Jahn-Teller distortion induced magnetic phase transition in cubic BaFeO_3

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Abstract

Using density functional theory (DFT) with the local spin density approximation (LSDA) and the generalized gradient approximation (GGA) functionals, with and without a Coulomb U term, the electronic and magnetic structures of cubic BaFeO_3 (BFO) in the ferromagnetic (FM) and antiferromagnetic (AFM) states are studied. Our LSDA/GGA and LSDA+ U /GGA+ U results show that cubic BFO has a FM ground state, in agreement with recent experimental studies. Two types of Jahn-Teller (JT) distortions, denoted as JT1 and JT2, are considered. The source of the distortion in the JT1 (JT2) case is the displacement of the oxygen (iron) atoms from their equilibrium positions. We find FM to ferrimagnetic (FIM) and FM to AFM magnetic phase transitions in the JT1 and JT2 distortions, respectively. Larger strains are required for the FM-AFM transition as compared to the FM-FIM. DFT+ U calculations also show that the magnetic moments dramatically decrease at large strains due to strong overlapping between the iron and oxygen atoms. The origin of these transitions is discussed in terms of a competition between double exchange and superexchange interactions. From these results it is possible to conclude that oxygen and iron displacements are responsible for the magnetic phase transitions and the reduction of the magnetic moments. **We also show that JT distortion in BFO can be stabilized in the $(\text{BFO})_2/(\text{BaTiO}_3)$ superlattice.**

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I. INTRODUCTION

Iron-based oxides have very interesting properties due to the different oxidation states of Fe, which give rise to different crystal structures and stoichiometries. Well known examples are FeO and Fe₃O₄ where Fe can exist in Fe²⁺ and Fe^{2+/3+} states, respectively. All these materials are antiferromagnetic (AFM) or ferrimagnetic (FIM) insulators. Fe-containing ferroelectric oxides are currently attracting tremendous attention, not only due to their magnetic properties but also due to their applications. Particularly, those oxides that exhibit magnetic and ferroelectric characteristics simultaneously, known as multiferroics, can have practical device applications such as spin transistor memories, whose magnetic properties can be tuned by electric fields through the lattice strain effect.¹ A lot of work has been done on perovskite materials to understand the origins of multiferroic behavior.² Perovskite materials containing Fe, e.g., BiFeO₃³ and SrFeO₃ (SFO)^{4,5}, have very complicated magnetic structures that promote such type of behaviors.^{6,7} In cubic SFO, which is AFM and metallic down to low temperatures^{4,5}, Fe is surrounded by six O atoms and it is in the Fe⁴⁺ state. SFO is of particular interest due to its simple crystal structure and helical magnetic structure. Recently, the helical spin order in Fe perovskites has been investigated using a double exchange (DE) model including oxygen 2*p* orbitals.⁸ In particular, it was found that G-type helical magnetic structure could be changed to A-type by reducing the superexchange (SE) interactions.⁸

Another example of perovskites is BaFeO₃ (BFO), which is one of the few oxides where iron has an oxidation state of +4.⁹ In bulk, BFO normally assumes a hexagonal crystal structure, although various polymorphs have been observed with oxygen deficiency.⁹⁻¹³ Bulk hexagonal BFO exhibits an interesting AFM to FM transition at 160 K.¹⁴ Recent experiments observed however ferromagnetism in cubic BFO, where the metastable cubic structure was shown to be stable down to 8K,¹⁵ and a field-induced switching from AFM to FM. BFO has also spin spiral magnetic order, but it is different from that of SFO. As a consequence, SFO needs larger external fields than BFO for the AFM to FM transition. Callender *et al.*¹⁶ have grown epitaxially cubic BFO on STO and found weak ferromagnetism with a transition temperature of 235 K. Similarly, Matsui *et al.*¹⁷ have also reported ferromagnetic (FM) in pseudocubic BFO on STO. Very recently, Li *et al.*¹⁸ used DFT+*U* to investigate the helical structure of cubic FM BFO and SFO and found AFM to FM transitions under external

pressure. The structural FM stability of cubic BFO has also been studied experimentally and it was found that cubic BFO remains FM up to 40 GPa.²⁰ The magnetic structure of BFO can also be tuned by external small magnetic field (0.3 T).²⁰ Such experimental and theoretical results indicate that magnetic phase transitions (AFM to FM) can easily be affected by external perturbations. Motivated by this recent experimental work on cubic BFO, here we demonstrate that this BFO structure shows FM to AFM/FIM phase transitions due to Jahn-Teller(JT) type distortions, which can be used to engineer BFO for applications.

