Signature of half-metallicity in BiFeO$_3$

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BiFeO$_3$ has drawn a great attention over last several decades due to its promising multiferroic character. In the ground state the bulk BiFeO$_3$ is found to be in the rhombohedral phase. However, it has been possible to stabilize BiFeO$_3$ with tetragonal structure. The importance of tetragonal phase is due to its much larger value of the electric polarization and the possible stabilization of ferromagnetism as in the rhombohedral phase. Furthermore, the tetragonal structure of BiFeO$_3$ has been reported with different $c/a$ ratio, opening up the possibility of a much richer set of electronic phases. In this work, we have used density functional theory based first-principle method to study the ferromagnetic phase of the tetragonal BiFeO$_3$ structure as a function of the $c/a$ ratio. We have found that as the $c/a$ ratio decreases from 1.264 to 1.016, the tetragonal BiFeO$_3$ evolve from a ferromagnetic semiconductor to a ferromagnetic metal, while passing through a half-metallic phase.

This evolution of the electronic properties becomes even more interesting when viewed with respect to the volume of each structure. The most stable half-metallic phase initially counter-intuitively evolve to the magnetic-semiconducting phase with a reduction in the volume, and after further reduction in the volume it finally becomes a metal. So far, this type of metal to insulator transition on compression was known to exist only in alkali metals, especially in Lithium, in heavy alkaline earth metals, and in some binary compound.

I. INTRODUCTION

The discovery of the unusual electronic property, commonly known as half-metallic ferromagnetism, in Mn-based Heusler alloys [1] had started an intense research to find the existence of it in other materials both theoretically as well as experimentally, which continues unabated till today. In a half-metal, the Fermi energy is populated by electrons with only one type of spin character, either up or down. This unique character of the charge carriers of a half-metal makes it one of the most suitable candidate for the spintronic devices [2 3]. Half-metallic ferromagnetic phase are mostly found in Heusler alloys, and in some zinc-blende structures, colossal-magnetoresistance materials, transition metal dioxides, double perovskites and sulfides [4]. More recently, existence of half-metallicity has been predicted in some Fe based perovskites such as,(BaFeO$_3$) [5] and (CaFeO$_3$) [6]. While the half-metallicity has been found in bulk (BaFeO$_3$) at ambient pressure, it is found in the surface states of (CaFeO$_3$). In a parallel development, the search for a suitable material with the possibility of external electrical control had been quite intense for last couple of decades and multiferroic materials, especially Bismuth Ferrite ((BiFeO$_3$)), has emerged as one of the most promising candidate in this endeavor. The coexistence of coupled magnetic order and electric polarization has catapulted BiFeO$_3$ (BFO) as one of the leading contenders in this race. BFO has been found in various forms having different crystal symmetries [7 8]. In its ground state, bulk BFO has R3c symmetry with a rhombohedral perovskite structure. It has a large electric polarization along the [111] direction of the pseudocubic unit cell along with a G-type anti-ferromagnetic ordering of Fe$^{3+}$ spins. The anti-ferromagnetic ordering is superimposed with a long-wavelength cycloidal modulation [9 12]. BFO started receiving intense attention ever since the possibility of weak ferromagnetism (FM) induced by the Dzyaloshinski-Moriya interaction was predicted [13 14] in this R3c structure. However, the cycloidal modulation forces the spins to cant which induces a spin-density-wave instead of the uniform FM state. A crucial step to obtain the uniform FM phase is to suppress the cycloidal modulation of the spins. There are evidences that this modulation can be suppressed in thin films [19]. A large magnetic field can achieve this in the bulk BFO as well [13 15]. In 2003, magnetic moments as large as 1$\mu_B$/Fe [10] was reported in heteroepitaxially constrained BiFeO$_3$ thin film while others [17 19] claim to find much smaller or even non-existent FM moments in this system. However, there are further experimental evidences in favor of the weak FM in BFO films [20].

Although, the existence of large ferromagnetic moment in the rhombohedral BFO (R-BFO) is still a debated issue, there are growing experimental evidences that BFO can host FM moments [21] and it could be quite large under certain conditions. Interestingly, the heteroepitaxially constrained BFO structure belongs to $P4_{2}nm$ space group with a body centered tetragonal unit cell. In a subsequent first-principle based calculation, Ederer and...
Spaldin [23] predicted the thin-film tetragonal (T) BFO structure with G-type anti-ferromagnetic (G-AFM) ordering to have much larger ferroelectric polarization as (≈ 150µC/cm²) compared to the R phase. Furthermore, using strain induced calculation, they have studied all the types of anti-ferromagnetic ordering in T-BFO [24]. This prediction of larger polarization has been confirmed experimentally [25], although the measurement of the polarization has not been done on pure T-BFO phase, but rather on the mixed phase of T-BFO and R-BFO.

