Bonding Analysis of $BiFeO_3$ Substituted by Gd^{3+}

M. Pugaczowa-Michalska* and J. Kaczkowski

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

We present results of first-principles calculations for $Bi_5GdFe_6O_{18}$ compound in idealized the rhombohedral $R3c$ structure for a variety of magnetic ordering. Within DFT+U approach it is found that the insulating ground state with the G-type antiferromagnetic arrangement of Fe sublattice gives a minimal total energy for $BiFeO_3$ substituted by magnetically active Gd^{3+}. The $Bi_5GdFe_6O_{18}$ compound has nonzero total magnetic moment, which arises from antiparallel spin moments on Fe sites and reduced spin moment on Gd. Chemical bonding of the studied compound is analyzed using partial density of states, electron localization function and charge density distribution.

1. Introduction

$BiFeO_3$ is mentioned in literature as a prime candidate for device integration for spintronics applications due to strong coupling between the magnetic and electric degrees of freedom [1, 2]. In $BiFeO_3$ the magnetization comes from the partially filled $3d$ orbitals of the Fe^{3+} ions and the magnetic ordering exists up to $T_N = 640$ K, while the polarization is mostly caused by the lone pair of Bi^{3+} (s^2 orbital) and ferroelectric ordering survives up to $T_C = 1100$ K. Bulk $BiFeO_3$ has distorted rhombohedral perovskite structure with the space group $R3c$ which is noncentrosymmetric and has a G-type antiferromagnetic (AFM) order. The small canting of the Fe moments caused by the local magnetoelectric coupling to the polarization leads to a cycloid-type spacial spin-modulation. Unfortunately, this AFM order in $BiFeO_3$ prevents the observation of any net magnetization and the linear magnetoelectric effect in the bulk material. However, numerous investigations show that the partial ionic substitution is necessary for obtaining spontaneous magnetization in bulk $BiFeO_3$ [3]. Improvement of electrical, magnetic properties like induced magnetization, structure modification of $BiFeO_3$ have been achieved by minor substitution of Bi^{3+} by lanthanides ions. The effect of Gd substitution is observed in the magnetic properties as an increase in magnetization compared to the parent $BiFeO_3$. Magnetically active Gd^{3+} caused that ferroelectric and magnetic orders coexist in $Bi_{1-x}Gd_xFeO_3$ ($x = 0.05$, 0.1) at room temperature [4]. The measurements for higher concentration of Gd in $BiFeO_3$ revealed a sequence of the composition-driven structural phase transitions: $R3c \rightarrow Pn2_1a$ (at $x \approx 0.1$) and $Pn2_1a \rightarrow Pnma$ ($0.2 < x < 0.3$) [5]. Taking into account the earlier experimental studies, in this work we discussed the results of the electronic structure calculations of $BiFeO_3$ substituted by Gd ions. Here $Bi_5GdFe_6O_{18}$ has been explored using accurate density functional theory (DFT) calculations on the basis of

30 atoms supercell. The cation was substituted periodically, thus no disorder effects were considered. In our study we assumed the rhombohedral $R3c$ structure of $Bi_5GdFe_6O_{18}$ compound and focused on the possibility of spontaneous magnetization in the studied compound. The analysis of electron localization function and charge density distribution are also presented.

2. Method of calculations

The calculations are performed in the DFT method, which is implemented in the software Vienna *ab initio* simulation package (VASP) code [6, 7]. The exchange-correlation effects are accounted within the Perdew–Burke–Ernzerhof (PBE) functional [8]. In the frame of the DFT+U we have used the rotationally invariant approach of [9]. The choice of DFT+U allows for a correct treatment of the intra-atomic Coulomb interaction among $3d$ and $4f$ electrons. The values of U are assumed: $U = 4.5$ eV for Fe $3d$-electrons and $U = 11$ eV for Gd $4f$. The $R3c$ crystal structure of $Bi_5GdFe_6O_{18}$ is adopted as follows: The unit cell doubling is intrinsic for $R3c$ due to the counter-rotations of the two oxygen octahedra that are coupled with the polar displacement along [111]. The calculation unit cell contains six formula units of $BiFeO_3$, thus the final supercell contains 30 atoms. One Gd ion substituted in the place of the Bi ion. The final relaxation was for all atomic position and volume of the supercell. The other details of calculation were similar to [10].

