Evolution of the electronic and lattice structure with carrier injection in BiFeO₃

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We report a density-functional study on the evolution of the electronic and lattice structure in BiFeO₃ with injected electrons and holes. First, the self-trapping of electrons and holes was investigated. We found that the injected electrons tend to be localized on Fe sites due to the local lattice expansion, the on-site Coulomb interaction of Fe 3*d* electrons, and the antiferromagnetic order in BiFeO₃. The injected holes tend to be delocalized if the on-site Coulomb interaction of O 2*p* is weak (in other words, U_0 is small). Single-center polarons and multicenter polarons are formed with large and intermediate U_0 , respectively. With intermediate U_0 , multicenter polarons can be formed. We also studied the lattice distortion with the injection of carriers by assuming the delocalization of the secarriers. We found that the ferroelectric off-centering of BiFeO₃ increases with the concentration of the electrons injected and decreases with that of the holes injected. It was also found that a structural phase transition from *R*3*c* to the nonferroelectric *Pbnm* occurs, with the hole concentration over 8.7×10^{19} cm⁻³. The change of the off-centering is mainly due to the change of the lattice volume. The understanding of the carrier localization mechanism can help to optimize the functionality of ferroelectric diodes and the ferroelectric photovoltage devices, while the understanding of the evolution of the lattice with carriers can help tune the ferroelectric properties by the carriers in BiFeO₃.

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I. INTRODUCTION

In transition-metal oxide perovskites, there is a strong correlation between the degrees of freedom of charge and the lattice. When extra charges are injected into those materials, they interact with the lattice, causing a novel phenomenon. Unlike in conventional insulators and semiconductors, the change in BiFeO₃ (BFO) with injected carriers cannot be seen as a mere rigid shift of the band. The lattice distorts with carrier injection, and the injected carriers can be trapped due to lattice distortion. Here we investigate the behaviors of the injected carriers and the lattice in BFO with first-principles methods.

BFO has been of great interest for many years [1], because its large ferroelectric polarization and relatively small band gap [2–6] make it a good choice for semiconductor and optoelectronic material [7,8] in devices such as a ferroelectric diode [9–11] and a ferroelectric photovoltaic device [12,13]. In these devices, carriers are injected into BFO either by electric field or optical excitation. One of the most important issues regarding carriers is whether they tend to be localized or delocalized, as this greatly affects their mobility and lifetime as well as the leakage current in BFO. Therefore, the understanding of the carrier behavior in BFO is crucial for revealing the mechanisms behind its abundant properties, as well as for the development of the devices.

There is some evidence showing that the carrier has the tendency to be trapped in BFO. The electronic conductivity in nondoped and *p*-type BFO follows the $\log \sigma \propto 1/T$ law, implying the polaron hopping mechanism [14–16]. Hole doping was achieved by substituting Bi or Fe ions with acceptor cations (such as Ca²⁺, Sr²⁺, Ba²⁺, Ni²⁺, and Mg²⁺) [15,17–19]. The large concentration of acceptor cations tends to break the symmetry of the bulk. For example, by substituting

about 10% Bi ions with Ca ions, there is a monoclinic-totetragonal phase transition in BFO thin films [18]. While it is

Another important issue is how the lattice deforms if the injection of carriers is delocalized. The injected carriers, which are affected by the lattice, affect the lattice in return, thus they can modulate the ferroelectric distortions. In ferroelectrics, the off-centering of ions, which is stabilized by the long-range Coulomb interaction, tends to be unstable with free charge, as

difficult to achieve *n*-type doping, substituting Fe ions with Ti^{4+} or Nb⁵⁺ decreases the conductivity in BFO [19,20]. In chemically doped BFO structures, it is not clear whether the polarons are bounded to dopants or self-trapped. Schick et al. studied the dynamics of the stress in BFO due to the excited charge carriers with ultrafast x-ray diffraction, and they found that the carriers tend to be localized [21]. Yamada et al. found that photocarriers can be trapped by means of transient absorption and photocurrent measurements [22]. The trapping of the carriers can happen because of the defects or the self-trapping effect in BFO. In the latter case, the carriers reduce their energies due to the local lattice distortion and form small polarons. The states of the trapped carriers are in the band gap, thus these carriers need energy to be excited and become conducting. In-gap states were observed in absorption spectra and photoluminescence measurements [23–26], while it is not yet clear whether these states should be attributed to defect states or self-trapped states. There has been extensive study of defect states [27–29], whereas study of the self-trapped state is lacking. In this work, we investigate the self-trapping of injected electrons, and we found that the electrons tend to be localized even when the defects are absent. The localization of injected holes was also studied. We found that the holes tend to be delocalized, to form multicentered polarons, and to form single-centered polarons if the on-site Coulomb interaction of O 2p electrons is weak, intermediate, and strong, respectively. The lattice distortions near the localized electrons/holes were also studied.