The tetragonal structure is metastable [7], with the possibility of a wide range of c/a ratio [8, 16, 26–28]. Major efforts have been devoted to understand and to enhance the electric polarization in the T-BFO structure [27, 28]. However, the issue of ferromagnetism has not been explored in pure T-BFO structure as extensively as in the case of R-BFO phase, although, there are density-functional theory (DFT) based first principle calculations on doped T-BFO systems [29, 30].

In this work, we study the ferromagnetic phase of the T-BFO structure using DFT based first principle calculations. We have systematically studied the four different T-BFO structures (I, II, III and IV), having different c/a ratios and which have already been reported experimentally [16, 27]. The c/a ratio decreases monotonically from structure-I to structure-IV. We have found that in the presence of the uniform FM order, the structure-II is energetically the most stable out of all the four structures. Interestingly, this structure also hosts half-metallicity, while structure-I is a magnetic semiconductor and the other two structures have metallic character. Additionally, we have found that the electrical properties in this system evolves counter-intuitively, i.e., there is a transition from the half-metallic phase of structure-II to the semiconducting phase of structure-I along with a significant decrease in the volume. Half-metallicity has been predicted in doped T-BFO [30] system and in some BFO-based heterostructures [31–33]. However, to the best of our knowledge, this is the first time the half-metallicity is being reported in the pure T-BFO structure.

The paper is organized as follows: we have first discussed the computational details in Sec. II followed by the structural, electronic and magnetic properties in Sec. IIIA, IIIB, IIIC respectively. In Sec. IIID we have discussed...
the role of the molecular orbitals, charge density and hybridization. Finally, we conclude our results in Sec. IV.

II. COMPUTATIONAL DETAILS

To systematically explore the effect of the uniform ferromagnetic state in the T-BFO structure, we have performed DFT-based first-principle calculations by the pseudopotential method as implemented in the Quantum Espresso (QE) package \[34\]. The pseudopotentials with Projected Augmented Wave (PAW) \[35\] type basis sets that have been used in our calculation consists of 15 valence electrons (5d10 6s2 6p3) for bismuth (Bi), 16 valence electrons (3s2 3p6 3d4 4s2) for iron (Fe) and 6 valence electrons (2s2 2p4) for oxygen (O). We have used GGA + U method with Perdew-Burke-Ernzerhof (PBE) \[36\] type exchange correlation functional. An energy cut-off of 80 Ry has been used for the subsequent calculations. The Hubbard U parameter has been taken into account for the Fe-3d orbital and its strength has been set to 4.5 eV. With this choice of the Hubbard U, the theoretical band gap has been found to be reasonably close to the experimentally reported value in T-BFO \[37\] \[38\]. BiFeO3 crystallizes in a tetragonal phase with space group \(P\bar{4}mm\) (99) with different possible \(c/a\) ratios. Since it is well known that in the ground state the magnetic moments are ordered in G-type anti-ferromagnetic arrangement, we have used a \(2 \times 2 \times 2\) supercell (sc) composed of 8 formula units to compare the energies of the FM and G-AFM phases. A \(6 \times 6 \times 6\) Monkhorst-Pack k-point grids \[39\] has been used for the self-consistent calculation. The Methfessel and Paxton type smearing is used with a width of 0.01 Ry \[40\]. Ionic relaxation has been performed with the convergence threshold of the interatomic forces being less than \(10^{-3}\) Ry/bohr. We have used collinear spin-polarized calculation to study the FM phase.

III. RESULTS AND DISCUSSION:

A. Structural properties

In this work, we have used the experimentally reported parameters of the T-BFO unit-cell (\(P\bar{4}mm\) space-group and \(C4v\) point group) \[16\] \[27\]. The highest \(c/a\) ratio is 1.264 (structure-I) \[27\] and for the rest of the structures it is 1.233 (structure-II), 1.049 (structure-III) \[20\] and 1.016 (structure-IV) \[16\]. The lattice parameter ‘a’ of these structures are 3.67, 3.77, 3.88 and 3.93 Å respectively. The ionic relaxations have been performed for all the structures while keeping the lattice constant \(a\) and the \(c/a\) ratio fixed before studying the electronic and magnetic properties. The relaxations have been carried out after imposing the magnetic ordering.

In Fig. II(a), we have shown the unit-cell of the T-BFO. The FeO6 octahedra has been shown in the Fig. I(b), wherein, the axial oxygen has been named as ‘O1’ while the two equatorial oxygen have been designated as ‘O2’ and ‘O3’ respectively. The lattice plane perpendicular to the [001] direction has been pointed out in Fig. I(c). In Fig. II(a), the supercell has been introduced with the oxygen octahedra. The G-AFM and the FM type of spin-orderings, that have been used in our study, have been shown in Fig. II(b) and (c) respectively.

