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# BiFeO<sub>3</sub> Electronic Band Structure Calculations

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Bismuth ferrite belongs to magnetoelectric compounds which join, in the same crystal phase, two mutually excluding order parameters like magnetic and ferroelectric. In case of BiFeO<sub>3</sub> both of these transition temperatures are considerably above room temperature what is important from the point of view of applications. In this paper electronic band structure calculations are presented. In the calculations, hybrid exchange interaction potential is applied, which gives the possibility to obtain correct insulating character of the compound without application of arbitrary Hubbard  $U$  parameter. The calculated densities of electronic states and magnetic properties are described.

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## 1. Introduction

Magnetoelectrics belong to a wider group of the multiferroic materials. Multiferroics are the materials that exhibit more than one ferroic order parameter simultaneously, like ferromagnetism, ferroelectricity, ferroelasticity, or ferrotoroidicity [1]. Magnetoelectrics are materials that exhibit, in the same phase, magnetic and electric orderings and are characterized by the existence of a coupling between magnetic and electric systems which is pronounced by a magnetoelectric effect.

One of the most important and widely studied magnetoelectric is bismuth ferrite BiFeO<sub>3</sub>. This is among only a few compounds which have electric polarization and magnetic order at room temperature. The ferroelectric Curie temperature is considerably high and is approximately,  $T_C = 1100$  K. At room temperature, bismuth ferrite is a G-type antiferromagnet and is in this magnetically ordered state up to the Néel temperature,  $T_N = 643$  K [1].

Bismuth ferrite, at room temperature, adopts an  $R\bar{3}c$  rhombohedral (no. 161) structure. The unit cell in the hexagonal coordinate system (Fig. 1a) is indeed distorted perovskite-like crystal structure and belongs to trigonal perovskites, typified by the (3, 3) phase LaAlO<sub>3</sub> at room temperature. The unit cell is the result of a rotation of FeO<sub>6</sub> octahedra about a trigonal axis normal to a triangular octahedron face, compared to the cubic parent structure [2]. In hexagonal unit cell contains six formula units with lattice parameters  $a = 5.5787$  Å and  $c = 13.8688$  Å ( $a_r = 5.6343$  Å,  $\alpha_r = 59.348^\circ$  in rhombohedral coordinates) [3].

The aim of the paper is to present the usefulness of one-parameter on-site hybrid exchange correlation potential in correct description of strongly correlated  $3d$  electrons in oxides. According to our knowledge, this is the first report that describes the application of the potential to BiFeO<sub>3</sub>.

## 2. Experimental procedure

The electronic band structure was calculated by the *ab initio* self-consistent full-potential linearized augmented plane waves (FLAPW) method, as implemented in the WIEN2k code [4]. The generalized gradient approximation (GGA) in the parameterization of Perdew–Burke–Ernzerhof, revised for solids (PBEsol) [5], was employed. Since it is well known that GGA method does not treat very well strongly correlated electrons such as  $d$ -electrons in oxides, the one-parameter on-site hybrid functional method has been used for iron  $3d$  orbitals [6]. The advantage of the method over conventional GGA+ $U$  is that the results of the calculations are not dependent on the value of the Hubbard parameter  $U$ . The iron magnetic moments were set antiparallel to obtain antiferromagnetic solution of G-type. The crystal structure parameters and atom positions were set according to the data presented in [3]. The BiFeO<sub>3</sub> unit cell ( $R\bar{3}c$ ) and magnetic moments alignment used in the calculation are presented in Fig. 1a.

## 3. Results and discussion

Calculation of total and partial spin resolved electronic density of states (DOS) are presented in Fig. 1b. The valence band is split into two regions. The lower one which is narrow and starts at about  $-6.5$  eV and ends around  $-5$  eV, is formed mainly by  $s$  and  $p$  states of O