3. Results

In order to clarify the magnetic ground state properties of $Bi_5GdFe_6O_{18}$ the following configurations are considered: (1) nonmagnetic (NM), (2) ferromagnetic (FM), (3) antiferromagnetic (AFM). In the third case we assume the G-type of antiferromagnetic ordering in the studied supercell of $Bi_5GdFe_6O_{18}$. Both intra-plane and inter-plane coupling between atoms are antiferromagnetic at the G-type. In practice $BiFeO_3$ is observed to be nearly G-AFM. The introduction of rare-earth substituent can change the anisotropy constant, thus, the presence of the spatially modulated structures would be energetically unfavorable [3]. The examination

———————

*corresponding author; e-mail: maria@ifmpan.poznan.pl

of collinear magnetic structure in $BiFeO_3$ doped by Gd atoms is acceptable from this point of view.

Our results suggest that the collinear *G*-AFM spin arrangements will lower the energy of the systems. The energy of $BiFeO_3$ for *R3c* with *G*-AFM is at least 3.159 eV/f.u. lower than with PM and lower about 0.239 eV/f.u than with FM order in the cell. Upon substitution Bi by Gd an insulating behavior of $Bi_5GdFe_6O_{18}$ is maintained, giving a calculated band-gap at least of 1.78 eV.

Figure 1 presents the calculated total and partial orbital-resolved densities of states (DOS) of $Bi_5GdFe_6O_{18}$ for *G*-AFM. There are two groups of bands in the valence energy region (−8 eV; 0 eV). The lower part of spin-polarised subbands (−8 eV; −6 eV) is strongly dominated by Fe derived $3d$ states, whereas $2p$ states of O and $6p$ states of Bi build up mainly in the upper parts. The energy position of O $2p$ states overlaps partially with that of Fe $3d$ states. This result indicates that the Fe $3d$ hybridizes in a certain extent with O $2p$ below the Fermi level (FL). This is similar to the fluorescence spectra obtained for $BiFeO_3$ by Higuchi et al. [11]. The presence of magnetically active Gd ions in $BiFeO_3$ leads to an asymmetry between the spin-up and the spin-down electronic states of the studied $Bi_5GeFe_6O_{18}$. The Gd contribution to the DOS as a sharp peak we can see in the majority DOS at the energy about −7 eV. The position of unoccupied $4f$ states of Gd in the DOS is at 5 eV above the Fermi level. The macroscopic magnetic states of the stud-
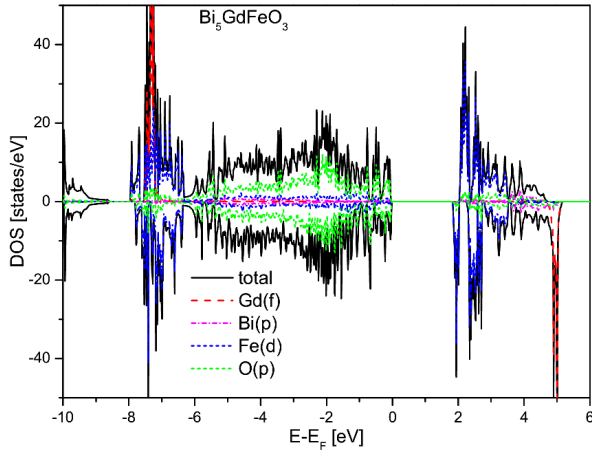
ture on the Fe subsystem as well as the lone pair electrons are presenting at Bi sites, one could expect anisotropy in the exchange interaction.