II. COMPUTATIONAL METHOD

We performed calculations in the framework of density functional theory (DFT)²¹ using linear combinations of atomic orbitals (LCAO) as implemented in the SIESTA code²². We used a double- ζ polarized (DZP) basis set for all atoms. We employed both the local spin density approximation (LSDA) as parametrized by Ceperly and Adler,²³ and the generalized gradient approximation (GGA) as parametrized by Wu and Cohen²⁴ for the exchange-correlation functional. We used standard norm-conserving pseudopotentials²⁵ in their fully nonlocal form.²⁶ We carefully checked the convergence of the cutoff energy for the real-space grid, since the lattice parameters and magnetic moments in this system were rather sensitive to this parameter. This energy cutoff defines the energy of the most energetic plane wave that can be represented on such grid, i.e., the larger the cutoff the smaller the separation between points in the grid ($E \sim G^2 \sim 1/d^2$, where $\vec{G}$ is a reciprocal vector and d is the separation between points). We found that 400 Ry was enough to converge the lattice parameters and magnetic moments. Similarly, we performed the Brillouin zone integrations using different Monkhorst-Pack grids. We found that the magnetic moments and lattice parameters were converged with a $24 \times 24 \times 24$ mesh. With such optimized computational parameters, we obtained 3.88 and 3.94 Å for the the LSDA and GGA lattice constants a , respectively, which are comparable to the experimental lattice constant, 3.99 Å²⁷ or 3.97 Å.²⁰ Using such optimized lattice constants, we obtained magnetic moments per Fe atom of $3.40 \mu_B$ and $3.58 \mu_B$ for LSDA and GGA, respectively, which are also comparable to the experimentally determined magnetic moment $\sim 3.50 \mu_B$.²⁰ Notice however that the local magnetic moments at the Fe and O atoms are smaller, $2.74 \mu_B$ and $0.23 \mu_B$, respectively. We also carried out additional simulations using planewaves and all-electron projector aug-

mented wave (PAW) potentials, as implemented in the Vienna Ab Initio Simulation Package (VASP) code^{28,29} and plane waves plus pseudopotentials as implemented in the Quantum Espresso (QE) code³⁰, to further test the validity of the previous results. We expanded the electron wave function in plane waves up to a cutoff energy of 400 eV and we employed only the LSDA functional. We used these parameters for both geometry optimization and electronic-structure calculations. We found a magnetic moment per iron atom of $\sim 3.35\mu_B$, in reasonable agreement with SIESTA LSDA calculations and experiment.²⁰

We performed the LSDA+ U and GGA+ U calculations with the LSDA and GGA calculated lattice constants. In order to determine the influence of different U 's and cutoff radii and see how the results compare to previous experiments and calculations, we studied first the typical case of bulk oxide FeO,³¹ where DFT is known to give qualitatively different behavior (metallic instead of insulating character)³² than experiments. **It has become customary to attribute the Coulomb interaction U an effective value that incorporates the exchange correction $U_{eff} = U - J$.³³ Note that the calculations presented in this work were done with U replaced by $U_{eff} = U - J$ and $J = 0$ as applied previously.**³⁴ We performed calculations with $U = 4$ eV and $U = 4.5$ eV, which is the range of values most used in the literature for iron^{32,37}, and used projectors with different radii. The parameters that best fitted the experiments and previous calculations for FeO were, $U = 4.0$ eV and $r_c = 5.5$ Bohr for GGA+ U , and $U = 4.5$ eV and $r_c = 5.0$ Bohr for LSDA+ U , which gave a gap of approximately 2.4 eV. This value is in excellent agreement with the previous value of 2.4 eV given in Ref. (31). Of course, one has to be cautious because FeO is an insulator whereas BFO is a half-metal, which means that in principle the U could be different for both materials. However, our optimized value of $U = 4.0$ eV for BFO is the same that was used by Li *et al.*¹⁸ to simulate BFO and SFO and obtain a helical spin order in these materials. The quantitative and qualitative agreement of our LSDA/GGA and LSDA+ U /GGA+ U results with previous theoretical and experimental works guarantees the computational approach used in the present study.

