Unexpected robustness of the band gaps of TiO$_2$ under high pressures

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Abstract

Titanium dioxide (TiO$_2$) is a wide band gap semiconducting material which is promising for photocatalysis. Here we present first-principles calculations to study the pressure dependence of structural and electronic properties of two TiO$_2$ phases: the cotunnite-type and the Fe$_2$P-type structure. The band gaps are calculated using density functional theory with the generalized gradient approximation, as well as the many-body perturbation theory with the GW approximation. The corresponding pressure coefficients are significantly smaller than that of diamond and silicon carbide, whose pressure coefficient is the smallest value ever measured by experiment. The robustness originates from the synchronous change of valence band maximum and conduction band minimum with nearly identical rates of changes. A step-like jump of band gaps around the phase transition pressure point is expected and understood in light of the difference in crystal structures.

1. Introduction

Pressure is a powerful tool for tuning the atomic and electronic structures of materials. Both inorganic and organic substances, such as Si, Ge, H$_2$O, SiO$_2$ and C$_6$H$_6$, can exhibit complex condensed phases under high pressures [1–5]. With the application of high pressure, people are able to synthesize some novel compounds that do not exist at ambient conditions [6]. Tremendous studies have demonstrated that the electronic properties of materials can be effectively manipulated by compression, through which the metal-to-semiconductor [7, 8] or insulator-to-metal transitions [9–15] take place. It is conjectured that insulators and semiconductors always metallize under sufficiently high external pressures [16]. The most notable examples may be the prediction of possible metalization and superconductivity in solid state hydrogen [17–19], and the observation of high-$T_c$ superconductivity in hydrogen sulfide under high pressures [20, 21].

In principle, the electronic structures of materials under high pressures can be probed by experimental measurements on the quantities such as electrical conductivity, optical conductivity and reflectivity [22, 23]. To date, however, measurements on the electronic properties of wide band gap semiconductors are limited to pressures of several to tens GPa. At extreme pressures below the pressure point of metallization (rarely attainable in experiment), typically $\sim 100–200$ GPa, little is known about the characteristics of electronic structures of the intermediate states of wide band gap semiconductors. This may be due to the technique difficulties in accurate determination of electronic band structures at the presence of high pressure devices like the diamond anvil cell (DAC), or the intrinsic or impurity absorption edges of diamond in conventional optical spectroscopy [22]. There lacks the knowledge about the global behavior of electronic structures across a wide range of pressures, in particular, pressures spanning an interval with the width of $\sim 100$ GPa or larger.

In this work, we study the effects of pressure on titania (TiO$_2$), one of the most extensively studied wide band gap semiconductors [24–26], at pressures spanning over an interval of $\sim 150$ GPa. As an important photocatalyst for harvesting solar energy, the alignments of energy levels near the valence and conduction bands play a key role.
is the external potential due to ions, \( y \) is the Green’s function, \( G \) is the kinetic energy operator of electrons, and \( \Sigma \) are the parameters to be determined, and \( c_p = \frac{\partial E_T}{\partial P} \) is the so-called pressure coefficient [36–39], which is a key parameter describing the pressure dependence of band gaps. It is unclear whether equation (1) would be applicable or not to wide band gap semiconductors at \( P \geq 100 \) GPa. From the data reported in literatures [36–50], previous studies are focused on the pressure coefficients (\( c_p \)) at ambient or moderate pressures, at which the values of \( c_p \) can be either positive or negative, with an order of magnitude of \( 10^{-2} \)–\( 10^{-1} \) eV GPa\(^{-1}\) for most systems. By contrast, our studies based on first-principles calculations find that, the band gaps of the two high-pressure phases of TiO\(_2\) are surprisingly robust to compression. Within a wide range of pressures (50–200 GPa for the cotunnite-type, and 110–260 GPa for the Fe\(_2\)P-type), the pressure coefficients of TiO\(_2\) are significantly smaller than that of diamond (\( \sim 5 \) meV GPa\(^{-1}\)) [41, 42] and silicon carbide (SiC) (\( \sim 1.9 \) meV GPa\(^{-1}\)) for the cubic SiC [43], and \( \sim 2 \) meV GPa\(^{-1}\) for 6H-SiC [44]), the smallest value ever measured experimentally. Furthermore, we find that the pressure dependence of the band gaps of both phases is well described by a modified form of equation (1).