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the free carriers can screen the Coulomb interaction. However, ferroelectric metal, in which ferroelectric displacement coexists with conducting carriers, was predicted by Anderson and Blount [30] and then identified in LiOsO₃ [31]. In some ferroelectrics, the ferroelectric displacement can survive within a range of carrier concentration. For example, BaTiO₃, another ferroelectric perovskite, undergoes a phase transition from the ferroelectric tetragonal phase to cubic with the injection of electrons above a critical concentration [32,33]. Can the ferroelectricity of BFO sustain the carrier injection? If it can, how is the ferroelectric displacement tuned by charges? In this work, we also studied the evolution of the lattice structure with the injection of carriers. We found that a structural phase transition from R3c to the nonferroelectric Pbnm structure occurs if the hole concentration is over a criterion of 8.7×10^{19} cm⁻³. This indicates that hole injection can be used as an efficient way of depolarization of BFO if holes tend to be delocalized, whereas the free electrons do not destabilize the ferroelectric distortion, but they enhance the structural off-centering of BFO, which supports the idea that long-range ferroelectric order can be driven by short-range interactions [34].

II. METHODS

Density-functional-theory (DFT) calculations have been performed using the local spin density approximation [35] (LSDA) and the projector augmented wave method [36] as implemented in the Vienna *ab initio* simulation package (VASP) [37]. A plane-wave basis set with an energy cutoff of 450 eV was used to represent the wave functions.

The localization of the carrier depends on whether the localized electronic state can form within the band gap. Therefore, a good description of the band gap is needed. Local-density approximation (LDA) and generalized-gradient approximation (GGA) calculations always underestimate the band gap and tend to fail in predicting the localization of carriers. Our LDA calculation gives a band gap of 0.5 eV, while the experimental band gap of BFO is about 2.8 eV. The DFT+U method can improve the description of the electronic properties in BFO [38] by adding a Hubbard U [39,40] correction. Goffinet *et al.* [41] compared the results of DFT+U and hybrid functionals, and they found that both can describe the structural properties well. The band gap with the hybrid functional B1-WC calculation is 3.0 eV, while the LDA+U calculation with $U_{\rm Fe} = 3.8$ eV gives a 2.0 eV band gap. We used the more computationally inexpensive LDA+Ucorrection in all our calculations. An effective $U_{\text{Fe}} = 4 \text{ eV}$, which can give qualitative and subquantitative correct results for the structural, magnetic, and electronic properties in BFO, is used throughout this paper unless otherwise stated. In the calculations of the hole polarons, various U_0 's ranging from 0 to 12 eV were used. Adding Hubbard U to O 2p was found to be an effective way to calculate the hole polarons in titanite perovskites [42], in which the valence-band maximum (VBM) is mostly O2p states.

Bulk BFO adopts the symmetry with space group *R3c*, which can be viewed as pseudocubic structure with a ferroelectric polarization along the [111] direction. We constructed $\sqrt{2} \times \sqrt{2} \times 2$, $2 \times 2 \times 2$, and $2\sqrt{2} \times 2\sqrt{2} \times 2$ pseudocubic supercells, and by adding (removing) one electron from the supercells, the concentration of the electrons (holes) in these supercells is 1/4, 1/8, and 1/16 u.c.⁻¹, respectively. The $\sqrt{2} \times \sqrt{2} \times 2$ and $2\sqrt{2} \times 2\sqrt{2} \times 2$ supercells are constructed from the structure in Cc phase. The structures in Cc phase and R3c phase are very close. If the structures of the two phases are both put in $2 \times 2 \times 2$ supercells, the only difference between them would be that the angles $(\alpha, \beta, \text{ and } \gamma)$ of the lattice parameters for the R3c phase are all about 89.9°, while α and γ are fixed to 90° in the Cc phase. The localized electrons and holes break the symmetry of the bulk. Here, a $5 \times 5 \times 5$ Γ centered k-point grid was used to integrate the Brillouin zone. G-type antiferromagnetic structure was assumed in all the calculations. The image charge correction [43] and the potential-alignment correction [44] were utilized in the DFT calculations with the adding and removing of the electrons.