III. RESULT AND DISCUSSION

We carried out total energy calculations of cubic BFO in nonmagnetic (NM), FM, and AFM states. We will only discuss GGA+ U data, but comparison with LSDA+ U /LSDA/GGA

will be made wherever necessary. We found that at ambient pressure BFO has a FM ground state. Figure 1 shows the **LSDA+U** calculated total and projected density of states (PDOS). The electronic structure of BFO shows typical half metallic behavior, which has important applications in spin based electronic devices (spintronics). Strong bonding of Fe t_{2g} -O p orbitals can be seen around the Fermi energy both in the majority and minority spin states. The t_{2g} -O p hybridization is essential for ferromagnetism and can be perturbed either by external pressure or by distorting the local environment around the Fe atoms. Two sharp peaks, contributed by t_{2g} electrons, in the valence spin-up and conduction spin-down states can be seen. This shows that the local magnetic moment of Fe is mainly contributed by the t_{2g} orbitals. The calculated electronic structure is in agreement with the recent work of Li *et al.*¹⁸ It is important to mention that our calculated LSDA/GGA electronic structures showed metallic behavior, which is also in agreement with the previous DFT calculations.¹⁹ We therefore believe that including an optimum value of U is essential to describe the true electronic structure of BFO.

We mainly considered two types of distortion δ denoted as JT1 and JT2. In JT1 (see Fig. 2), the atomic position of the Fe atom is fixed at the center of the cell, whereas the six O atoms surrounding Fe are distorted by $\delta = \{0, 0.01, \dots, 0.10\}$ Å along the z direction in such a way that the elongation of some of them is compensated by the contraction of the other. We denote these systems as $\delta 0, \delta 0.01, \dots, \delta 0.10$. A double unit cell ($1 \times 1 \times 2$) was used to take into account AFM(001) coupling between the Fe atoms as well, which would model AFM coupling along the direction perpendicular to the surface of the layers. Modeling other configurations of AFM coupling would require larger unit cells, which is beyond the scope of the present study. We nonetheless believe that such configurations would be close in energy to the AFM(001) configuration and the main conclusions of our study would also apply to such cases. Notice BFO has BaO and FeO₂ layers. The two Fe atoms in Fig. 2 are bonded through the O atoms of a BaO layer. We denote these oxygen atoms as O_c. In the ideal case (no distortion), the in-plane bond angle O-Fe-O is 90°, the out of plane bond angle Fe-O_c-Fe is 180° and the bond lengths is ~ 1.94 Å. The distortion of the octahedron around the Fe atoms directly affects the bond lengths and bond angles between Fe and the oxygens. Since different O atoms are moving in opposite direction, it is expected that consecutive Fe atoms will have different bond lengths and therefore there will be two different kinds of Fe atoms, i.e., Fe_I and Fe_{II} (see Fig 2). In the second type of distortion JT2 (Fig. 2), the atomic

positions of the O atoms are fixed and the Fe atoms are displaced along the z direction by δ from its ideal positions, i.e., $(0.5, 0.5, 0.50 + \delta)$. Notice that in both types of distortions the bond lengths and bond angles are perturbed but the atomic volume is conserved.

The total energy was calculated for each distortion in the FM and AFM states. The energy difference between the FM and AFM states ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$) gives an approximate value of the exchange integral J . In the following we will show how J changes with δ and the exchange correlation functional (without and with U). The LSDA/GGA and LSDA+ U /GGA+ U calculated ΔE of JT1 is shown in the left panel of Fig 3. Negative (positive) ΔE corresponds to FM (AFM) configurations. In both LSDA and GGA the unstrained BFO is in the FM state but as the strain increases, ΔE decreases and changes sign around 0.03 Å. Such reversal of sign is an indication of magnetic phase transition, FM $\rightarrow$ AFM. Notice that such magnetic phase transition induced by JT distortion is also observed in other perovskites.^{35,36} BFO remains in the AFM state in the strained region (0.03 to 0.07 Å). Beyond 0.07 Å, BFO has however zero ΔE , i.e., FM and AFM are isoenergetic. These calculations demonstrate that BFO has to cross an energy barrier ~ 0.1 eV per cell to transit from one magnetic state (FM) to another magnetic state (AFM). When the calculations were repeated with LSDA+ U /GGA+ U , a similar magnetic phase transition was obtained. Including U , however, decreases the barrier height (~ 0.05 eV), shifts the phase transition region to higher strains and reduces the isoenergetic region.