2. Theoretical methods

The first-principles calculations were carried out by the Vienna \textit{ab initio} simulation package (VASP) [51, 52], which is based on density functional theory (DFT). A plane wave basis set and the projector-augmented-wave potentials [53, 54] are employed to describe the electron-ion interactions. The exchange-correlation interactions of electrons are described by the generalized gradient approximation (GGA) within the PBE formalism [55]. The energy cut-off for plane waves is 600 eV. For the structural optimization and total energy calculations, a 6 × 10 × 5 and 6 × 6 × 10 Monkhorst–Pack k-mesh [56] is generated for sampling the Brillouin zone (BZ) of the cotunnite-type and Fe\(_2\)P-type structure, respectively. These set of parameters yield convergence of total energies to within a level of \( 10^{-2} \) meV/Ta\(_2\)O\(_5\) unit. Since DFT is a ground state theory and not suitable to estimate the band gap values, we have employed the GW method [57, 58], which explicitly includes the many-body effects (exchange and correlation) of electrons to calculated the energy levels of low-lying excited states and consequently the band gaps of TiO\(_2\) under high pressures. Specially, we take the one-shot GW approach implemented in the VASP code [59] to calculate the energy spectrum. The quasiparticle energies and wave functions are obtained by solving a Schrödinger-type equation [58]:

\[
(T + V_{\text{ext}} + V_H)\psi_{\alpha k}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}', \mathbf{r}; E_{\beta k})\psi_{\beta k}(\mathbf{r}') = E_{\alpha k}\psi_{\alpha k}(\mathbf{r}),
\]

where \( T \) is the kinetic energy operator of electrons, \( V_{\text{ext}} \) is the external potential due to ions, \( V_H \) is the electrostatic Hartree potential, \( \Sigma \) is the electron self-energy operator, and \( E_{\alpha k} \) and \( \psi_{\alpha k}(\mathbf{r}) \) are the quasiparticle energies and wave functions, respectively. Within the GW approximation proposed by Hedin [57], the term \( \Sigma \) can be calculated as follows:

\[
\sum(\mathbf{r}, \mathbf{r}'; E) = \frac{1}{2\pi} \int d\omega e^{i\omega} G(\mathbf{r}, \mathbf{r}'; E + \omega) W(\mathbf{r}, \mathbf{r}'; \omega),
\]

where \( G \) is the Green’s function, \( W \) is the dynamically screened Coulomb interaction, and \( \delta \) is a positive infinitesimal. In the GW calculations on the cotunnite-type and Fe\(_2\)P-type TiO\(_2\), a \( 4 \times 6 \times 3, 4 \times 4 \times 6 \) k-mesh is used to sample the BZ, respectively. The number of energy bands involved in the GW calculations is 192 for both systems. This ensures the calculated GW band gaps to converge within an error bar of \( \sim 0.1 \) eV. More details of the GW calculations are provided in supplementary texts, which are available online at stacks.iop.org/JPCO/1/055014/mmedia.
3. Results and discussion

3.1. Lattice parameters and enthalpy as a function of pressure

The dependence of the lattice parameters with pressure is shown in figures 1(a) and (b), for the cotunnite-type and Fe₂P-type TiO₂. For both phases, the lengths of cell axes decrease almost linearly with pressure. Rate of compression is $2.34 \times 10^{-3} \text{ Å GPa}^{-1}$ in $a$-axis, $1.42 \times 10^{-3} \text{ Å GPa}^{-1}$ in $b$-axis, $2.19 \times 10^{-3} \text{ Å GPa}^{-1}$ in $c$-axis for cotunnite-type TiO₂; and $1.47 \times 10^{-3} \text{ Å GPa}^{-1}$ in $a$-axis (and $b$-axis), $1.15 \times 10^{-3} \text{ Å GPa}^{-1}$ in $c$-axis for Fe₂P-type TiO₂. Due to their large bulk moduli [32, 33, 60], both phases show considerable incompressibility.

The calculated enthalpy ($H = U + PV$, where $U$ is the total energy obtained by DFT calculations, and $P$ is pressure and $V$ is volume of the system. The symbol f. u. is the abbreviation for formula units (equivalently, Ta₂O₅ unit).)

![Figure 1](image_url)

Figure 1. Pressure dependence of the lattice parameters of the cotunnite-type (a) and Fe₂P-type (b) TiO₂. (c) The enthalpies of the two high-pressure phases of TiO₂, as a function of pressure. The enthalpy $H = U + PV$, where $U$ is the total energy obtained by DFT calculations, and $P$ is pressure and $V$ is volume of the system. The symbol f. u. is the abbreviation for formula units (equivalently, Ta₂O₅ unit).
The predicted phase transition pressure (~115 GPa) is ~45 GPa smaller than previously reported (~160 GPa for DFT–GGA calculations) [33], which may arise from the difference of simulation parameters (see 1 for details).

