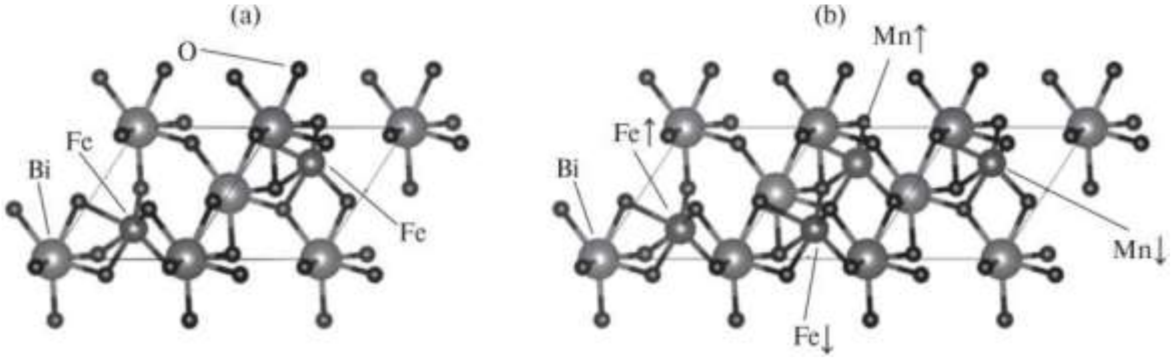

Fig. 1. Visualization of the model structures used: (a) is the unit cell of BiFeO$_3$ with rhombohedral axes; (b) is the BiFe$_{0.5}$Mn$_{0.5}$O$_3$ supercell size 2 x 1 x 1 (arrows shows the magnetic-moment direction).

It should be noted that weak ferromagnetism also affects the density of electronic states, resulting in some asymmetry (Fig. 2). The energy-gap width is 1.28 and 1.48 eV for the spin-down and spin-up states, respectively. The valence band is predominantly formed by O2*p* states with a small admixture of other ions. In this case, the interband transitions for both spin channels are probably of the indirect-band type. To clarify this, further calculations of the dispersion of electron bands along special points of high symmetry of the first Brillouin zone are required, which is not the purpose of this work.

Near the top of the valence band for spin-down states, a narrow band (0.2—0.3 eV) is observed, formed by the contribution of oxygen and manganese ions, which indicates a connection between the magnetic moment of manganese ions and nearby oxygen ions. The conduction band is formed by the 3*d* states of iron ions with a small admixture of the 3*d* states of manganese ions, localized in the form of three narrow bands with a width of 0.2—0.4 eV near the bottom of the band, which is consistent with the results obtained for BiFeO$_3$ [23]. With increasing energy, asymmetric extended bands of the 3*d* states of manganese ions practically without iron impurity 3*d* states are observed, which indicates the manifestation of orbital order inherent in BiMnO$_3$. However, due to the large distance between manganese ions (6.63 A), the indirect mechanism is not sufficient to establish long-range order leading to ferromagnetic ordering, as in BiMnO$_3$. The only interaction observed is between the *d* orbitals of manganese and the *p* orbitals of oxygen, which leads to polarization of the latter and a nonzero magnetic moment.

The analysis of orbital populations allows not only to study the features of the electronic structure of an atom during the transition from a free state to a chemically bound state, but also to determine the value of the atomic magnetic moment. The most common population analysis is Mulliken population analysis, the basic idea of which is to decompose the electron density in such a way that the overlap population is divided equally between nearby atoms. We note that the overlap population is not equivalent to the overlap integral, although it includes the latter. The difference in the sums of the populations of all pseudo-atomic orbitals with different spin orientations gives the magnetic moment of the atom. Since this method is developed for analysis of the electronic structure of finite systems, the quantitative results obtained in the case of periodic systems, especially those including magnetic ions, should be taken into account with possible inaccuracies of the approximation. As an additional tool, one can use Voronoi population analysis, which involves integrating the electron density over the Voronoi (Voronoi—Dirichlet) polyhedra that fill the crystalline space. In this case, the problem of the influence of the completeness of the basis on the population that arises when using the Mulliken approach is removed, since integration is carried out over the electron density within the framework of a polyhedron, the volume of which (the Voronoi volume) depends on the distance between atoms and does not depend on the presence of translational symmetry. The results of population analysis using both methods are presented in Table 1.