In Appendix A, we have presented relative energies of these four structures with G-AFM and FM type magnetic ordering. We have found that the G-AFM ordering is energetically more favorable than the FM phase irrespective of the \(c/a\) ratio. However, the energy follows a similar pattern in the presence of each type of magnetic ordering, that is, structure-II is energetically most stable for a given type of magnetic ordering, followed by structure-I, structure-III and structure-IV. Since our primary interest is in the nature of the FM phase, in the following sections we present the results of T-BFO with only FM ordering. To understand the relation between the energy of a given structure and its \(c/a\) ratio, we have studied the Fe-Ox-Fe angle, and the O1-Fe and Fe-Ox bond length of...
The total density of states (TDOS) corresponding to the FM phase in (a) structure-I, (b) structure-II, and (c) structure-IV respectively.

The local density of states (LDOS) corresponding to the FM phase in (a) structure-I, (b) structure-II, and (c) structure-IV respectively.

Table I. Top row: The angle Fe-O_e-Fe (in unit degree, °), where O_e is the equatorial oxygen O2/O3. Second row: the bond-length Fe-O1 (in unit Å) Third row: Fe-O_e bond-length (in unit Å). Bottom row: the volume of the unit-cell BFO (in unit Å³).

| Structures | str-I | str-II | str-III | str-IV |
|------------|------|--------|---------|--------|
| c/a ratio  | 1.264| 1.233  | 1.049   | 1.016  |
| Fe-O_e-Fe  | 146.59| 144.01 | 163.31  | 165.04 |
| O1-Fe      | 1.85 | 1.83   | 1.89    | 1.88   |
| Fe-O_e     | 1.92 | 1.98   | 1.96    | 1.98   |
| Volume     | 62.48| 66.07  | 61.27   | 61.67  |

each structure after performing the ionic relaxation. Here O_e represent the equatorial oxygen atoms. These results are presented in Table I. The direct correlation between the energy and the Fe-O_e-Fe angle is quite apparent. Similar to the energy, from structure-I to structure-II, Fe-O_e-Fe angle initially decreases and then it increases monotonically. The bond length between ‘Fe’ and the two type of oxygen, i.e., the axial oxygen O1 and the two equatorial oxygen O_e have also been measured. The O1-Fe bond length decreases slightly from the structure-I to the structure-II and then increases in structure-III. This bond length remains almost unchanged in structure-IV, compared to structure-III. The trend is almost identical with the pattern followed by the energy of each structure, that is, similar to the energy, this bond length is the lowest in the case of structure-II. Interestingly, the structure-II shows the half-metallic character. However, a similar correlation is not observed between the Fe-O_e bond length and the energy. While the Fe-O2 and Fe-O3 bond lengths are observed to be the same, the lowest Fe-O_e bond length is found in the case of structure-I. This bond length increases in structure-II and then remains more or less constant till structure-IV. In the later sections, we are going to explore in detail the relation between the c/a ratio of each structure and its electronic properties.

B. Electronic properties

For a systematic understanding of the electronic properties, we have computed the band structure, total density of states (TDOS), local density of states (LDOS) and
the projected density of states (PDOS) for each structure. In Fig. 3, we have presented the spin-resolved band structure of structure-I, II and IV. The fundamental nature of the band structure of structure-III is identical with the structure-IV, and it has been studied in Appendix B. From the Fig. 3(a), it is clear that for the highest ratio, i.e., in structure-I, no states are available at the Fermi energy from either of the spin channel. However, the band gap is not the same for the two spin channels. The band gap corresponding to the spin-up channel is estimated to be ~0.53 eV, while it is ~1.61 eV for the spin-down channel. The band gaps have been calculated at the zone center. This shows that structure-I is a magnetic semiconductor similar to the R3c phase of BFO [11]. From Fig. 3(c), it is obvious that structure-IV is a metal as both the spin channels contribute states at the Fermi level. A similar behavior is observed in structure-III (Appendix B).

However, in between these two limits of the c/a ratio, in the intermediate structure with c/a = 1.233, i.e., structure-II surprisingly has a non-zero contribution at the Fermi energy only from the spin down channel. This makes the structure-II behave like a half-metal. In this case a band-gap of ~0.89 eV is observed in the spin-up channel. The band structure is presented in Fig. 3(b). A closer look at the systematic change in the electronic properties with respect to the volume of each structure reveals a fascinating phenomena, which has not been reported so far in a pure compound to the best of our knowledge. A simple analysis shows that the volume of the structure-II is the highest, while the structure-I has a lower volume than the structure-II. Structure-III and IV occupy almost the same volume and is less than that of the structure-I. This indicates that the
change from the semiconducting state of the structure-I to the half-metallic phase of the structure-II is quite counter-intuitive, since the volume effectively increases from the structure-I to the structure-II. It is generally expected that under pressure (with reduction of volume), the insulator/semiconductor turns into a metal. Interestingly, our results indicate an opposite trend to this general expectation. Furthermore, the semiconducting state of the structure-II becomes a metal in the structure-III and remains a metal in structure-IV. This change is in tune with the general expectation of the insulator/semiconductor to metal transition under pressure, as the volume of structure-III/IV is lower than that of the structure-II. Interestingly, this kind of metallic to insulating/semiconducting and back to metallic transition has been observed in pure Li, which becomes a semiconductor at 80 GPa [42] and then it becomes a metal once again at 120 GPa [43]. Experimental evidences of this kind of counter-intuitive metal to insulator transition under high pressure have also been reported earlier in Na [44], FCC-Ca [45], [46], and Ni [47], and in the binary compound ClLi4 [48].