To find whether the electron injected into the BFO is delocalized or localized, we compared the two states with and without the bulk symmetry being broken. By following the recipes of Deskins et al. [45], we first elongate the Fe-O bonds around one Fe site to break the transition symmetry. Then we set the initial magnetic moment of the specific Fe site 1 less than those of the other Fe sites; since the Fe^{3+} ion has the $3d^5$ high spin electronic configuration, adding one electron will reduce the net magnetic moment. By using this as the initial state and relaxing the structure, the localized polaronic state can be obtained if there is a localized state within the band gap of BFO. A similar method can be applied in the calculation related to the hole localization. The initial structures were constructed by stretching or compressing the bonds near the hole center. In BFO without injected holes, O2p states are almost fully occupied, thus they have 0 spin. A $1\mu_B$ magnetization was set as the initial value for the O ion where the hole is assumed to be localized.

To see how the lattice distorts with the carrier concentration, the symmetries of the lattices are fixed to a few low-energy phases, namely R3c, Cc, $R\bar{3}c$, Pbnm, and $Pbn2_1$, respectively. A $5 \times 5 \times 5 \Gamma$ -centered k-point mesh was used with these calculations.

III. RESULTS AND DISCUSSION

A. Bulk properties

Here we look into the bulk properties of BFO. The primitive cell of BFO with R3c symmetry is shown in the inset of Fig. 1. There are 10 atoms in the primitive cell, including two 2 Bi atoms, 2 Fe atoms, and 6 O atoms. Each Bi atom has 12 neighboring O atoms, and each Fe atom has 6 neighboring O atoms, which make an octahedron. The calculated structural parameters with various U's are given in Table I, which agree well with experimental data [46] and previous calculations (e.g., in Ref. [38]).

The partial density of states of BFO is shown in Fig. 1. The states at the conduction-band minimum (CBM) are mostly Fe 3d states. Consequently, the injected electrons mainly stay at the Fe sites. The valence-band maximum (VBM) consists of O2p, Fe 3d, and Bi 6s states. Though the Bi 6s states are deep below the Fermi energy, the strong hybridization between the Bi 6s and O2p orbitals leads to considerable Bi 6s DOS at



FIG. 1. The density of Bi 6s and 6p, Fe 3d, and O 2p states. The inset shows the primitive cell of BFO with R3c symmetry. The results were calculated with $U_{\text{Fe}} = 4 \text{ eV}$ and $U_{\text{O}} = 0 \text{ eV}$. Changing the values of U_{Fe} and U_{O} does not change the nature of the VBM and CBM.

the VBM. The electron lone pair, which is the driving force of the ferroelectricity in BFO, is related to the Bi6s-O2p antibonding states at the VBM [47]. We must investigate at which site the injected holes are localized (if they tend to be localized).

B. Self-trapping of electrons

Electrons injected into the BFO lattice can be either delocalized or localized, depending on how they interact with the lattice. The delocalized electrons stay on the CBM and the symmetry of the lattice is preserved, whereas the localized electrons break the symmetry of the lattice and change the local chemical bonds to lower the energy, forming an in-gap state, i.e., forming a small polaron. To understand the behavior of the injected electrons, we compared the two kinds of electron states with the DFT+U calculations. Figures 2(a) and 2(b) show the electron density isosurfaces for the localized and the delocalized state, respectively. The localized electron resides

TABLE I. The structural parameters of BFO with R3c symmetry calculated with various U's. The Wyckoff positions are Bi 2a(x,x,x), Fe 2a(x,x,x), and O 6b(x,y,z).

$(U_{\rm T}, U_{\rm C})$		$(4,0)^{a}$	$(4.0)^{\mathbf{b}}$	$(1 8)^{a}$	$(4.12)^{a}$	Evnt ^c
(0 _{Fe} ,00)		(4,0)	(4,0)	(4,0)	(4,12)	Елрі.
Bi (2a)	x	0	0	0	0	0
Fe (2 <i>a</i>)	x	0.226	0.227	0.227	0.227	0.221
O (6b)	x	0.540	0.542	0.538	0.536	0.538
	у	0.942	0.943	0.942	0.940	0.933
	z	0.397	0.397	0.398	0.399	0.395
a_{rh} (Å)		5.52	5.52	5.49	5.47	5.63
α (deg)		59.79	59.84	59.82	59.72	59.35

^aResult from LDA+U calculation, this work.