The values of the effective charge of magnetic ions are close for both methods, while for bismuth and oxygen ions it is underestimated, although the sign is determined correctly. Voronoi population analysis restores the effective charges of bismuth and oxygen, slightly changing the effective charges of magnetic ions. A combined analysis of the populations shows that bismuth and oxygen are predominantly involved in the formation of the chemical bond, while iron and manganese form the magnetic order. The atomic magnetic moments for bismuth are negligible for both methods, whereas in the case of oxygen they increase by about an order of magnitude. At the same time, according to Mulliken, the atomic magnetic moment of manganese is 0.6 $\text{ц}_\text{в}$ greater than that of iron, which is explained by the greater value of the overlap integral due to the orientation of *d* orbitals of manganese ions

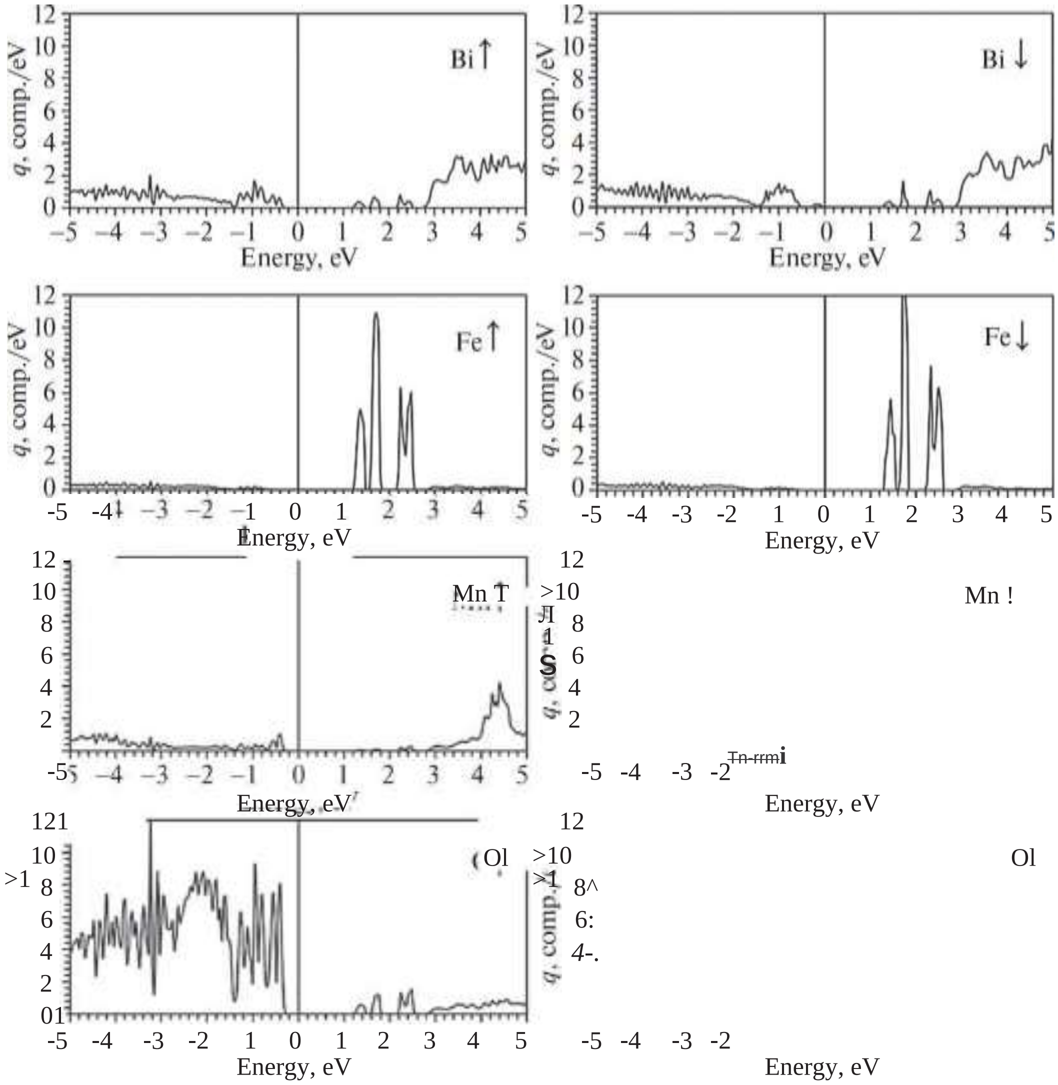

Fig. 2. Atomic-projected spin-allowed density of electronic states q in BiFe$_{0.5}$Mn$_{0.5}$O$_3$ (the top of the valence band for spin-down states is taken as zero).

in the direction of oxygen atoms. In the case of iron this does not happen, which is confirmed by the values of the atomic magnetic moments in Voronoi analysis, where the difference between the magnetic moments between manganese and iron decreases by an order of magnitude. This suggests that there is orbital order in the first coordination sphere of manganese, as in the case of BiMnO$_3$; however, due to the large distance between

Table 1. Analysis of average values of populations and magnetic moments of ions according to Mulliken and Voronoi

Ion	Average effective charge value		Atomic magnetic moment >>	
	according to Mulliken	according to Voronoi	according to Mulliken	according to Voronoi
Bi	+0.18	+2.40	0.023	0.012
Fe	+ 1.26	+ 1.68	4.650	4.160
Mn	+ 1.31	+ 1.56	5.250	4.230
O	-0.66	-1.34	0.112	0.086

manganese ions, it is not enough to form ferromagnetic ordering in $BiFe_{0.5}Mn_{0.5}O_3$ due to the competing magnetic order formed by iron ions.

