Biaxial strain effect induced electronic structure alternation and trimeron recombination in Fe₃O₄

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The Verwey transition in Fe₃O₄ is the first metal-insulator transition caused by charge ordering. However, the physical mechanism and influence factors of Verwey transition are still debated. Herewith, the strain effects on the electronic structure of low-temperature phase (LTP) Fe₃O₄ with P21/c and Cc symmetries are investigated by first-principles calculations. LTP Fe₃O₄, with each space group has a critical strain. With P21/c, Fe₃O₄ is sensitive to the compressive strain, but it is sensitive to tensile strain for Cc. In the critical region, the band gap of LTP Fe₃O₄, with both two symmetries linearly increases with strain. When strain exceeds the critical value, DOS of spin-down tₓᵧ electron at Fe(84) with P21/c and Fe(B42) with Cc changes between dₓ²₋ᵧ² and dₓ + dᵧ. The trimerons appear in Cc can be affected by strain. With a compressive strain, the correlation of trimeron along x and y axes is strengthened, but broken along the face diagonal of Fe₃O₄, which is opposite at the tensile strains. The results suggest that the electronic structure of Fe₃O₄ is tunable by strain. The narrower or wider band gap implies a lower or higher transition temperature than its bulk without strains, which also gives a glimpse of the origin of charge-orbital ordering in Fe₃O₄.

As an ancient magnet, Fe₃O₄ has been used as compass with a history about 3000 years. With more in-depth understanding of Fe₃O₄, its novel properties including half-metallicity and high Curie temperature of about 860 K have potential applications in spintronic devices. At ambient conditions, the high-temperature phase Fe₃O₄ has a face-center cubic lattice with a Fd3m symmetry. As a mixed-valence iron oxide with an inverse spinel lattice, Fe₃O₄ is formally written as Fe₂⁺[Fe³⁺Fe²⁺]O₄. Two Fe₂⁺ atoms have one spin-down tₓᵧ electron in 3d orbitals. Rapid hop of the electron between two neighbor Fe₂⁺ forms the conductive mechanism of Fe₃O₄.

In 1939, Verwey found that the conductivity of Fe₃O₄ drops about two orders by cooling down to 125 K. The lattice symmetry transforms from cubic to monoclinic simultaneously. The first-order approximation given by Verwey is an order-disorder transition of charge distribution at Fe₂⁺. The lattice structure of low-temperature phase (LTP) Fe₃O₄ once puzzled us. Gradually, the lattice structure of LTP Fe₃O₄ was clarified by X-ray diffraction, Raman and infrared spectroscopy in recent thirty years. Below Tᵥ, the lattice is a supercell of -√2aₓ × -√2aᵧ × 2a₁ (a₁ is the cubic lattice constant) with Cc symmetry. The charge ordering has been observed by Magnetic Compton scattering, resonant multiwave X-ray diffraction and selected area electron diffraction. With the P21/c or Cc space group, some theoretical calculations on the charge-orbital distribution give the results that is consistent with the experiments, which describe the ionic distribution, complex charge-orbital ordering pattern and ferroelectricity.

Recently, Senn et al. proposed a new type of quasiparticle named as “trimeron” by both the experimental and theoretical results, where an anomalously short distance of the Fe₂⁺ and Fe³⁺ appears. The minority-spin tₓᵧ electron is delocalized in a polaron that is composed of one Fe²⁺ donor and two Fe³⁺ acceptors. Owing to the weak interactions, trimeron can be regarded as an orbital molecule, where three Fe ions locally coupled within an orbital ordered solid state. The trimeron model provides a new idea for understanding the Verwey transition. However, the case at a lattice strain may be different. High quality Fe₃O₄ samples grown on SrTiO₃ and Co₃O₄ have been investigated, where the transition temperature shows a significant difference of about 10 K. So the strain may play an important role in the transition of Fe₃O₄, which should be studied in details.