^bResult from LDA+U calculation, Ref. [38].

^cExperimental result, Ref. [46].



FIG. 2. The isosurface of the (a) localized and (b) delocalized charge corresponding to the density of $1/8 e^{-1}/u.c.$ The green, brown, and red spheres represent the Bi, Fe, and O ions, respectively.

mostly on one Fe site, and the delocalized electron distributes on all Fe sites.

To see whether the in-gap state is stable, we calculated the electronic structures of the BFO with a localized and a delocalized injected electron. The total density of states (TDOS) of the $2 \times 2 \times 2$ supercell is shown in Fig. 3. The TDOS of BFO without injected electrons is used as a reference. In the localized case, there is an in-gap state of about 0.6 eV below the CBM, which corresponds to the localized electron state. The in-gap states are 0.5 and 0.7 eV below the CBM in the supercells with an electron concentration of 1/4 and 1/16 u.c.⁻¹, respectively. As for the delocalized state, the change is not just a Fermi energy shift within rigid bands either. A split in the formerly unoccupied Fe t_{2g} band can be clearly seen. The possible reasons for this are the change in the lattice and the electron-electron interaction, which shift the occupied bands down and the unoccupied bands up.

The electron self-trapping energy E_{EST} is defined as

$$E_{\text{EST}} = E_{\text{tot}}(\text{BFO} : e_{\text{CBM}}^{-}) - E_{\text{tot}}(\text{BFO} : e_{\text{polaron}}^{-}),$$

where $E_{\text{tot}}(\text{BFO}: e_{\text{CBM}}^-)$ is the total energy of the BFO cell with an injected electron at the CBM, and $E_{\text{tot}}(\text{BFO}: e_{\text{polaron}}^-)$ is the



FIG. 3. The total density of states of BFO in the $2 \times 2 \times 2$ supercell (a) without an injected electron, (b) with one localized injected electron, and (c) with one injected delocalized electron. The states with the energies below the dashed line are occupied.

TABLE II. The lengths of Fe-O bonds. In each Fe-O octahedron, the six Fe-O bonds can be divided into two groups of three long bonds and three short bonds, labeled by the subscript L and S, respectively. The superscript e means that a localized electron resides in the octahedron. l_L and l_S are the lengths of bonds in the octahedron farthest away from the localized electron. All units are Å.

Electron concentration	l_L^e	l_S^e	l_L	l_S
no injection			2.05	1.94
1/16e ⁻ /u.c.	2.11	2.01	2.05	1.93
$1/8e^{-}/u.c.$	2.12	2.01	2.07	1.94
$1/4e^{-}/u.c.$	2.15	2.04	2.11	1.94

total energy of BFO with a localized electron. A positive value means that the small polaronic state is energetically preferable. The $E_{\rm EST}$ of the supercells with electron concentrations of 1/4, 1/8, and 1/16 u.c.⁻¹ is 0.66, 0.50, and 0.39 eV, respectively.

We analyzed the possible mechanism for the self-trapping of electrons, and we found that the self-trapping is driven by the local lattice expansion and the Coulomb repulsion of the Fe 3d electrons, and it is stabilized by the antiferromagnetic structure.

One reason for the self-trapping of electrons is the distortion of the lattice surrounding the electrons. The most obvious change of the lattice is the expansion of the Fe-O octahedra where the injected electrons are localized. In ferroelectric BFO, the six Fe-O bonds of each Fe ion can be divided into two groups, namely the longer bond group and the shorter bond group, as the Fe atoms do not reside at the center of the oxygen octahedra. We found that both groups of Fe-O bonds near the injected electrons are elongated, as listed in Table II. The elongation of the bonds can be easily understood as a consequence of the Coulomb repulsion between the injected electron and the negatively charged oxygen ions. Because of the elongation of the Fe-O bonds, the Coulomb energy of the injected electrons is reduced. Meanwhile, this elongation reduces the Fe 3d-O 2p overlap, suppressing the hopping of the injected electrons and increasing the tendency of localization.

The higher the carrier concentration, the larger is the elongation, as the elongation of the Fe-O bonds increases the elastic energy of the surrounding lattices. The difference of the energy between the localized state and the CBM is larger in the structure with higher electron concentration, which is consistent with the longer local Fe-O bonds, as shown in Table II. On the other hand, the $E_{\rm EST}$ is smaller in the structure with lower electron concentration because of the increasing of the elastic energy cost.