The total density of states (TDOS) corresponding to the above mentioned band structures have been shown in Fig. 4. In Fig. 4(a), the TDOS has been presented for the structure-I, and it is clear that a band gap exists for both the spin components, although they are unequal. It is also clear that the band gap is smaller for the spin-up component. The TDOS of structure-II has been presented in Fig. 4(b). While there are no states at the Fermi energy from the spin-up channel, there exists a small but finite number of states from the spin-down component, which is the typical signature of a half-metal. It is clear from the Fig. 4(c), that both the spin components contribute to the conductivity in the case of structure-IV, although the contribution is more from the spin-up component.

In order to examine the orbital contribution of different atoms to the electronic properties in the T-BFO structures, we have computed the local density-of-states (LDOS). These results are presented in Fig. 5. In Fig. 5(a), the results for the structure-I has been presented. It is clear that there are no states at the Fermi energy and there exists a band gap for both the spin channels. However, as the $c/a$ ratio is lowered from structure-I to structure-II, one can observe in Fig. 5(b) that a finite amount of electronic states appear at the Fermi energy. Interestingly, only the spin-down channel of the Bi-6p orbital appears to make the contribution to the TDOS at the Fermi energy. In the molecular orbital analysis (Sec. III D), we have found contributions from the Fe-3d and O-2p orbitals. In Fig. 5(c), we have presented the results for the structure-IV, which is found to be a metal from its band structure. However, there are some interesting features to observe in the charge carriers and its spin type. ‘Bi’, more specifically Bi-6p orbital, contributes electron carriers from both the spin channels, while Fe-3d and O-2p orbitals contribute hole carriers to
the system only from the spin-up channel.

It is important to note that, like the ferromagnetic rhombohedral phase, in Fig. we can also observe an indication of strong hybridization between the Fe-3d and O-2p orbitals in both the valence and the conduction bands. Furthermore, a hybridization can also be observed between Bi-6p and O-2p in the conduction band. The hybridization between Fe-3d and O-2p is mainly found in the spin-up channel of the valence band and in the spin-down channel of the conduction band close to the Fermi energy. It is also important to note that the Bi-6s orbital contribution is found far below the Fermi level at around $-1.5\text{eV}$, which indicates that these Bi-6s lone pair electrons are localized in this system. However, Bi-6s orbital takes part in the hybridization process. In Sec. we have discussed the type of hybridization and the role of specific atomic orbitals in more details.

To further understand the contribution of the individual orbitals, we have calculated the projected density of states (PDOS), and the results have been presented in Fig. From Figs. (a),(d), and (g), it is clear that there is a band gap in both the spin channels. It is also clear that in this structure the band just above the Fermi energy has contributions from Bi-6p$_z$, Fe-3d$_{xz}$ and O1-2p$_z$ orbitals. Interestingly, all of these orbitals belong to the spin-down channel. On the other hand, the band just below the Fermi energy has contributions only from Fe-3d$_{yz}$ and O2-2p$_y$, and O3-2p$_x$. These orbitals belong to the spin-up channel. It is interesting to note that there is no contribution from the Bi atom in this band. Surprisingly, as the $c/a$ ratio is lowered in the structure-II, the spin-down channel of Bi-6p$_z$ moves below the Fermi level. This is very evident from Fig. (b). The spin-down channels of the Fe-3d$_{xy}$ and O1-2p$_z$ orbitals also move below the Fermi energy. However, they have vanishingly small but finite contributions to the PDOS. Their presence has been detected by the molecular orbital study, which has been discussed in Sec. Interestingly, the spin-up channels of the orbitals, which were the closest to the Fermi energy in the structure-I are pushed further down in energy in the structure-II, giving rise to the half-metallic character to the T-BFO. As the $c/a$ ratio is lowered further in the structure-IV, both the spin channels of the Bi-6p$_z$ orbital move further below the Fermi energy, while only the spin-up component of the $e_g$ band of Fe along with the O1-2p$_z$, O2-2p$_y$, and O3-2p$_x$ orbitals crosses over the Fermi level, thereby making the structure-IV a ferromagnetic metal. Furthermore, it is also clear from the Figs. (c), (f) and (i), that ‘Bi’ contributes only electron carriers of both types of spin to the system, while the other orbitals mentioned above contribute only hole carriers, that too from the spin-up channel, to the system. It is also important to note that the Bi-6p$_z$ orbital consistently moves towards the Fermi level from above and then crosses over the Fermi energy as the $c/a$ ratio is decreased gradually. On the other hand, other orbitals systematically moves closer to the Fermi energy from below and finally crosses over with the decrease in the volume from the structure-I to the structure-IV.