Our calculations for $Bi_5GdFe_6O_{18}$ suggest that the presence of Gd atom can change local magnetic moment on the Fe sites, in comparison with $BiFeO_3$. For parent $BiFeO_3$ the net magnetic moment at the Fe site is around 4.3 μ_B. The local magnetic moment at Fe is varying between ±4.09 μ_B and ±4.07 μ_B in $Bi_5GdFe_6O_{18}$. The spin magnetic moment of Gd is about 1.021 μ_B. To shed a light on the very essence of the bonding created in $Bi_5GdFe_6O_{18}$ we discuss below a charge density and an electron localization function (ELF) pictures. The charge density (Fig. 2a) reveals that the bonding between Fe and O atoms has mixed ionic-covalent nature. In general, such mixed ionic-covalent character of the Fe–O bond may lead to ferroelectricity in materials. The DOS (discussed above) may be an evidence of dominant ionic bonding between the Fe and O atoms with some covalent character. The finite charges between Bi and O as well as between Gd and O confirm the presence of finite covalent bonding between these atoms. The presence of pure ionic bonding between atoms prevents ferroelectricity because short-range repulsion between nearest neighbors ions is stabilized for symmetric structures. Ravindran et al. [13] emphasize that the existence or absence of ferroelectricity is determined by a balance between short-range repulsions, which favor the nonferroelectric symmetric structure and additional bonding considerations which act to stabilize the distortions necessary for ferroelectric phase of $BiFeO_3$.

The picture of ELF is very useful for separation of the spatial regions characterizing the shared-electron interaction like in covalent and metallic bonding, and the unshared-electron interaction such as ionic bonding. The ELF first introduced in [14] as measure of the probability of finding an electron in the neighborhood of another electron with the same spin. The ELF can be expressed as

$$ELF = \left(1 + \left(\frac{D(r)}{D_h(r)}\right)^2\right)^{-1},$$

where D is the kinetic energy of the system under study and D_h is the kinetic energy of a homogeneous electron gas.

D has the physical meaning of the excess local kinetic energy density due to the Pauli repulsion. Where electrons are alone or form pairs of antiparallel spin, the excess local kinetic energy has a low value and ELF is close to 1. However, the excess local kinetic energy has a large value if the probability of finding parallel spin electrons close together is high. In this situation the ELF is small. In the absence of significant electronic populations, ELF dwindles to zero. The ELF plot for $Bi_5GdFe_6O_{18}$ is displayed in Fig. 2b. The isosurface (Fig. 2b) enclosed points for which ELF > 0.8.
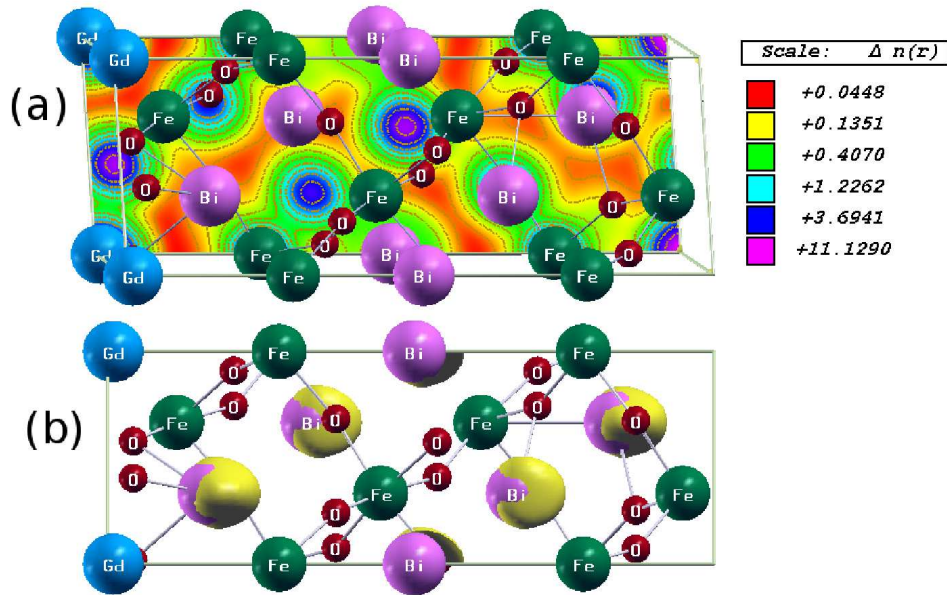

Fig. 1. Spin-resolved total and partial DOS of $Bi_5GdFe_6O_{18}$ in AFM states.

ied $Bi_5GdFe_6O_{18}$ originate from two distinct sublattices of spins. The Fe transition metal provides one sublattice, which mainly consist of $3d$ spins, and the Gd gives rise to a second sublattice with spins mainly localized in the $4f$ shell. We call attention to the fact that Gd^{3+} ions are magnetically active and possess their own large magnetic moment ($m_{eff} = 7.9 − 8$ μ_B). The magnetic moments of Gd ions are aligned by exchange coupling with Fe subsystem (f–d exchange interaction). The magnetic order on the Gd substituted ions can modify the electronic struc-

Fig. 2. (a) Valence electron charge density calculated for $Bi_5GdFe_6O_{18}$, (b) Isosurface of the ELF of $Bi_5GdFe_6O_{18}$ for value 0.8. Charge density and ELF was visualized by using XCrysDen software [12].