The second type of strained BFO, JT2, exhibits a different behavior (see right panel of Fig. 3). The LSDA/GGA calculations show that BFO retains its FM configuration up to 0.07 Å but beyond that point it transits to an AFM state. This shows that large strains would be required for such magnetic phase transition. The phase transition is shifted to even higher strained regions 0.10 Å when U is included. Interestingly, ΔE has a local minimum around 0.04 Å, which is exactly the amount of strain where a FM-AFM transition was observed in the JT1 case. Comparing JT1 and JT2, we see that when some of the oxygen atoms are moved away from the Fe atoms distorting the octahedra the Fe atoms couple antiferromagnetically beyond some strain limit. From this it is possible to infer that O displacements suppress DE and favor SE beyond some critical strain. Changes in the exchange integral J due to strain will, therefore, have significant effect on DE and SE interactions, as will be discussed below. Moving the Fe atoms away from the oxygen atoms brings however the FM order to lower energy states. These calculations suggest that small

atomic displacements are crucial for the magnetic ground state structure.

The calculated total magnetic moments per unit cell of BFO in the FM and AFM states of JT1 are shown in Fig. 4. The magnetic moments saturate at small displacements and are rather robust against small strains. In the small strain region the total magnetic moment per cell in the LSDA+ U /GGA+ U is $\sim 8.0 \mu_B$, i.e., $\sim 4.0 \mu_B$ per Fe atom, suggesting that the nominal oxidation state of Fe in this region is Fe^{4+} , which is consistent with the charge neutrality of BFO and agrees with experimental results.²⁰ However, there is a drastic change in the magnetic moments around $0.04 \text{ \AA}$, since they tend to sharply decrease beyond this value. This is the region where the magnetic phase transition is also observed. Beyond $0.08 \text{ \AA}$, the total magnetic moments in the FM state saturates at $\sim 4.0 \mu_B$ per cell. In this region, LSDA/GGA and LSDA+ U /GGA+ U almost give the same magnetic moments per unit cell. To understand this drastic (about 50 %) decrease in the value of the magnetic moment, we analyzed the Mulliken charges of the Fe atoms. The main drop in the magnetic moment comes from Fe_I . This drop is due to the O_c atoms, which are displaced towards Fe_I (see the local magnetic moments of Fe_I and Fe_{II} in Fig. 4). Such displacement decreases the bond length and angle between O_c and Fe_I and strongly increases the overlap, which reduces the magnetic moment of Fe_I .

The total magnetic moments per unit cell of JT1 in the AFM state (shown in Fig. 4) are also analyzed. In the unstrained case, BFO has zero total magnetic moment per cell which is consistent with a true AFM structure. However, when the structure is distorted, i.e., when the octahedral symmetry is lowered, BFO develops a non zero magnetic moment. Therefore, changing the atomic positions of the O atoms not only changes the local magnetic moments of the Fe atoms, but it also transforms BFO to an AFM structure with non zero total magnetic moments per cell, i.e., a FIM. It is interesting to note that starting from an AFM structure, the electronic self-consistent cycle converges to a FIM structure whenever some strain is imposed in the JT1 case. More importantly, it is also possible to see a more severe change in the total magnetic moments than that found in the FM calculations, i.e., beyond $0.07 \text{ \AA}$, the total magnetic moment converges to $\sim -4.0 \mu_B$. Interestingly, in both FM and AFM calculations, the magnetic moments of the unit cell converge to $\sim |4.0| \mu_B$, which suggests that FM and AFM states are isomagnetic in this high-strain region. Notice that similar considerations were also derived from the total energy calculations (see Fig. 3)