| Structures | str-I | str-II | str-III | str-IV |
|------------|-------|--------|---------|--------|
| $c/a$ ratio | 1.264 | 1.233  | 1.049   | 1.016  |
| TM         | 0.0000| 0.0000 | 0.0000  | 0.0000 |
| Bi         | $\pm0.0000$ | $\pm0.0000$ | $\pm0.0000$ | $\pm0.0000$ |
| Fe         | $\pm3.5996$ | $\pm3.6031$ | $\pm3.6152$ | $\pm3.6127$ |
| O          | $\pm0.1823$ | $\pm0.2195$ | $\pm0.1417$ | $\pm0.1343$ |

Table III. Estimation of the total magnetic moment (TM) and the individual magnetic moments (in $\mu_B$) contributed by ‘Bi’, ‘Fe’ and ‘O’ corresponding to the ferromagnetic (FM) phase.

| Structures | str-I | str-II | str-III | str-IV |
|------------|-------|--------|---------|--------|
| $c/a$ ratio | 1.264 | 1.233  | 1.049   | 1.016  |
| TM         | 40.0000 | 40.0000 | 39.9500 | 39.8300 |
| Bi         | 0.0146 | 0.0117 | 0.0071  | 0.0063 |
| Fe         | 3.7300 | 3.6900 | 3.8300  | 3.8200 |
| O          | 0.2240 | 0.2584 | 0.2453  | 0.2450 |

C. Magnetic properties

In this section, we discuss the magnetic properties of the T-BFO structure and its dependence on the $c/a$ ratio. In the FM phase, the total magnetic moment (TM) is found to be around 40 $\mu_B$ for all of the four structures, which also agrees well with the results of the ferromagnetic R3c phase of BFO. Contribution of different atoms to the magnetization in the FM phase are listed in the Table. To understand the crucial differences in the contribution towards magnetization from different atoms compared with the anti-ferromagnetic phase, we have presented a similar analysis for the G-AFM phases in the Table. The major difference that we have found is that in the case of G-AFM phases ‘Bi’ doesn’t contribute anything to the total magnetic moment for all the four structures, while in the case of FM phases it has a finite contribution to the total magnetic moment. This behavior is similar compared to the R3c structure. In the T-BFO, the contribution decreases monotonically with the $c/a$ ratio from structure-I to structure-IV. As expected, Fe’s contribution towards the total magnetic moment has been found to be the largest among all the
atoms in both the FM and G-AFM phases. Furthermore, the Fe’s magnetic moment has been found to be larger in the FM phase, and this trend is also similar to the rhombohedral phase \[41\]. However, in the T-BFO phase Fe’s magnetic moment has been observed to be lower compared to the rhombohedral phase.

A similar scenario is found in the case of ‘O’ atom as well, which agrees with the R3c structure, i.e., it contributes much more towards the total magnetization in the FM phase as compared to the G-AFM phase \[41\]. However, in comparison to the rhombohedral structure, the magnetic moment of the ‘O’ atom is significantly higher in the G-AFM phase of the T-BFO structure, while they are comparable in the FM phase. In this phase, in the case of structure-IV and structure-III, the TM is less than \(40\ \mu_b\), while in the structure-II it is exactly \(40\ \mu_b\). This is consistent with our conclusions based on the band structure and the TDOS results presented in Figs. 3(a), (d), and (g). In the LUMO, i.e., in Fig. 6(b) contributions of Bi-6p and a tiny contribution from the equatorial oxygens can be seen. In the spin-down channel, contributions of the Fe-3dxz orbital and the equatorial oxygens are found in the HOMO, shown in Fig. 6(c), while the Fe-3dz2 orbital and the O1-2px contribute to the LUMO, plotted in Fig. 6(d). In the case of structure-II, for the spin-up channel, the composition of the HOMO and the LUMO shown in Figs. 5(a) and (b) respectively is identical with the same of the structure-I. In the case of spin-down channel which shows the conducting property, we have plotted the molecular orbital which is shown in Fig. 5(c). In this case, the contributions from Bi-6pz, Fe-3dz2 and the O1-2pz are very prominent and retain their own character while the contributions from equatorial oxygens and other Fe-3d orbitals i.e., Fe-3dxz and Fe-3d-t2g orbitals have lost their own characters due to strong hybridization.