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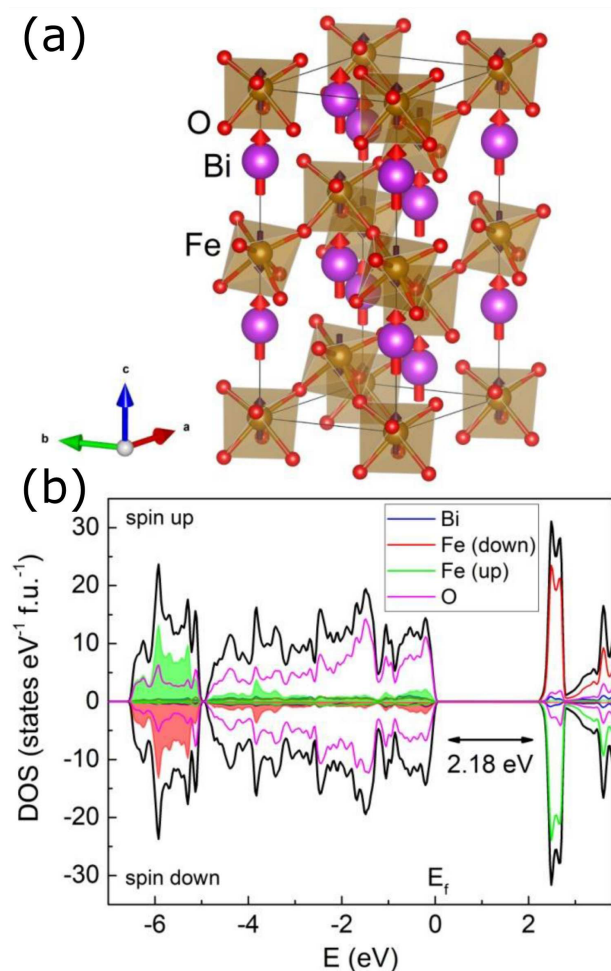


Fig. 1. (a)  $\text{BiFeO}_3$  unit cell (red arrows — direction of electric polarization, black arrows — magnetic moments alignment), (b) calculated density of states (DOS).

which is hybridized with  $d$  states of Fe. The hybridization suggests existence of covalent contribution in Fe–O bond. The upper and much wider band ranges from about  $-5$  eV up to the Fermi level and is formed mostly by  $s$  and  $p$  states of oxygen with a minor contribution of electronic states, originated from the rest of atoms. The shapes of the DOS curves of all electrons of the valence band are similar with similar position of the maxima. This is probably the reason of very strong mixing of these electrons and formation of chemical bonds. The valence band is separated from a conduction band by 2.18 eV energy band gap. This confirms the insulating character of  $\text{BiFeO}_3$  and is in a good agreement with experimental data 2.36–2.50 eV [7].

The spin up and spin down resolved bands are mutual mirror reflections, which is characteristic for antiferromagnetic behavior. The calculated iron spin magnetic moment is  $4.033 \mu_B$  and is in reasonable agreement with the value of  $3.75 \mu_B$  measured from neutron diffraction [2]. The magnetic moments are not integer values due to hybridization of iron cations with neighboring

oxygen. Because of the hybridization, small magnetic moment is induced at O with value of  $0.048 \mu_B$ . Due to similar reasons, even smaller magnetic moment of about  $0.003 \mu_B$  is evidenced on Bi. The induced magnetic moments are polarized along the same direction as the nearest iron moment. This leads to total compensation of the magnetic moments and total unit cell magnetic moment is vanished.

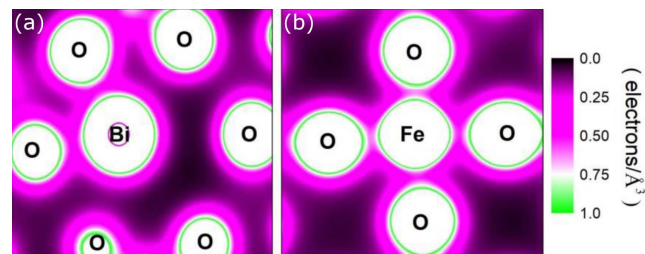


Fig. 2. Valence electrons density maps in first coordination shells of Bi, Fe.

Valence electrons density maps in first coordination shells of Bi and Fe are shown in Fig. 2. It can be easily observed that in a region between the metal cations and oxygen atoms, there is no vanishing electron density in the middle, in the direction of chemical bond formation. This indicates partial covalent character of the bonds [8].

#### 4. Conclusion

The electronic band structure calculations were conducted for  $\text{BiFeO}_3$  to study chemical bonding, magnetic, and electric properties. The partially covalent character of Fe–O bond was confirmed and strong hybridization of all electrons in the valence band were observed. The used exchange correlation potential is able to correctly predict the isolating character of the studied compound with the energy band gap of about 2.18 eV without usage of arbitrary  $U$  parameter. The calculated magnetic properties confirmed antiferromagnetic character of the compound with iron magnetic moment of about  $4.03 \mu_B$ .

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