The magnetic moments of BFO in the FM and AFM states were also examined in

the JT2 case. The calculated magnetic moments in the FM states are shown Fig. 4. LSDA+ U /GGA+ U gives as before a magnetic moment per unit cell $\sim 8.0 \mu_B$ in the low strained region. Upon imposing strain, a drastic change in the magnetic moments is observed around $0.06 \text{ \AA}$. Beyond this strain the total magnetic moments converge to $\sim 4.0 \mu_B$ in the FM state, similar to the JT1 case. This drastic change in the magnetic moment is due to Fe-O_c strong bonding, as discussed in the JT1 case. In the JT2 case, both Fe atoms are moved towards the O_c atoms, which are fixed. At some strain both types of atoms bond strongly, which decreases the magnetic moments of Fe_I and Fe_{II} (**shown in Fig. 4**). In the strained AFM case, which is more stable than the FM case, Fe_I and Fe_{II} have -1.82 and $1.82 \mu_B$ magnetic moments, respectively, for $\delta 0.09$, where the Fe_I-O_c (Fe_{II}-O_c) bond length is $\sim 1.24 \text{ \AA}$ ($2.94 \text{ \AA}$). The net magnetic moment per unit cell in this case is zero, i.e., a true AFM structure. This implies that moving the Fe atoms transforms BFO from FM to AFM at large strains. This magnetic phase transition is different from that of the JT1 case, which transformed FM to FIM at large strains. Notice that the deformation of the cubic structure through JT distortions lowers the symmetry, which tends to decrease the energy relative to the symmetric structure. This is related to the tendency of the cubic phase of BFO, which is stable in thin-film geometries, to transform to some other structure, e.g., a hexagonal AFM structure that has lower symmetry. Such phase transition would occur however in films with large numbers of layers, which are beyond the thin film geometries studied here.

To elucidate the origin of these magnetic phase transitions and the reduction of the magnetic moments beyond some critical strain, we focus on the effect of distortions on the electronic structure of BFO. As we previously showed, pristine BFO has a half metallic electronic structure where t_{2g} and e_g states are separated from each other due to a crystal field splitting (see Fig.1). The calculated DOS for the JT1 case in the FM and AFM states for a strain of $0.03 \text{ \AA}$, which is very close to the FM-AFM/FIM transition, are given in Fig. 5. As can be seen, the electronic structure remains half metallic but now the low lying t_{2g} band is splitted into two energy states, particularly in the Fe_I d band. A broad majority t_{2g} band is also formed just below the Fermi energy, which shows a strong bonding with the O_c atom connecting Fe_I and Fe_{II}. Both Fe atoms have different local magnetic moments and exchange splittings, which implies that strain changes the local symmetry and distorts differently the electronic structure of each atom. Similar behavior can be seen in the AFM DOS as well. The Fe- t_{2g} state is split due to the JT distortion and the majority t_{2g} states

become occupied with 3 electrons. Therefore, the integer magnetic moment of $3.0\mu_B$ is mainly coming from the t_{2g} levels of the high spin state of Fe^{4+} (3 t_{2g} up electrons and 1 e_g electron). The remaining $\text{Fe}-e_g$ electron hybridizes with the O atoms and induces magnetic moments at the O sites. Such hybridization reduces the magnetic moment from $4.0\mu_B$ to $3.0\mu_B$. Further increases in the JT distortion may transform the Fe^{4+} from a high spin state to a low spin state (2 t_{2g} up, 2 t_{2g} down) of $0.12\mu_B$ (see JT1 $\delta 0.09$ discussed in next pages).

We consider now the electronic structure in the strained region, where AFM/FIM is the ground state structure, to have a clear understanding of such magnetic phase transition. Figure 6 shows the electronic structure of JT1 BFO under $0.05 \text{ \AA}$ ($\delta 0.05$) in the FM and AFM states. The most noticeable feature of this electronic structure is a clear splitting of the low lying Fe t_{2g} band, in both the FM and AFM states. At this strain, the JT distortion is almost completed at the Fe_I site, while Fe_{II} shows a similar JT distortion at higher strains. The FM-AFM/FIM magnetic phase transition is mainly caused by such JT distortion at the Fe_I site, which destabilizes the FM ground state and reduces the local magnetic moment, as compared with the pristine and low strained systems. The oxygen PDOS associated to O_c is also significantly changed, and becomes partially occupied. Therefore, the FM state becomes unstable when the PDOS of O_c in the spin-up state touches the Fermi energy. At larger strains the O_c PDOS further crosses the Fermi energy, which stabilizes the AFM/FIM state (see also Fig. 7).