In perovskite oxides (ABO₃), B site is at the center of O octahedra and covalently bonding with the nearest O atoms. Some previous results show that the tilting or rotation of the O-octahedra has an influence on the band structure of Fe₃O₄. Similar results should be looked forward to the cases at a lattice strain.
gap of perovskite\textsuperscript{24,25}. It is well known that the change of bond angle or bond length modifies the crystal field and band structure. Borisevich \textit{et al.}\textsuperscript{25} indicate that the enlarged Fe-O-Fe angle and a higher symmetry can reduce the band gap of BiFeO\textsubscript{3}. By doping a ion with a larger atomic radium at B-site, Jiang \textit{et al.} successfully tuned the band gap in CaFeO\textsubscript{3}\textsuperscript{26}.

In order to investigate the strain effect on the charge-orbital ordering and electronic structure of LTP Fe\textsubscript{3}O\textsubscript{4}, the first-principles calculations are carried out on LTP Fe\textsubscript{3}O\textsubscript{4} with $P\overline{2}/c$ and $Cc$. It is found that the orbital ordering and band structure of LTP Fe\textsubscript{3}O\textsubscript{4} can be tuned by the external strain. The band gap of Fe\textsubscript{3}O\textsubscript{4} with both two symmetries can be changed by a strain with a critical region, where the trimeron shows a complex relation with the external strain.

**Calculational Details**

The electronic structures of the LTP Fe\textsubscript{3}O\textsubscript{4} with structure (I) $P\overline{2}/c$ and structure (II) $Cc$\textsuperscript{19} are calculated by using the potential projector augmented wave method in Vienna Ab initio Simulation Package\textsuperscript{27,28}. The calculations are based on the generalized gradient approximation plus on-site Coulomb interaction (GGA + $U$)\textsuperscript{29–31}. The energy cutoff is 400 eV. The Monkhorst-Pack grid of $k$-points for structure (I) is $6 \times 6 \times 2$ and that for structure (II) is $3 \times 3 \times 2$. The on-site Coulomb interaction parameter $U = 4.5$ eV and on-site exchange interaction parameter $J = 0.89$ eV for all the Fe ions are used in the two structures\textsuperscript{16}. The lattice constants and atomic positions in the two structures are used as that in refs 1 and 19, respectively. The same parameters except for $k$-points of $3 \times 3 \times 3$ are used to calculate the high-temperature phase (HTP) Fe\textsubscript{3}O\textsubscript{4} with structure (III) $Fd\overline{3}m$ symmetry.

The stress is defined by the change of lattice constants as $S = (a - a)/a \times 100\%$, where $S$, $a$ and $a$ represents the strain, lattice constant without and with strain, respectively. Biaxial lattice strain is applied by fixing the in-plane lattice constants ($a$ and $b$) and relaxing $z$ direction throughout the calculations. The tensile and compressive strains are defined as $S > 0$ or $S < 0$. In order to clarify the strain effects on the charge-orbital ordering, the structural optimization for structures (I) and (II) with lattice constants are carried out, where the atomic positions are fully relaxed. Then, the lattice strain is taken into considerations. The structure optimization will stop until the total energy change is less than $10^{-5}$ eV and the Hellman–Feynman forces of optimized structure fall below $10^{-2}$ eV/Å.