Furthermore, the electronic charge density denotes the nature of the bonding among the different atoms. The charge density calculations along the \{001\} plane gives the details of the sharing of the chemical/ionic bonding between ‘Bi’, ‘Fe’ and ‘O’ ions. From the charge density plots of Fig. 7 we find that in the case of structure-I and structure-II the charges are localized which shows the charge sharing is less between ‘Bi’, ‘Fe’ and ‘O’. But in the lowest \(c/a\) ratio, i.e., in case of the structure-IV, the charges are delocalized, which indicates greater charge sharing between ‘Bi’, ‘Fe’ and ‘O’. This gives the confirmation of the ferromagnetic metallic phase which we obtained earlier in the case of structure-IV. In general, the amount of charge sharing between the ions, i.e., the anion and the cation decide the type of bonding that exists in the system whether it is ionic or covalent. In this case, we find greater charge difference between ‘Bi’ and ‘O’. This type of charge difference has also been found

D. Molecular orbital, Charge density and Hybridization:

For further understanding about the orbital contributions, we have investigated the nature of the molecular orbitals in the vicinity of Fermi energy. In Fig. 7 we have presented the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for both the spin channels corresponding to the structure-I. From Fig. 7(a) it is clear that the HOMO corresponding to the spin-up channel has contribution from the Fe-3dx2−y2 orbital and the 2p orbitals of the equatorial oxygen, more specifically from the O2-2py and O3-2px orbitals. This is consistent with the PDOS results presented in Figs. 6(a), (d), and (g). In the LUMO, i.e., in Fig. 7(b) contributions of Bi-6p and a tiny contribution from the equatorial oxygens can be seen. In the spin-down channel, contributions of the Fe-3dxz orbital and the equatorial oxygens are found in the HOMO, shown in Fig. 7(c), while the Fe-3dz2 orbital and the O1-2pz contribute to the LUMO, plotted in Fig. 7(d). In the case of structure-II, for the spin-up channel, the composition of the HOMO and the LUMO shown in Figs. 5(a) and (b) respectively is identical with the same of the structure-I. In the case of spin-down channel which shows the conducting property, we have plotted the molecular orbital which is shown in Fig. 5(c). In this case, the contributions from Bi-6pz, Fe-3dz2 and the O1-2pz are very prominent and retain their own character while the contributions from equatorial oxygens and other Fe-3d orbitals i.e., Fe-3dxz and Fe-3d-t2g orbitals have lost their own characters due to strong hybridization.

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between ‘Fe’ and ‘O’. Hence we can conclude that the ‘Bi’ and ‘Fe’ cations create ionic bond with electronegative oxygen. The perovskite BiFeO$_3$ can be viewed as a structure with a central metal (either Bi or Fe) surrounded by electron rich ligands, i.e. O. Here, in this case, we find that ‘Fe’ plays the role of principal central metal atom as it has more contribution than ‘Bi’ to the hybridization, which we find from Löwdin charges. In this study, modified $sp^3d^4$ hybridization has been found in all the cases which we have discussed in Appendix C. In any such inorganic cluster, there is a direct electron donation from the ligand to the metal atom. It may happen that the metal atom may give back some electrons to the ligand LUMO. In the case of structure-II, the electron bridging between O-Bi-O and O-Fe-O makes the hybrid orbitals, which might play an important role in the half-metallicity.

IV. CONCLUSION:

In conclusion, in this work we have used DFT based first-principle calculation to explore the evolution of the ferromagnetic phase of the tetragonal BiFeO$_3$ structure as a function of the $c/a$ ratio. We have found that the ferromagnetic TBFO structure harbors rich set of electronic phases, including the half-metallic phase, incidentally which is also the most stable electronic phase among all the possible ferromagnetic phases. Additionally, we have also found that the electronic phase shows a half-metal to an insulator, and finally to a metal transition on compression, which is contrary to the commonly anticipated behavior of electronic phases under pressure. We have found that Bi-$6p_z$ orbital plays a very crucial role in determining the degree of metallicity in the ferromagnetic TBO structure. The structure with the highest $c/a$ ratio was found to be a magnetic-semiconductor. With the reduction of the $c/a$ ratio, initially only one spin channel of the Bi-$6p_z$ orbital crosses the Fermi energy from above, providing the half-metallic character to BFO, and finally both the spin channels cross the Fermi energy on further reduction of the $c/a$ ratio. From our molecular orbital analyses, we have found contribution of the Fe-3$d$ and O-2$p$ orbitals towards the half-metallicity in this system. Since, typically fabricating stable structures with half-metallicity experimentally is a challenging task, our findings are going to be quite useful, especially from the point of view of spintronic applications, as the tetragonal BFO structures are fabricated quite routinely.

Appendix A: Energy vs $c/a$ ratio

The relative energy is calculated with respect to the G-AFM energy possessed by the structure-II.

$$\text{Relative Energy} = \frac{E_{\text{structure-x}}^{\text{G-AFM/FM}} - E_{\text{structure-II}}^{\text{G-AFM/FM}}}{E_{\text{G-AFM}}} \times 100$$

where, $E_{\text{structure-x}}^{\text{G-AFM/FM}}$ is the energy of any structure with either G-AFM or FM ordering.

The energy of each structure has been represented relative to the energetically most favorable structure, that is the structure-II with G-AFM ordering. It is clear from Fig. 10 that the G-AFM type magnetically ordered phase is lower in energy than the corresponding FM phase irrespective of the $c/a$ ratio. Interestingly, the energy of the FM phase also follows a similar pattern to that of the G-AFM phase, that is, the structure-II is the most stable one among all the possible structures with FM ordering. The lowest energies found in the structure-II with the G-AFM ordering and FM ordering are $-10883.8911$ Ry and $-10883.7638$ Ry respectively. The energy difference for the most stable G-AFM and the FM phase is $0.1273$ Ry which belongs to the structure-II. The next higher energy differences have been found to be $0.1976$ Ry, $0.2288$ Ry and $0.2391$ Ry for the cases of structure-I, structure-IV and structure-III respectively.