Figure 7 shows the PDOS in the FM and AFM states of JT1 $\delta 0.09$. Compared with the unstrained BFO in the FM state, the t_{2g} states of Fe are shifted now towards the Fermi energy. There are also unoccupied d states which were occupied in the unstrained case. The exchange splitting of the Fe_I d band significantly decreases, which reduces its magnetic moment to $0.12 \mu_B$ in the FM state (this could be due to the low spin state (2 t_{2g} up, 2 t_{2g} dn) of Fe). However, Fe_{II} still carries a large magnetic moment **as presented in Fig. 4**. The local moments of both Fe atoms are therefore different (see also their PDOS), which implies the presence of different crystallographic environments.³⁸ In such different local environments the Fe atoms generate a FIM-type behavior, similar to FIM Fe_2O_3 . The band structure in the AFM case is similar and shows that Fe_I and Fe_{II} are not coupled antiferromagnetically but ferrimagnetically, which is consistent with the local magnetic moments of Fe_I and Fe_{II} . The DOS also demonstrates the existence of an electronic phase transition (half metal to metallic) at large strains. The magnetic phase transition is therefore accompanied by an

electronic phase transition at large strains, mainly contributed by t_{2g} and O p orbitals.

To shed more light on the mechanism of the phase transition we look now into the spin densities of different systems in the FM and AFM states in the (110) plane. This analysis will further help us to understand the origin of magnetic phase transitions and the reduction of magnetic moments at large strains. Figure 8 shows the spin densities of JT1 $\delta 0$, $\delta 0.09$ and JT2 $\delta 0.09$. The spin density of $\delta 0$ exhibits a large spin polarization at O_c , both in the FM and AFM states and a large spin density at the Fe sites. Also, a clear antiferromagnetic coupling between Fe_I and Fe_{II} can be seen in the AFM state. Notice that as we increase the strain the magnetic moment at the Fe_I site starts decreasing because the O_c atom connecting Fe_I and Fe_{II} moves towards Fe_I , which decreases its magnetic moment. This behavior can be seen in Fig. 8, where Fe_{II} has a large spin polarization, whereas Fe_I has a smaller magnetic moment of $\sim 0.12 \mu_B$ ($\sim -1.05 \mu_B$) in the FM (AFM) state (also see **Fig. 4**). Notice also the spin polarization at the O_c site is reduced. This behavior shows again that the FM-AFM/FIM transition is mainly governed by strong Fe_I - O_c bondings. In the JT2 $\delta 0.09$ the spin densities of both Fe atoms decrease again due to the strong overlap with the O_c atom but their shape is indistinguishable, which is expected since the local environments are the same.

The origin of the FM-AFM/FIM phase transition can be discussed in terms of SE and DE models. Generally, compressing a lattice parameter a leads to the increase of the hopping integral t , represented by $pd\sigma$. In this particular case t personifies the orbital hybridization between O p and Fe $3d$. Since DE and SE energies are proportional to t and t^4 , respectively, increasing t enhances SE as compared with DE.⁸ In our case the lattice constant a of BFO is fixed at its optimized value, and we only changed the bond angle/length between the atoms in such a way that it strongly modifies the electronic structure. As we have shown (see all DOS figures) when the strain increases, the hybridization between the Fe and O orbitals also increases. At a large strains t becomes very strong and BFO transitions to AFM/FIM. This shows that SE is enhanced by strain, since the oxygen band width increases and favors AFM/FIM. On the other hand, at low strain the overlap between Fe $3d$ and O $2p$ is relatively weak and DE wins, which compels BFO to be in the FM state. This competition between DE and SE is consistent with our total energy calculations, i.e., FM vs. AFM states. At large strain the energy difference J increases, suggesting that t also increases, which agrees with the DOS figures. In such competition, the magnetic moments decrease due to the

strong t . Changing a can also change the magnetic structure of BFO, i.e., A-type or G-type helical spin structures. In particular, decreasing a produces a G-type structure.¹⁸ Such magnetic structural changes are again mainly caused by t . In the light of the phase diagrams presented in Ref. (8) (Fig.3), where it is shown that the transition from FM to a helical magnetic (HM) phase transition depends on $pd\sigma$ and oxygen-oxygen hopping amplitudes t_{pp} , it is possible to infer that large t_{pp} is also important for the stabilization of the HM state. In our case, straining BFO produces AFM or FIM magnetic states, depending on the nature of the strain. Therefore, we believe that the experimentally observed magnetic phase transition at high pressure or external magnetic fields²⁰ may distort the local environment of the Fe and O atoms in BFO and such distortion can favor FM-FIM/AFM magnetic phase transitions. To the best of our knowledge there is no experimental work on JT distortion-induced magnetic phase transitions in BFO. Therefore, further experimental work would be required to explore such magnetic phase transitions in this material.