**Results and Discussions**

**Electronic & lattice structure with $P\overline{2}/c$ symmetry.** In Fig. 1, the unique equivalent site of Fe\textsubscript{2} in structure (III) breaks into Fe(B1a), Fe(B1b), Fe(B2a), Fe(B2b), Fe(B3) and Fe(B4) in structure (I) as the symmetry reduces\textsuperscript{1,3}. The coordinate system of monoclinic structure rotates by 135° around $z$ axis\textsuperscript{1}. Figure 2 shows the electronic structure of structure (I) and (III). HTP Fe\textsubscript{3}O\textsubscript{4} shows a half metallic characteristic, where the spin-down
states near Fermi level comes from the extra minority electron of Fe\textsubscript{B} \textit{t}_2 \textit{g} orbits\textsuperscript{2,5}. In Fig. 2(b), the band gap of structure (I) is opened by 0.51 eV at Fermi level, which is a bit larger than the spectroscopic 0.14 eV\textsuperscript{10}. Figure 2(c) shows the partial DOS at different Fe\textsubscript{B} sites. The minority electron of Fe\textsubscript{B} is localized at Fe(B1a), Fe(B1b) and Fe(B4), which is consistent with previous results\textsuperscript{1,3,16}. These results suggest that Fe(B1a), Fe(B1b) and Fe(B4) are Fe\textsuperscript{2+} and Fe(B2a), Fe(B2b) and Fe(B3) are Fe\textsuperscript{3+}. In Table 1, the bond-valence sum (BVS) of Fe\textsubscript{B} is in well agreement with DOS. Herewith, the BVS expression is \( \text{BVS} = \sum_i \exp \left( \frac{R_i - R_0}{b} \right) \), where \( R_0 \) is the bond-valence parameter\textsuperscript{32}. For Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, \( R_0 \) is 1.734 and 1.759, respectively. \( R_i \) refers to the \( i \)-th bond length and \( b \) is a constant of 0.37 Å\textsuperscript{32}.

In order to investigate the strain effects, the strain of \(-5\%\), \(-2.5\%\), 0\%, +2.5\% and +5\% are set. In Fig. 3, the orbit of spin-down \( t_{2g} \) electron at Fe(B4) (\( B4\textit{t}_{2g}\downarrow \)) is almost in the \( xy \) plane at \( S = -2.5\% \), 0\%, +2.5\% and +5\%. At \( S = -5\% \), the \( B4\textit{t}_{2g}\downarrow \) orbit shows a different style from others. In Fig. 3(a) and (b), the charge density of \( B4\textit{t}_{2g}\downarrow \) are projected onto (1\,\overline{1}0) and (1\,\overline{1}0) plane at \( S = 0\% \) and \(-5\% \). At \( S = 0\% \), the charge density of \( B4\textit{t}_{2g}\downarrow \) plotted on both planes shows ellipsoidal shape. At \( S = -5\% \), the charge density of the electron plotted on (1\,\overline{1}0) plane still shows ellipsoidal shape, but the charge density plotted on (1\,\overline{1}0) plane shows a flower shape. This phenomena manifests

| Atom site | BVS  | \(<\text{Fe}_B\text{-O}>\) (Å) |
|-----------|------|-----------------|
| Fe(B1a)   | 2.238| 2.101           |
| Fe(B1b)   | 2.238| 2.101           |
| Fe(B2a)   | 2.942| 2.023           |
| Fe(B2b)   | 2.942| 2.023           |
| Fe(B3)    | 2.882| 2.034           |
| Fe(B4)    | 2.255| 2.098           |

Table 1. The BVS calculation results of Fe\textsubscript{B} in structure (I). The bond-valence parameters for Fe\textsuperscript{2+}-O\textsuperscript{2−} = 1.734 and Fe\textsuperscript{3+}-O\textsuperscript{2−} = 1.759\textsuperscript{32}. The average Fe\textsubscript{B}-O bond lengths in Fe\textsubscript{B}O\textsubscript{6} at different Fe\textsubscript{B} sites are also shown.
that the $B_4t_{2g}^{\downarrow}$ orbit lies in the $(110)$ plane at $S = -5\%$. In order to figure out the critical strain, the electronic structure is also calculated at $S = -3\%$ and $-4\%$. Figure 3(c) shows the $B_4t_{2g}^{\downarrow}$ charge density projected onto $(100)$ plane with a strain from $0\%$ to $-5\%$. The $B_4t_{2g}^{\downarrow}$ orbit still lies in the $xy$ plane until the strain decreases to $-5\%$. Therefore, the compressive strain of $-5\%$ is the critical value for $P2_1/c$ symmetry. Meanwhile, DOS of $3d$ orbits of $\text{Fe}(B_4)$ also shows the same change. In Fig. 3(d), at $S = -5\%$, the $B_4t_{2g}^{\downarrow}$ orbit changes from $d_{xy}$ to $dy_z + dx_z$ by comparing the DOS at $S = 0\%$. Actually, the $B_4t_{2g}^{\downarrow}$ orbit changes from $d_{xy}$ to $d_{yz}$ in HTP Fe$_3$O$_4$ coordinate system because of the rotation of coordinate