In $Bi_5GdFe_6O_{18}$ we have combination of large value of ELF as well as the presence of finite covalent bondings between Bi and O atoms. Both features lead to a stronger lone pair, which is more stereochemically active. The anisotropic nature of electrons at Bi sites observed on studied system gives rise to the tendency to the ferroelectric distortion.

4. Conclusions

The magnetic ground state of $Bi_5GdFe_6O_{18}$ ($R3c$ structure) has nonzero total magnetic moment. The total magnetic moment of $Bi_5GdFe_6O_{18}$ arises from an antiparallel arrangement of spin moments on Fe sites and reduced moment on the Gd site. The presence of magnetically active Gd ions in the studied $Bi_5GdFe_6O_{18}$ leads to an asymmetry between spin-up and spin-down DOS. The calculated DOS gives evidence of insulating character of the ground state of $Bi_5GdFe_6O_{18}$. In comparison with $BiFeO_3$ our calculations showed that the value of the band gap in $Bi_5GdFe_6O_{18}$ is above 1.78 eV. The bonding between the atoms in $Bi_5GdFe_6O_{18}$ is not purely ionic. The analysis of partial DOS together with charge density and ELF lead to the conclusion that covalent character of bonding between Fe and O, between Bi and O, between Gd and O atoms reveals in the charge density picture. The obtained ELF of $Bi_5GdFe_6O_{18}$ exhibits that the $6s^2$ lone pair of Bi^{3+} ions still played important role in chemical bonding and may give rise to the ferroelectric distortion.

Acknowledgments

References

[1] H. Béa, M. Bibes, S. Cherifi, F. Nolthing, B. Warot-Fonrose, S. Fusil, G. Herranz, C. Deranlot, E. Jacquet, K. Bouzehouane, A. Barthélémy, *Appl. Phys. Lett.* **89**, 242114 (2006).

[2] L.W. Martin, Y.-H. Chu, Q. Zhan, R. Ramesh, Shu-Jen Han, S.X. Wang, M. Warusawithana, D.G. Schlom, *Appl. Phys. Lett.* **91** 172513 (2007).

[3] A.M. Kadomtseva, Yu.F. Popov, A.P. Pyatakov, G.P. Vorob'ev, A.K. Zvezdin, D. Viehland, *Phase Transit.* **79** 1019 (2006).

[4] P. Uniyal, K.L. Yadav, *Mater. Lett.* **62** 2858 (2008).

[5] V. Khomchenko, V. Shvartsman, P. Borisov, W. Kleemann, D. Kiselev, I. Bdikin, J. Vieira, A. Kholkin, *Acta Mater.* **57**, 5137 (2009); *Appl. Phys. Lett.* **93** 262905 (2008).

[6] G. Kresse, J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

[7] G. Kresse, D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).

[8] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[9] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).

[10] M. Pugaczowa-Michalska, J. Kaczkowski, A. Jezierski, *Ferroelectrics* **461**, 85 (2014).

[11] T. Higuchi, Y.-S. Lui, P. Yao, P.-A. Glans, J. Guo, C. Chang, A. Wu, W. Sakamoto, N. Itoh, T. Shimura, T. Yogo, T. Hattori, *Phys. Rev. B* **78**, 085106 (2008).

[12] A. Kokalj, *Comput. Mater. Sci.* **28**, 155 (2003).

[13] P. Ravindran, R. Vidya, A. Kjekshus, H. Fjelvåg, O. Eriksson, *Phys. Rev. B* **74**, 224412 (2006).

[14] A.D. Becke, K.E. Edgecombe, *J. Phys. Chem.* **92**, 5397 (1990).