Before presenting our summary, it would be worth commenting on the stabilization of JT distortion in BFO, which should be addressed if such systems are to be used in practical applications. Usually, the structure can be stabilized by doping with La, Nd or Bi at the Ba site,^{39–41} by combining it with another structure in a superlattice⁴² or by adding hydrostatic pressure.⁴³ We decided to use the superlattice approach, and want to investigate whether JT distorted structure is stable or not when it is deposited on a substrate, e.g., BaTiO₃ (BTO). We carried out LSDA calculations of BFO on top of BTO, i.e. (BFO)₂/(BTO). First, we optimized the lattice constant of BFO/BTO, which is $\sim 3.91\text{\AA}$. We deposited then BFO on BTO with the Ti and O atoms displaced from their symmetric positions (this is the most stable structure of BTO, as proven by experiments⁴⁴) and relaxed all the atoms. After relaxation, we found that the atomic positions of the BFO atoms were also displaced from their ideal positions, giving rise to a clear distortion. This shows that JT distortions in BFO can form a stable structure by combining it with other materials in superlattices. To check whether the bulk results are still valid in the superlattice configuration, **we considered JT1 and JT2 and carried out calculations for $\delta 0, 0.01, \dots$ using (BFO)₂/(BTO) superlattice configurations for both FM and AFM states. We plotted the LSDA calculated energy density ρ (eV/ $\text{\AA}^3$) vs distortion (see Fig. 9(a)) in the FM states of (BFO)₂/(BTO) for JT1 and JT2. Although, we do not see any spontaneous stabilization of JT distortion, but both JT1 and JT2 have the stable structure**

due to its positive curvature (lack of soft modes of phonons). We found similar behavior in the AFM calculations (not shown here). If these JT1 and JT2 in the FM/AFM states were not stable then it could have shown negative curvature, which we did not observe indicating that both JT1 and JT2 are stable in the cubic phase of BFO. Other type of JT distortions may destabilize the cubic phase of BFO which may give birth to some other phases (crystal structures) of BFO or may induce spontaneous distortions.³⁴. However, such calculations are beyond the scope of the present work, and this manuscript is explicitly dealing with magnetic phase transition induced by JT distortions. To see how BTO will affect the magnetic phase transition, we show the calculated total energy difference (FM-AFM) vs distortion of $(\text{BFO})_2/(\text{BTO})$ in Fig. 9 (b). Fig. 9 (b) shows that both JT1 and JT2 have magnetic phase transitions (FM to AFM/FIM) similar to bulk BFO. However, we noticed that in the heterostructure the phase transition regions are shifted to lower distortions as compared with the bulk LSDA calculations. This can be suggested that BTO lowers the value of strain (distortion) needed for magnetic phase transition. The total magnetic moments of the cell and local magnetic moments of Fe_I and Fe_II in $(\text{BFO})_2/(\text{BTO})$ showed bulk BFO like behavior. AFM structures would be more difficult to stabilize because the required distortions are higher, but these could be achieved through doping at the Ba site³⁹⁻⁴¹. Therefore, we can safely conclude that JT in BFO can easily be stabilized by combining it with BTO, either in superlattices or in composites. Further experimental and theoretical work would be needed to investigate and stabilize JT distortions in $(\text{BFO})_n/(\text{BTO})$ superlattices.

IV. SUMMARY

Cubic BaFeO_3 (BFO) was investigated using density functional theory (DFT) within the generalized gradient approximation (GGA) and the local spin density approximation (LSDA). The effect of on site Coulomb interaction U was also considered. We showed that BFO has a ferromagnetic (FM) ground state in all cases. This FM ground state is in agreement with recent experimental work. The electronic and magnetic structure of BFO was modified by two different types of Jahn-Teller (JT) distortions, denoted as JT1

and JT2. We showed that JT frustrates the magnetic structure of BFO and induces FM to antiferromagnetic (AFM) and FM to ferrimagnetic (FIM) transitions. Such magnetic phase transitions are governed by the displacements of the O and Fe atoms from their ideal positions. The DFT and DFT+ U calculations revealed that a larger JT distortion is needed for the FM to AFM transition as compared to the FM to FIM transition. The Coulomb interaction mainly shifted the magnetic phase transition to higher strains. The JT distortions also reduced the magnetic moments of the Fe atoms. The mechanisms of the transitions were elucidated using partial densities of states and spin density contours. These results suggest that different magnetic phase transitions can be induced in BFO by different types of strain. **We also showed that JT distortions in (BFO)₂/(BaTiO₃)-type superlattice are stable with less distortion needed for magnetic phase transition as compared with the bulk BFO.**