Since the conductivity of Fe$_3$O$_4$ is related to Fe$B_4t_{2g}^{\downarrow}$ and BO$_6$ distortion, it is necessary to investigate the O-octahedral distortion at different Fe$B_4$ sites. In Fig. 4(a), the band gap shows a positive correlation with the increased $\Delta V$ except for $S = -5\%$. Herewher, $\Delta V$ is the average volume difference between Fe$^{2+}$O$_6$ and Fe$^{3+}$O$_6$. $E_g$ is the energy gap near Fermi level. By linear fitting $E_g$ at different strains, we get $E_g = 0.946\Delta V - 0.651$, where $E_g$ at a compressive strain of $-5\%$ is not included. Quantitatively, the volume of Fe$O_6$ shows the magnitude of its crystal field. Since Fe$^{3+}$ has a stronger interaction with surrounded O$^{2-}$ than Fe$^{2+}$, the volume of Fe$^{3+}$O$_6$ is smaller than that of Fe$^{2+}$O$_6$, but the electrostatic potential is higher than that of Fe$^{2+}$O$_6$. The results mean that the larger volume difference is, the more energy is needed when the electron hopes between Fe$^{2+}$ and Fe$^{3+}$. Therefore, as the tensile strain increases, the gap becomes larger. Simultaneously, the competition between the band gap and thermal activation energy has a relation with the metal-insulator transition (MIT) temperature. Therefore, the MIT temperature of Fe$_3$O$_4$ could be tuned by external strain. At a compressive (tensile) strain, the band gap becomes narrow (wide) and the MIT temperature of Fe$_3$O$_4$ becomes lower (higher).

However, the above demonstration on the relation between $\Delta V$ and $E_g$ is not proper for the case at $S = -5\%$. Therefore, the Fe-O bond length in Fe$O_6$ at Fe$B_4$ is further analyzed. Since the charge density of Fe$B_4$ shows an obvious change and all the Fe$B_4$ atoms are equivalent with the same ambient ionic conditions, in Fig. 4(b), Fe$B_4$ at $1c/8$ height is selected as a candidate. O(17), O(21), O(25), O(29) and Fe$B_4$ are almost in horizontal plane and O(2)-Fe($B_4$)-O(14) is parallel to $z$ axis. Table 2 lists the Fe($B_4$)-O distances at different strains.

Figure 3. Charge density of $B_4t_{2g}^{\downarrow}$ plotted on (110) and (110) planes in structure (I) with (a) 0% and (b) $-5\%$ lattice strain are shown, respectively. Charge density of $B_4t_{2g}^{\downarrow}$ plotted on (100) plane for 0%, $-2.5\%$, $-3\%$, $-4\%$ and $-5\%$ lattice strain are showing in (c). The atom shown in white square is Fe ($B_4$). The PDOS of Fe($B_4$) plotted on 3d orbits with 0% strain (upper panel) and $-5\%$ (lower panel) are shown in (d).
weak bond interaction between Fe(3) distribution and crystal field. At a larger strain, the orbital ordering pattern becomes unstable. The outermost longer. The bond lengths of Fe(0% to 0.15 Å longer than that at Fe(0% to 0.28 eV than that at Fe(0% to 0.5% is larger by about 0.28 eV than that at Fe(0% to 0.5%). At Fe(0% to 0.5%, the length of O(2)-Fe(0% to 0.5%) is about 0.15 Å longer than that at S = −4%. The above phenomenon shows that the strain can tune the mode of ionic distribution and crystal field. At a larger strain, the orbital ordering pattern becomes unstable. The outermost 3d electrons of Fe(B4) have a strong Column repulsive interaction with surrounded O2− in horizontal plane. Owing to the change of the distribution of 3d orbits, the electrostatic energy can be partially released along the O(25)-Fe(B4)-O(21) and Fe(B4)-O(25) show an anomalous shortage, but the Fe-O bond length along z direction shows a sudden enlargement. At S = −5%, the length of O(2)-Fe(B4)-O(14) is about 0.15 Å longer than that at S = −4%. The above phenomenon shows that the strain can tune the mode of ionic structure (I) with −4% and −5% compressive strain in left and right panel, respectively.