CONCLUSIONS

Ab initio methods allow us to investigate the electronic structure and magnetic properties of rhombohedral bismuth ferromanganite $BiFe_{0.5}Mn_{0.5}O_3$, which is a substitutional solid solution in the $BiFeO_3$—$BiMnO_3$ system. This structure is a model for the orthorhombic solid solution $BiFe_{0.5}Mn_{0.5}O_3$ and allows the obtained results to be extended to it with significantly lower computational costs.

Studies have shown that Mulliken population analysis is less applicable for both assessing the effective charges of ions and their atomic magnetic moments, which is due to the structural features of the compound under study and the presence of orbitally polarized ions with different occupancies of *d* orbitals. For a more accurate assessment of the values of the specified characteristics, it is recommended to use Voronoi population analysis, which shows that the magnetic moments of iron and manganese ions are close (4.16 and 4.23 MB respectively). This is what should be expected for antiferromagnetic ordering. Analysis of the population of the electronic states showed that the 3*d* states of iron ions are localized, and the 3*d* states of Mn ions are delocalized and asymmetric. The detected small resulting magnetic moment of the unit cell (0.024 MB on the supercell) is caused by the nonequivalence of the positions of iron and manganese ions, which leads to the formation of an energy gap with a width of 1.28 and 1.48 eV for spin-down and spin-up channels, respectively.

The obtained results make it possible to establish the factors that determine the type of structural distortions, the nature of exchange interactions between iron and manganese ions and their magnetic moments. This significantly expands existing knowledge about the structure and properties of $BiFeO_3$—$BiMnO_3$ magnetoelectric compounds.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflict of interest.

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