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FIG. 1. (Color online) The LSDA+ U calculated total (a) and partial (b) densities of states (PDOS) in the FM states of cubic BaFeO₃. Solid (red), dotted (blue), and dashed (green) lines represents the Fe- t_{2g} , Fe- e_g , and O- p orbitals respectively. The total DOS is represented by solid thick (black) lines. The Fermi energy is set to zero.

FIG. 2. (Color online) Schematic representation of JT1(a) and JT2 distortions(b). Thin (green) arrows on the oxygen atoms show the direction of the distortion δ along z axis. Red (green) balls show Fe (O) atoms, whereas empty circles show Ba atoms. The dashed lines show that unit cell that is used in the calculations. Thick (red) arrows show the direction of magnetic moments. In JT2 (b), the green (red) arrows show the direction of distortion (spin magnetic moment) on Fe atoms. The oxygen atom O_c connecting Fe_I and Fe_{II} is also shown.

FIG. 3. (Color online) Total energy difference $\Delta E/\text{cell}$ (in eV) vs. distortion δ (in Å) for JT1 (left panel) and JT2 (right panel) systems calculated with (a) GGA/LSDA and (b) GGA+ U /LSDA+ U . Empty (filled) squares represent GGA (GGA+ U) data whereas empty (filled) circles represent LSDA (LSDA+ U) results.

FIG. 4. (Color online) The calculated total magnetic moments per cell (in μ_B) vs distortion δ (in Å) for the JT1 in the FM (a) and AFM (b) states, and for JT2 in the FM (c) state. Up (down) triangles represent LSDA (GGA) results. Empty (filled) triangles represent results without (with) U . The GGA+ U calculated local magnetic moments (in units of μ_B) of Fe_I and Fe_{II} for JT1 (d) and JT2 (e) are also presented. Empty (filled) symbols represent the local magnetic moments of Fe_I and Fe_{II} in AFM(FM) states.

FIG. 5. (Color online) GGA+ U calculated PDOS in the FM (left panels, labeled as (a)) and AFM (right panels, labeled as (b)) states for JT1, δ 0.03. Solid (red), dotted (blue), and dashed (green) lines represent Fe- t_{2g} , Fe- e_g , and O- p orbitals, respectively. The local magnetic moments of the Fe atoms are also shown in each panel. The Fermi energy is set to zero.

FIG. 6. (Color online) GGA+ U calculated PDOS in the FM (left panels, labeled as (a)) and AFM (right panels, labeled as (b)) states for JT1, δ 0.05. Solid (red), dotted (blue), and dashed (green) lines represent Fe- t_{2g} , Fe- e_g , and O- p orbitals, respectively. The local magnetic moments of the Fe atoms are also shown in each panel. The Fermi energy is set to zero.

FIG. 7. (Color online) GGA+ U calculated PDOS in the FM (left panels, labeled as (a)) and AFM (right panels, labeled as (b)) states for JT1, δ 0.09. Solid (red), dotted (blue), and dashed (green) lines represent Fe- t_{2g} , Fe- e_g , and O- p orbitals, respectively. The local magnetic moments of the Fe atoms are also shown in each panel. The Fermi energy is set to zero.

FIG. 8. (Color online) Spin densities in the FM (left) and AFM (right) states for $\delta=0$ (top) and $\delta=0.09$ (middle) of JT1 and $(\delta=0.09)$ of JT2. Cyan, red, and green balls represent Ba, Fe and O atoms, respectively. The scale is also shown at the bottom of the figure.

FIG. 9. (Color online) (a) The LSDA calculated energy density ρ (eV/Å³) vs. distortion δ (in Å) in the FM state of (BFO)₂/(BTO) supercell for JT1(empty circles) and JT2 (filled circles). (b) The LSDA calculated $\Delta E/\text{cell}$ vs. distortion δ (in Å) of (BFO)₂/(BTO) supercell for JT1(empty triangles) and JT2 (filled triangles).