Table 2. The bond lengths (Å) between Fe(B4) at 1c/8 and surrounded O2− in structure (I) with the strain changing from +5% to −5%. The two longest bond lengths in the xy plane are shown in bold.

| Strain/Atom site | +5% | +2.5% | 0% | −2.5% | −3% | −4% | −5% |
|------------------|-----|-------|----|-------|-----|-----|-----|
| O(2)             | 2.0019 | 2.0163 | 2.0277 | 2.0360 | 2.0370 | 2.0413 | 2.1389 |
| O(14)            | 2.0440 | 2.0664 | 2.0854 | 2.1052 | 2.1087 | 2.1144 | 2.1685 |
| O(17)            | 2.2159 | 2.1690 | 2.1314 | 2.0858 | 2.0777 | 2.0612 | 2.0618 |
| O(21)            | 2.2170 | 2.1702 | 2.1317 | 2.0882 | 2.0802 | 2.0688 | 1.9828 |
| O(25)            | 2.1926 | 2.1461 | 2.1052 | 2.0598 | 2.0526 | 2.0530 | 1.9645 |
| O(29)            | 2.1932 | 2.1456 | 2.1054 | 2.0576 | 2.0500 | 2.0523 | 2.0566 |

In the horizontal plane, at S ≥ −4%, the bond length of Fe(B4)-O(17) and Fe(B4)-O(21) are longer than that of Fe(B4)-O(25) and Fe(B4)-O(29). At S = −5%, the distances Fe(B4)-O(17) and Fe(B4)-O(29) become much longer. The bond lengths of Fe(B4)-O(21) and Fe(B4)-O(25) show an anomalous shortage, but the Fe-O bond length along z direction shows a sudden enlargement. At S = −5%, the length of O(2)-Fe(B4)-O(14) is about 0.15 Å longer than that at S = −4%. The above phenomenon shows that the strain can tune the mode of ionic distribution and crystal field. At a larger strain, the orbital ordering pattern becomes unstable. The outermost 3d electrons of Fe(B4) have a strong Column repulsive interaction with surrounded O2− in horizontal plane. Owing to the change of the distribution of 3d orbits, the electrostatic energy can be partially released along the O(25)-Fe(B4)-O(21) direction. O2− has been pushed away along z direction due to the electronic interaction. The Fe-O bond length distortion in horizontal plane also appears at Fe(B2) and Fe(B3). However, the Fe-O bond lengths at Fe(B1) do not change. Since the inversion centers and partial face centers are occupied by Fe(B1), the symmetry of Fe(B1) is higher than other FeB sites, where the ambience of Fe(B1) is more stable than other FeB sites. Therefore, the mode of ionic distribution does not change at Fe(B1).

In the band structure, the energy of spin-down conduction-band minimum at S = −5% is higher by about 0.28 eV than that at S = −4%. However, in Fig. 4(c), the valence-band maximum of FeB t2g orbit is still just below Fermi level. The compressive strain of −5% can change the structure of O-octahedra at FeB sites. Simultaneously, the Fe-O Column interaction can raise the conduction band energy. So, in Fig. 4(a), the band gap of structure (I) at S = −5% is larger by about 0.28 eV than that at S = −4%.

Furthermore, the nearest six Fe-Fe distances around different FeB sites are analyzed. Unlike Column's law, the <Fe2+.Fe3+> distance shows an anomalous shortage, which is even less than the <Fe2+.Fe2+> distance at Fe(B1) without strain. The phenomenon is consistent with trimeron model. As the tensile strain is applied, the weak bond interaction between Fe3+.Fe2+.Fe4+ becomes tighter around Fe(B1). When the compressive strain is applied, the trimerons around Fe(B1) become weak. However, the distance between Fe(B4) and Fe(B3) becomes shorter than the Fe2+.Fe4+ distance around Fe(B4). So, a more complex structure of trimeron forms, which will be demonstrated in the next section.