Another reason for the self-trapping of the electrons is the Coulomb repulsion effect of the electrons. To see how this influences the localization of the electrons, we calculated the electronic structure with various effective U_{Fe} 's ranging from 0 to 6 eV. The self-trapping happens only if $U_{\text{Fe}} > 2$ eV. We found that the difference between the energy of the in-gap state and that of the lowest unoccupied state is larger with larger U_{Fe} , as shown in Fig. 4(a). The in-gap state and the lowest unoccupied state are both Fe 3*d*, thus the former can be seen as the lower Hubbard band (LHB) and the latter as the upper Hubbard band (UHB). The on-site Coulomb



FIG. 4. The dependencies of (a) ΔE (the difference between the energy of the in-gap state and that of the lowest unoccupied state) and (b) the self-trapping energy E_{EST} . (c) The calculated band gap on U_{Fe} .

repulsion of the Fe 3*d* electrons shifts the LHB down and the UHB up, enlarging the difference between them. Because the Coulomb repulsion lowers the energy of the localized electron, the self-trapping of the electrons is stabilized. Therefore, the self-trapping energy is higher with larger U_{Fe} , as shown in Fig. 4(b).

In all the structures, our calculations gave the results of G-type antiferromagnetic order with a total magnetic moment of $1\mu_B$ when one electron is self-trapped. The projected density of states of Fe 3*d* orbitals is shown in Fig. 5. The in-gap state has the opposite spin with the other occupied 3*d* states on the same site. Therefore, the electronic configurations of the Fe ions are $d^5 \downarrow d^1 \uparrow$ and $d^5 \uparrow$ with and without the localized electron, respectively [Figs. 5(a) and 5(b)]. In the Fe sites neighboring that with a localized electron, the five



FIG. 5. The projected density of the 3d states of (a) the Fe site with an injected localized electron, and (b) the neighboring Fe site. The energies are shifted so that the states below the energy 0 eV are occupied.

FIG. 6. The isosurface of the density of injected holes in the forms of (a) delocalized holes, (b) multicenter hole polarons, and (c) single-center small polarons in a 2 × 2 × 2 supercell. Parts (d)–(f), (g), and (h) show the local lattice distortion near the multicenter polaron and the single-center polaron, respectively. In (d), (e), and (g), only Bi-O bonds are shown. In (f) and (h), only Fe-O bonds are shown. The bond lengths are written in the form of $l_0 + \Delta l$, where l_0 is the bond length in the bulk structure with no carrier injection, and Δl is the increment. Parts (b), (d), (e), and (f) were calculated with $U_0 = 8$ eV. Parts (c), (g), and (h) were calculated with $U_0 = 12$ eV. The green, brown, and red spheres represent the Bi, Fe, and O ions, respectively.

3*d* states with the same spin as the in-gap state are fully occupied, which makes the hopping to the nearest neighbors forbidden. Therefore, the antiferromagnetic order stabilizes the localization of the injected electron.

C. Self-trapping of holes

The self-trapping of holes was also investigated. In BFO, the top of the valence band is a mix of O2p, Fe 3d, and Bi 6s states, as shown in Fig. 1. Therefore, we need to know on what sites the polarons would reside if the holes are selftrapped. We found that the Fe-site centered small polaron is energetically unfavorable with a large range of $U_{\rm Fe}$ from 0 to 8 eV. The largest contribution to the top of the valence band is from the O2p states. We explored the self-trapping of holes by adding the Hubbard U to the O 2p states [42] while keeping $U_{\rm Fe} = 4$ eV. Using various $U_{\rm O}$ from 0 to 12 eV, we found that holes tend to be delocalized with $U_{\rm O}$ < 6 eV, small polarons centered on O sites are stabilized for $U_{\rm O} \ge 12$ eV, and multicenter polarons are formed if U_0 is between 6 and 12 eV. The delocalized holes, the multicenter polaron, and the single-center small polaron are shown in Figs. 6(a), 6(b), and 6(c), respectively. The delocalized hole mainly distributes uniformly at the O sites; the multicenter hole polaron stays on the hybridized orbital of Bi and O (mainly at three O sites