Appendix B: Results of structure-III

After increasing the $c/a$ ratio from 1.016 to 1.049, we have found that structure-III also shows purely metallic behavior, which is not very away from the properties of the structure-IV. Here, the band structure, TDOS, LDOS & PDOS have been studied like all other structures. The metallicity in the band structure, i.e., Fig. 11(a) is clearly visible, which agrees with the corresponding TDOS (Fig. 11(b)). In the LDOS we found that, like structure-IV, Bi-$6p$, Fe-3$d$ and O-2$p$ have contributions near the Fermi energy. Bi-$6p$ contributes electron carriers from both the spin channels, while Fe-3$d$ and O-2$p$ orbitals contribute hole carriers to the system from the spin up channel only which is also in the case of structure-IV. In PDOS, we find that the Bi-$6p_z$ orbital contributes

Figure 10. $c/a$ ratio versus relative energy (in %), where the relative energy of a structure is measured respect to the most stable G-AFM state, that is structure II.
in both the spin-channels, whereas the \( e_g \) band of ‘Fe’ contributes along with the O1-2p\(_z\), O2-2p\(_y\), and O3-2p\(_x\) orbitals. These bands cross over the Fermi level for the spin-up channel only, thereby making the structure-III to be a ferromagnetic metal.

**Appendix C: Löwdin charges**

From Löwdin charges analysis, it is found that the hybridization of the principal central metal ion ‘Fe’ are \( sp^2\,d^2\) (structure-I), \( sp^2\,d^2\,t^2\) (structure-II) and \( sp^2\,d^2\,t^2\) (structure-IV) respectively. So, the hybridization present in T-BFO can be called as the modified \( sp^2\,d^2\). Also, we have found that the Bi-5d does not have any contribution in the hybridization. The extra population of electrons in Fe-3p & Fe-3d may be the outcome of the back-bonding, which has been created due to the interplay between Bi-6s and Bi-6p.