Electronic & lattice structure with Cc symmetry. In Fig. 5, when the symmetry reduces to Cc space group, the LTP FeO lattice and the charge-orbital ordering pattern become more complex. The electronic structure of bulk without strain is firstly calculated. The band gap near Fermi level with and without structural optimization is about 1.0 and 0.7 eV, respectively. Figure 5(b) shows the total DOS of the optimized structure. The energy gap is larger than experimental result because the calculation is proceeded at 0 K. Then, the strain of −5%, −2.5%, +2.5% and +5% is applied to the Cc structure. Different from P2/c structure, the structure (II) is sensitive to tensile strain. So, we then calculated the electronic properties at S = +3% and +4% to figure out the critical value.

Figure 5(c) shows the spin-down charge density at a height of 3c/8 and 7c/8 as a tensile strain increases from 0% to +5%. At S < +4%, the Fe(42)t2g orbit [marked with white square in Fig. 5(c)] lies in the (110) plane at

![Figure 4.](https://example.com/figure4.png)

(a) The band gap E_g with the average FeO2 volume difference at different strains. (b) The local structure of Fe(B4) under P2/c symmetry. (c) The band structure of structure (I) with −4% and −5% compressive strain in left and right panel, respectively.
3c/8 and lies in the (110) plane at 7c/8. When the tensile strain exceeds the critical value at $S = +4\%$ and $+5\%$, the Fe($B_{42}$)$_{t_{2g^{↓}}}$ orbit rotates into horizontal plane. Figure 5(a) shows the atom sites of Fe($B_{42}$), which is labeled in dark blue. In Fig. 6(a), at $S = +4\%$ and $+5\%$, the DOS of Fe($B_{42}$) shows that the orbits of those Fe atoms change from $d_{xz}$ to $d_{x^{2}-y^{2}}$. The coordinate of structure (II) also rotates around $z$ axis by 135° from cubic Fe$_3$O$_4$, which is consistent with structure (I). Therefore, the orbit actually changes from $d_{xz}$ to $d_{xy}$ at 3c/8, which changes from $d_{yz}$ to $d_{xy}$ at 7c/8 within cubic coordinate. In the inset of Fig. 6(a), by comparing the DOS at $S = +4\%$ and $+5\%$, it is found that although the Fe($B_{42}$)$_{t_{2g^{↓}}}$ orbit changes at $S = +4\%$, it still has the residual states projected onto $d_{yz}$. The residual states come from the out-of-plane slope of $d_{x^{2}-y^{2}}$. Then, the relationship between $\Delta V$ and $E_g$ in structure (II) is investigated. In Fig. 6, $E_g$ shows a positive relation with the increased $\Delta V$ at $S < +4\%$, which can be described as $E_g = 0.370 \Delta V + 0.534$. However, the linear fitting parameters both slope and intercept are quite different from structure (I) due to the different structure and charge-orbital ordering pattern.

Since the orbital change at Fe($B_{42}$) is obvious, the Fe-O bond length and O-octahedra distortion at Fe($B_{42}$) are taken as an example, where Fe(85) (at 3c/8) is selected as a substitute for other equivalent Fe($B_{42}$) sites. Figure 7(a) shows the local structure of Fe(85). The O(77), O(90), O(109), O(122) and Fe(85) atoms are almost in horizontal plane. O(2)-Fe(85)-O(53) is almost parallel to $z$ axis. Table 3 lists the Fe(85)-O bond lengths at different strains, revealing the reason for the orbital change at Fe($B_{42}$). The FeO$_6$ distorts in horizontal plane at $S = +4\%$ and $+5\%$. The two shortest bonds are along (110) direction and the two longest bonds are perpendicular to (110) direction. When $+4\%$ and $+5\%$ strain is applied, both the shortest and longest bond are coexistent in diagonals. The Fe-O bond length along $z$ direction suddenly decreases by about 0.1 Å when the strain increases from $+3\%$ to $+4\%$. The obvious Fe-O bond length distortion in $xy$ plane also appears at Fe($B_{2b1}$), Fe($B_{31}$), Fe($B_{32}$), Fe($B_{34}$), Fe($B_{41}$), Fe($B_{43}$) and Fe($B_{44}$). Due to the tensile strain, the expansion of the equatorial plane of O-octahedra can release the electrostatic energy between the surrounded O$^{2-}$ and outside electron of Fe$^{2+}$. Correspondingly, the Column interaction along $z$ direction can also be weakened by the transformation of Fe($B_{42}$)$_{t_{2g^{↓}}}$ orbit, so the Fe-O bond length along $z$ direction becomes shorter. Since the equatorial face can further expansion at $S = +5\%$, more electrostatic energy can be released, where the Fe($B_{42}$)$_{t_{2g^{↓}}}$ orbit becomes more parallel to the $xy$ plane. In the inset of Fig. 6(a), at $S = +5\%$, the residual $d_{yz}$ states are less than that at $S = +4\%$. 