FIG. 7. Density of states in the $2 \times 2 \times 2$ supercell with one hole polaron (red curves). The red curves are the DOSs of the structure with one hole polaron. The cyan curves are the DOSs of BFO without hole injection and are plotted as reference. (a) Total DOS. Parts (b) and (c) are the partial DOSs of the Bi and O atoms where the localized holes reside, respectively. Parts (a), (b), and (c) were calculated with U_0 =8 eV. (d) Total DOS. (e) Partial DOS of the O atoms where the localized holes reside. Parts (d) and (e) were calculated with U_0 = 12 eV.

and the Bi site near their center); the single-center hole polaron mainly stays at one O site. The TDOSs calculated with $U_{\rm O} = 8$ and 12 eV are shown in Figs. 7(a) and 7(d), respectively. States inside the band gap of the structure emerge, which corresponds to the hole polarons. Larger $U_{\rm Fe}$'s were checked and the results were found to be qualitatively the same. The localization of holes on the O sites instead of on the Fe sites is consistent with the fact that the half-filling d^5 electronic configuration is more stable than the d^4 configuration. The electronic configuration of the Fe ion would be d^4 if a hole is localized on the Fe³⁺ (d^5) site. In perovskite Fe⁴⁺ oxides such as SrFeO₃ and CaFeO₃, the Fe ions were found to be d^5L rather than d^4 , where <u>L</u> means a ligand hole [48–50], which suggests that holes on the O sites are more energetically favorable.

The change of the band gap (E_g) with U_O is small since the O bands are almost fully filled in bulk BFO [Fig. 8(c)]. Adding

FIG. 8. The dependences of (a) the energy difference between the in-gap state and the valence-band maximum, (b) the hole self-trapping energy, and (c) the band gap of BFO on U_0 .

U to the O 2*p* state does not significantly improve the lattice structure results, as can be seen from Table I. Therefore, we do not intend to claim what value of $U_{\rm O}$ is most appropriate for describing the self-trapping of the holes. Thus we also do not claim whether and what kind of hole polarons tend to be formed here. Instead, we study the properties of the polarons by varying the $U_{\rm O}$.

Like the self-trapping of electrons, the self-trapping of holes is also stabilized by on-site electron Coulomb interaction. Since most of the hole states are O2p, the dependence on U_{Fe} is not significant. We studied the dependence of the self-trapping energy and the in-gap state energy on U_{O} . The hole self-trapping energy E_{HST} is defined as

$$E_{\text{HST}} = E_{\text{tot}}(\text{BFO}: h_{\text{VBM}}^+) - E_{\text{tot}}(\text{BFO}: h_{\text{polaron}}^+),$$

where $E_{tot}(BFO : h_{VBM}^+)$ is the total energy of the BFO supercell with an injected hole at the VBM, and $E_{tot}(BFO : h_{polaron}^-)$ is the total energy of the BFO supercell with a hole polaron. The U_O dependence of the E_{HST} was studied. E_{EST} increases with U_O , as shown in Fig. 8(b). In BFO without carrier injection, the O2p states are almost fully occupied. With the removal of one electron, the in-gap state and the occupied O2p states can be seen as the UHB and LHB of the O2p, respectively. The effect of U_O is to push the in-gap state (the UHB) up and the occupied O2p states (the LHB) down, which lowers the total energy. Figure 8(a) shows that the energy difference (ΔE) between the in-gap state and the VBM increases with U_O , which is consistent with the larger UHB/LHB splitting.

The multicenter hole polaron state is a mix of Bi 6s and O 2p states, indicating that the hybridization between them is strong and plays an important role. The PDOSs of Bi 6s and O 2p on the sites corresponding to the ions marked as A and B in Fig. 6(b) are shown in Figs. 7(b) and 7(c). It can be seen that both the Bi 6s and O 2p state components are in the in-gap state. Instead of pushing one O 2p orbital up into the band gap, the Hubbard U on O 2p pushes the hybridized (Bi 6s, O 2p) state up. The delocalization effect of

the hybridization competes with the localization effect of the on-site electron Coulomb interaction. With small $U_{\rm O}$ (<6 eV), the delocalization is predominant, leading to free holes. With large $U_{\rm O}$ (>12 eV), the localization becomes predominant, leading to single-center small polarons. With intermediate $U_{\rm O}$, multicenter polarons are formed.