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[1] R. A. De Groot, F. M. Mueller, P. G. Van Engen and K. H. J. Buschow, Physical Review Letters 50, 2024 (1983).
[2] I. Žutić, J. Fabian, and S. Das Sarma, Reviews of modern physics 76, 323 (2004).
[3] J. M. D. Coey, C. L. Chien, Mrs Bulletin 28, 720 (2003).
[4] M. I. Katsnelson, V. Yu. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, Reviews of modern physics 80, 315 (2008).
[5] Z. Li, T. Itatka and T. Tolyama, Physical Review B 86, 094422 (2012).
[6] Rui-Wuhan, Du-Shuai Ma, Jian-Min Zhang and Y. Yao, Physical Review B 103, 195115 (2021).
[7] P. Ravindran, R. Vidya, A. Kjekshus, H. Fjellvåg, and E. Eriksson, Physical Review B 74, 224412 (2006).
[8] O. Diéguez, E. O. González-Vázquez, J. C. Wojdeil and J. Íñiguez, Physical Review B 83, 094105 (2011).
[9] I. Sosnowska, T. P. Neumaier, and E. Steichele, Journal of Physics: Condensed Matter 18, 2069 (2006).
[10] J. Herrero-Albillos, G. Catalan, J. A. Rodriguez-Velamazán, M. Viret, D. Colson, and J. Scott, Journal of Physics: Condensed Matter 22, 256001 (2010).
[11] A. M. Kadomtseva, A. K. Zvezdin, Y. F. Popov, A. P. Pyatakov, and G. P. Vorob’ev, Journal of Experimental and Theoretical Physics Letters 79, 571 (2004).
[12] C. Ederer, and N.A. Spaldin, Physical Review B 71, 060401 (2005).
[13] D. Wardecki, R. Przenioslo, I. Sosnowska, Y. Skourski, & M. Loewenhaupt, Journal of the Physical Society of Japan 77, 103709 (2008).
[14] J. B. N. J. Wang, J. B. Neaton,H. Zheng, V. Nagarajan, S. B. Ogale, B Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare and N. A. Spaldin, Science 299, 1719 (2003).
[15] D. Albrecht, S. Lisenkow, W. Ren, D. Rahmanov, I. A. Kornev, L. Bellaiche, Physical Review B 81, 140401 (2010).
[16] W. Eerenstein, F. D. Morrison, J. Dho, M. G. Blamire, J. F. Scott, N. D. Mathur, J. Wang, A. Scholl, H. Zheng, S. B. Ogale, and D. Viehland, Science 307, 1203 (2005).
[17] H. Béa, M. Bipes, A. Barthélémy, K. Bouzehouane, E. Jacquet, A. Khodan, J. P. Contour, S. Fusil, F. Wyczisk, A. Forget, D. Lebeugle, D. Colson, and M. Viret, Applied Physics Letters 87, 072508 (2005).
[18] M. Ramazanoglu, M. Laver, W. Ratcliff II, S. M. Watson, W. C. Chen, A. Jackson, K. Kothapalli, S. Lee, S. W. Cheong, and V. Kryukhin, Physical review letters 107, 207206 (2011).
[19] M. C. Ramírez-Camacho, C. F. Sánchez-Valdés, J. J. Gervacio-Arciniega, R. Font, C. Ostos, D. Bueno-Baques, M. Curiel, J. L. Sánchez-Llamazares, J. M. Siqueiros and O. Raymond-Herrera, Acta Materialia 128, 451 (2017).
[20] A. Sil, D. S. Negi, M. H. Naik, M. Jain, R. Datta, R. Ranjan, and P. A. Kumar, EPL (Europhysics Letters) 126, 57003 (2019).
[21] C. Ederer and N. A. Spaldin, Physical review letters 95, 257601 (2005).
[22] C. Ederer and N. A. Spaldin, Physical Review B 81, 054109 (2010).
[23] J. X. Zhang, Q. He, M. Trassin, W. Luo, D. Yi, M. D. Rossell, P. Yu, L. You, C. H. Wang, C. Y. Kuo, and J. T. Heron, Physical Review Letters 107, 147602 (2011).
[24] H. M. Tüttüncü and G. P. Srivastava, Physical Review B 78, 235209 (2008).
[25] D. Rincinschi, K. Y. Yun and M. Okuyama, Journal of Physics: Condensed Matter 18, L97 (2006).
[26] D. Sando, B. Xu, L. Belhaiche, and V. Nagarajan, Applied Physics Reviews 3, 011106 (2016).
[27] Q. J. Wang, Q. H. Tan and Y. K. Liu, Computational Materials Science 105, 1 (2015).
[28] P. I. Rajan, S. Mahalakshmi and S. Chandra, Computational Materials Science 130, 84 (2017).
[29] N. Feng, W. Mi, X. Wang, Y. Cheng, and U. Schwinghammer, ACS applied materials & interfaces 7, 10612 (2015).
[30] W. Sun, W. Wang, D. Chen, G. Zhang, Z. Cheng and Y. Wang, Journal of Materials Chemistry C 7, 463 (2019).
[31] L. Yin, Q. Zhang, W. Mi and X. Wang, Journal of Applied Physics 120, 165303 (2016).
[32] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, and A. Dal Corso, Journal of physics: Condensed matter, 21, 395502 (2009).
[33] P. E. Blüchl, Physical Review B 50, 17953 (1994).
[34] J. P. Perdew, K. Burke and M. Ernzerhof, Physical review letters 77, 3865 (1996).
[35] P. Chen, N. J. Podraza, X. S. Xu, A. Melville, E. Vlasos, V. Gopalan, R. Ramesh, D. G. Schlom, and J. L. Musfeldt, Applied Physics Letters 96, 131907 (2010).
[36] C. Himcinschi, A. Bhatnagar, A. Talkenberger, M. Barchuk, D. R. Zahn, D. Rafaja, J. Cortus and M. Alexe, Applied Physics Letters 106, 012908 (2015).
[37] H. J. Monkhurst and J. D. Pack, Physical review B 13, 5188 (1976).
[38] M. P. A. T. Methfessel and A. T. Paxton, Physical Review B 40, 3616 (1989).
[39] H. M. H’Linh, E. M. Aguilar, J. A. García, J. R. Ariño, L. Mestres, P. Alemany, D.H. Galván, J. S. Beltrones and O. R. Herrera, Computational Materials Science 164, 66 (2019).
[40] T. Matsuka and K. Shimizu, Nature 458, 186 (2009).
[41] T. Matsuka, M. Sakata, Y. Nakamoto, K. Takahama, K. Ichimaru, K. Mukai, K. Ohta, N. Hirao, Y. Ohishi, and K. Shimizu, Physical Review B 89, 144103 (2014).
[42] Y. Ma, M. Eremets, A. P. Oganov, Y. Xie, I. Trojan, S. Medvedev, A. O. Lyakhov, M. Valle, and V. Prakapenka, Nature 458, 182 (2009).
[43] K. J. Dunn and F. P. Bundy, Physical Review B 24, 1643 (1981).
[44] R. A. Stager and H. G. Drickamer, Physical Review 131, 2524 (1963).
[45] A. K. McMahan and R. C. Albers, Physical Review Letters 49, 1198 (1982).
[46] X. Jin, X. J. Chen, T. Cui, H. K. Mao, H. Zhang, Q. Zhuang, K. Bao, D. Zhou, B. Liu, Q. Zhou and Z. He, Proceedings of the National Academy of Sciences, 113, 2366 (2016).
[47] W. E. Pickett, Physical review letters 77, 3185 (1996).