**Figure 5.** (a) The lattice structure under Cc symmetry. (b) Total DOS of structure (II). (c) Charge density map of spin-down electrons plotted on (001) plane at 3c/8 (left column) and 7/8 c (right column) with different strains. Fe($B_{42}$) is shown in the white square.
In Fig. 7(b), the conduction-band minimum at $S = +4\%$ is lower than that at $S = +3\%$, where the valence-band maximum is still just below Fermi level. As a result, the band gap becomes smaller as the strain increases. Furthermore, the model of trimeron presented by Senn et al. 18–20 is also observed in our calculations. It is found that the distribution of trimeron can be affected by external strain. When the strain increases from 0% to $+5\%$, the Fe-Fe distance along $x$ and $y$ axis changes faster than that along the face diagonal direction of Fe$_8$B$_4$O$_4$. The Fe-Fe distance along diagonal direction even reduces with the increased strain at some Fe$_8$B$_4$O$_4$ sites. The process of Fe$_8$B$_4$O$_4$ distortion is compared with an ideal model of equivalent volume deformation in tetragonal system. Figure 8 shows the sketch map of this ideal model, where $a$, $h$ and $l$ each respect the in-plane, out-of plane crystal edges and face diagonal. Lattice with tensile and compressive strain are superscripted with $'\text{}'$ and $'\text{''}$$'$, respectively. The volume of this tetragonal $V = a^2h$, so $h = V/a^2$ and the face diagonal $l = \sqrt{a^2 + h^2} = \sqrt{a^2 + (V/a^2)^2}$. The different coefficient of $l$ with respect to $a$ is $\frac{dl}{da} = \frac{d}{da} \left( \sqrt{a^2 + \left( \frac{V}{a^2} \right)^2} \right)$. At $0 < a < 3.367$, $\frac{dl}{da} < 0$. In our model, the case of $0 < a < 3$ is considered. As a result, the length of face diagonal reduces with the increased lattice constant. So, the

**Table 3.** The nearest Fe-O bond lengths at Fe(85) with different stresses in structure (II). The two longest bond lengths in the xy plane are shown in bold.

| Atom site | +5%  | +4%  | +3%  | +2.5% | 0%   | -2.5% | -5%  |
|-----------|------|------|------|-------|------|-------|------|
| O(33)     | 2.0252 | 2.0255 | 2.1162 | 2.1141 | 2.1331 | 2.1402 | 2.1426 |
| O(35)     | 2.0323 | 2.0329 | 2.1162 | 2.1141 | 2.1199 | 2.1225 | 2.1234 |
| O(77)     | 2.2188 | 2.1966 | 2.1673 | 2.1552 | 2.1218 | 2.0800 | 2.0460 |
| O(90)     | 2.2037 | 2.1797 | 2.0850 | 2.0755 | 2.0405 | 2.0049 | 1.9752 |
| O(109)    | 2.1986 | 2.1708 | 2.0969 | 2.0852 | 2.0466 | 2.0098 | 1.9787 |
| O(122)    | 2.1986 | 2.1731 | 2.1769 | 2.1658 | 2.1296 | 2.0853 | 2.0466 |

In Fig. 7(b), the conduction-band minimum at $S = +4\%$ is lower than that at $S = +3\%$, where the valence-band maximum is still just below Fermi level. As a result, the band gap becomes smaller as the strain increases.