Here we look into the local lattice distortion near the multicenter polaron. The multicenter polaron does not break the threefold rotation symmetry. The rotation axis is along [111] and through the Bi ion marked as A in Fig. 6(b). The lengths of the bonds between this Bi ion and O ions decrease as the polaron is formed [Fig. 6(c)]. Since the Bi 6s and O2p states are antibonding at the top of valence band, the decreasing of the Bi-O bond length enhance the Bi 6s-O2p hybridization and further pushes the unoccupied antibonding state up. Consequently, the in-gap state is stabilized by the lattice distortion. The change to the lengths of Fe-O bonds is relatively small [Fig. 6(e)].

The single-center hole polaron is mostly on one O2p orbital, as shown by the spatial distribution of the hole [Fig. 6(c)] and the PDOS [Fig. 7(e)]. For the single-center polaron state, the on-site energy plays a more important role than the intersite orbital hybridization. The lengths of the Bi-O bonds and Fe-O bonds for the O site where the hole is localized increase [Figs. 6(g) and 6(h)], i.e., the distances between the hole and the positively charged ions increase. Thus the Coulomb energy is reduced, which stabilizes the self-trapping of holes on the O site.

D. Lattice deformation with delocalized carriers

Here we investigate the distortion of the lattice under the assumption that the injected carriers are delocalized. We calculated the total energy of various structural arrangements (R3c, $Cc, R3c, Pbnm, Pbn2_1$) with the change of concentration of delocalized carriers. The structure of the Cc phase is very close to the R3c structure. Therefore, the energy difference between the R3c and Cc phase is almost zero, and we do not distinguish these two phases here. The $R\bar{3}c$ is the paraelectric phase of BFO at high temperature. The *Pbnm* phase is featured with antiferroelectric oxygen octahedron rotations, which compete with the ferroelectric distortion. In the $Pbn2_1$ structure, the antiferroelectric oxygen octahedron rotations coexist with Bi ion off-centering displacements. The results are shown in Fig. 9. The R3c structure is energetically preferable with electron injection. For hole concentration larger than 0.005 hole per BFO unit (about 8.7×10^{19} cm⁻³), the orthorhombic *Pbnm* structure, which is not ferroelectric, is energetically preferable. Therefore, BFO of R3c tends to be depolarized with hole injection. The estimated value of the critical hole concentration is quite rough, as the energy difference between the phases near the phase-transition point is small. It also depends on the functional used. The Perdew-Burke-Ernzerhof [51] (PBE) functional plus U with U = 4 gives a concentration of about 0.08 u.c.^{-1} (about $6.23 \times 10^{21} \text{ cm}^{-3}$). But the trend toward the phase transition is robust. Neither 0.005 nor 0.08 holes per unit cell is too large a number, which indicates that hole injection can be an efficient way to depolarize the BFO if the holes are delocalized.

FIG. 9. Calculated total energy difference vs injected carrier concentration with R3c structure in various possible structural arrangements. The dashed line at 0 eV denotes the energy of the R3c structure.

The details of the evolution of the lattice structure with the *R3c* symmetry kept are shown in Fig. 10. The volume of the lattice increases with electron injection and decreases with hole injection, as shown in Fig. 10(a). The absolute positions of the band edges shift in order to minimize the electronic energy, which is achieved by changing the volume. The ferroelectric off-centering of BFO has two main features, one being that the Fe site with the Wyckoff position 2a(x,x,x) deviates from the centrosymmetric position x = 0.25, and the other being that Fe-O bonds form two groups of longer and shorter bonds. The Wyckoff positions of Fe and the lengths of Fe-O bonds are shown in Figs. 10(b) and 10(c), respectively. The off-centering is stronger as the concentration of the injected electrons increases. The trends are opposite with the injection of holes into the BFO structure. In summary, the injection of

FIG. 10. The change of lattice with adding/removing delocalized electrons. (a) The volume of the BFO R3c primitive cell (two BiFeO₃ formula units). (b) The Wyckoff position of Fe. The central symmetry Wyckoff position of Fe is 0.25. (c) The Fe-O bond lengths.

depolarized electrons enhances the off-centering of the R3c, whereas that of the holes reduces the off-centering.

The change of the lattice structure with concentration of carriers is very much like the change with the hydrostatic strain. An *R3c* to *Pbnm* transition with hydrostatic pressure was predicted and found [47,52]. Diéguez *et al.* [53] proposed that the reduction in structural off-centering and the phase transition are because of the less directional Bi-O bonds caused by the decreasing of the lattice volume. Just like in the hydrostatic compressed structures, the volume of the unit cell, the off-centering of the Fe cations, and the difference in the short and long Fe-O bonds are reduced in the hole injected structure, as shown in Fig. 10.