Furthermore, the model of trimeron presented by Senn et al. 18–20 is also observed in our calculations. It is found that the distribution of trimeron can be affected by external strain. When the strain increases from 0% to $+5\%$, the Fe-Fe distance along $x$ and $y$ axis changes faster than that along the face diagonal direction of Fe$_8$B$_4$O$_4$. The Fe-Fe distance along diagonal direction even reduces with the increased strain at some Fe$_8$B$_4$O$_4$ sites. The process of Fe$_8$B$_4$O$_4$ distortion is compared with an ideal model of equivalent volume deformation in tetragonal system. Figure 8 shows the sketch map of this ideal model, where $a$, $h$ and $l$ each respect the in-plane, out-of plane crystal edges and face diagonal. Lattice with tensile and compressive strain are superscripted with $'\text{}'$ and $'\text{''}$$'$, respectively. The volume of this tetragonal $V = a^2h$, so $h = V/a^2$ and the face diagonal $l = \sqrt{a^2 + h^2} = \sqrt{a^2 + (V/a^2)^2}$. The different coefficient of $l$ with respect to $a$ is $\frac{dl}{da} = \frac{d}{da} \left( \sqrt{a^2 + \left( \frac{V}{a^2} \right)^2} \right)$. At $0 < a < 3.367$, $\frac{dl}{da} < 0$. In our model, the case of $0 < a < 3$ is considered. As a result, the length of face diagonal reduces with the increased lattice constant. So, the
trimerons along $x$ and $y$ direction break down by the tensile strain, but the correlation of trimerons along the face diagonal are strengthened. When a compressive strain is applied, the Fe-Fe distance along $x$ and $y$ direction becomes short and the Fe-Fe distance along face diagonal elongates. The trimerons along $x$ and $y$ direction are strengthened, but the trimerons along the face diagonal directions break down due to the compressive strain.

Figure 7. (a) The local structure of Fe(B42) under Cc symmetry. (b) The band structure under Cc symmetry with +3% and +4% compressive strain in left and right panel, respectively.

Figure 8. The sketch map shows the ideal model of deformation with equivalent volume. The Fe$_{26}$O$_4$ models without strain, with tensile or compressive strain are colored with blue, grey and orange, respectively. $a$, $h$ and $l$ each respects the in plane, out of plane direction Fe-O bond length and the Fe-Fe distance along face diagonal direction. The length of $a'$ and $a''$ is $(1 + 6\%)a$ and $(1 - 6\%)a$, respectively. The ratio of $a$, $a'$ and $a''$ is correspondent with the calculation results. The local structure of Fe$_{26}$O$_4$ is also shown in the lower right corner.
Conclusions
We have investigated the biaxial strain effects on the electronic structure of LTP FeO₃ with P2/c and Cc space group by GGA + U method. When the strain on the two structures are below their critical region, the distortion of O-octahedra can change the electrical potential difference between the nearest ferric and ferrous ions. As a result, the band gap shows a positive linear correlation with the strain. The narrower or wider band gap implies a lower or higher transition temperature. When the strain is above the critical value namely S < −4% in structure (I), the orbit of Fe(B4) changes from dₓz to dₓᵧ in HTP FeO₃ coordinate and the energy of conduction-band minimum increases. In structure (II), at S ≥ +4%, the orbit of Fe(B4) changes from dₓz to dₓᵧ in HTP FeO₃ coordinate and the energy of conduction-band minimum reduces. The trimeron appears in both the structure (I) and (II). The distribution of trimeron can also be affected by strain. The trimerons along x and y axes get broken (strengthened) at a tensile (compressive) strain. However, the trimerons along face diagonal are broken (strengthened) at a compressive (tensile) strain. These results can be ascribed to the change of Fe-Fe distance when different strains are applied, which can be estimated by geometric calculations.

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