Because of the similarity in the structural evolutions with carrier injection and hydrostatic pressure, the two kinds of evolutions can have the same origin. The reason for the weakening of the structural off-centering can be that the Bi-O bonds are less directional with the shrinking of the volume with the hole injection.

To see whether the above speculation is true or not, we analyzed the Bi-O bonds in BFO. With the electronic configuration of the Bi³⁺ ion being $6s^2p^0$, Bi ions can shift away from the central symmetric positions, forming Bi-O bonds on one side of Bi atoms and the lone pairs on the other side of Bi atoms [47]. The forming of the lone pairs costs energy, while the forming of Bi-O covalent bondings gains energy. Therefore, if the Bi-O covalent bonding is strong enough, the forming of lone pairs and directional Bi-O bonds is stabilized, leading to structural off-centering in BFO. In the R3c structure with ferroelectric polarization in the [111] direction, Bi ions have 12 O neighbors. Because of the threefold rotation symmetry, these bonds can be divided into four groups labeled I, II, III, and IV, as shown in Fig. 11(a). The Bi-O bonds on the [111] direction side (group I) are shorter than those on the opposite side (group IV), leading to the Bi lone pair opposite to the polarization in BFO, which can be seen from the electron localization function [54] in Fig. 11(b). We compared the evolution of the Bi-O bond lengths with carrier concentration shown in Fig. 11(c) to that with hydrostatic pressure in Fig. 11(d), and we found almost identical evolution patterns. The difference between the Bi-O bond lengths of groups I and IV reduces with hole injection, which is the same with the hydrostatic pressure. Therefore, we can reach the conclusion that the hole injection leads to a reduction in volume and causes less directional Bi-O bonds and weaker Bi lone pairs. Thus the structural off-centering is reduced. In the nonferroelectric Pbnm structure, the Bi-O bonds are less directional, which is compatible with the suppressing of the lone pair. Therefore, the nonferroelectric *Pbnm* phase is favored over the *R*3*c* phase.

The enhancement the structural off-centering with electron injection suggests that the screening of the long-range Coulomb interaction does not necessarily kill the off-centering. This supports the idea that ferroelectric long-range order can be driven by short-range interactions [34]. In the case of BFO, this short-range interaction is the cooperative shift of the Bi cations driven by the formation of lone pairs, which is not impaired by the screening of the long-range Coulomb interaction. On the contrary, the free electrons on the CBM (mostly Fe 3*d* bands) push the surrounding oxygen anions

FIG. 11. The directional Bi-O bonds and the Bi 6s lone pair. (a) The 12 Bi-O bonds of each Bi ion, which can be categorized into four groups labeled as I, II, III, and IV, respectively, because of the threefold rotation symmetry. (b) The contour map of the electron localization function in the cut of the diagonal plane of the R3c primitive cell. (c) The lengths of the Bi-O bonds vs the concentration of injected carriers. (d) The lengths of the Bi-O bonds vs the volume of the BFO unit with hydrostatic pressure. The black dashed lines present the point of the phase transition between R3c and Pbnm.

away, reducing the lengths of the Bi-O bonds labeled as I. Thus the lone pair and the structural off-centering are strengthened.

IV. CONCLUSION

In summary, we studied the electronic and lattice structure evolution of BFO with various concentrations of injected electrons and holes. We found that the electrons tend to be localized, which is stabilized by the electron-electron Coulomb repulsion and the expansion of the oxygen octahedron near the Fe site where the electron resides. The antiferromagnetic order also stabilizes the localization. The injected holes tend to be delocalized if the O 2p on-site Coulomb interaction is weak (in other words, if U_0 is small). Small polarons are formed on O sites if U_0 is large. With intermediate U_0 , multicenter polarons can be formed. The forming of hole polarons is also stabilized by the lattice distortion.

In the R3c structure with injected carriers, delocalized electrons tend to enhance the off-centering, indicating that the

ferroelectricity in BFO is not driven by long-range Coulomb interaction but the cooperative shift of Bi ions, whereas holes tend to reduce the off-centering. With hole concentration larger than 8.7×10^{19} cm⁻³, there is a phase transition from *R3c* structure to nonferroelectric *Pbnm* structure. The reduction of off-centering and the phase transition in BFO are due to the shrinking of the lattice. These results indicate that the carrier injection can be an efficient way to control the ferroelectric distortion if the holes tend to be delocalized.

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