On the other hand, the coincidence of the two enthalpy lines suggests the coexistence of both phases across a broad range of pressures. At T = 300 K, one can estimate the ratio of probability of finding the two phases (Fe2P-type versus cotunnite-type): \( r = \exp[-\Delta H/(k_B T)] \), which turns out to be 0.946, 1.066, 1.127, 1.826, 2.252, 3.400, for \( P = 110, 115, 120, 150, 160 \), and 200 GPa, respectively. Indeed, previous experimental work has shown that the cotunnite-type structure preserves at ambient pressure upon rapid decompression and quenched in liquid nitrogen (77 K) [61]. Moreover, the coexistence of different TiO2 phases below 60 GPa has also been experimentally demonstrated by compression-decompression method using the DAC technique [32]. Phase coexistence in the other transition metal dioxides, such as ZrO2, has also been reported recently [62]. In this context, the coexistence of the two high-pressure phases studied here is naturally expected for \( P > 100 \) GPa.

3.2. Band gaps as a function of pressure

The calculated band gaps of the cotunnite-type and Fe2P-type TiO2 are shown in figures 2(a) and (b), as a function of applied pressure. The band gap values obtained by using traditional DFT-GGA calculations (i.e., the Kohn–Sham gap) are shown along with those obtained using the GW method. Despite some minor fluctuations, the band gaps of both high-pressure phases of TiO2 are rather robust to compression. To get a deep understanding on this phenomenon, the data are least-squares fitted to a modified form of equation (1) as follows:

\[
E_g(P) = E_g(P_0) + \alpha(P - P_0) + \beta(P - P_0)^2,
\]

where \( \alpha \) and \( \beta \) have the same meanings as in equation (1); \( E_g(P_0) \) is the band gap at the starting point of pressure range under investigation. The value of \( P_0 \) is 50 GPa and 110 GPa, respectively, for the cotunnite-type and Fe2P-type TiO2. The fitting parameters are summarized in table 1. Consequently, the pressure coefficient is calculated as the first derivative of \( E_g \) with respect to \( P \):

\[
e_p = \alpha + 2\beta (P - P_0).
\]

This is a linear function of pressure \( P \). Specially, \( e_p = \alpha \) when \( P = P_0 \). The pressure variation of \( e_p \) is shown in figures 2(c) and (d), for the two phases. In the case of GGA calculations, the value of \( \alpha \) is 0.117 meV GPa~1 and \(-0.813 \) meV GPa~1, for the cotunnite-type and Fe2P-type TiO2, respectively. For the more accurate GW method, \( \alpha \) is 1.831 meV GPa~1 for the cotunnite-type and 0.489 meV GPa~1 for the Fe2P-type structure. As seen from table 1, all the values of \( \beta \) are the order of magnitude of \(~10^{-3} \) meV GPa~2, which result in the linear decrease of \( e_p \) with pressure. Meanwhile, the point \( e_p = 0 \) gives the pressure \( P_m = P_0 - \alpha/(2\beta) \), at which the band gap \( E_g \) reaches its maximum. For instance, from the parameters describing the GW band gaps (table 1), \( P_m \) is calculated to be ~180.1 GPa and ~140.0 GPa, for the cotunnite-type and Fe2P-type TiO2, respectively. Compared to the pressure coefficient of diamond (~5 meV GPa~1) [41,42] and that of SiC (~1.9 meV GPa~1) [43,44], which is the smallest value ever measured by experiments, the pressure coefficients of the two high-pressure TiO2 phases found in our work are still significantly smaller. In particular, the region in which \( |e_p| \leq 0.5 \) meV GPa~1, i.e., one order of magnitude smaller than that of diamond, is highlighted in figures 2(c) and (d). For the data obtained by GW calculations, the highlighted region spans a pressure interval of [144.6, 215.7 GPa] for the cotunnite-type, and [109.3, 170.7 GPa] for the Fe2P-type TiO2. The pressure interval is reduced to [165.9, 194.4 GPa] and [127.7, 152.3 GPa], in the case of \( |e_p| \leq 0.2 \) meV GPa~1, about one order of magnitude smaller than that of SiC. More generally, for \( |e_p| \leq \delta \), the pressure interval is \([P_0 + \frac{\delta - n}{2\beta}, P_0 - \frac{\delta + n}{2\beta}]\).

To make a comparison, the variation of the band gaps of rutile TiO2 under pressure is also studied (supplemental material, figure S1). The GW band gap (2.92 eV) of rutile at \( P = 0 \) compare well with the experimental value (~3 eV) at ambient pressure [28-30], and verifies the reliability of GW calculations. The fitting parameters are listed in table 1. From the data given by both GGA and GW calculations, the pressure coefficient of rutile turns out to be significantly larger than that of the cotunnite-type and the Fe2P-type TiO2. A simple comparison between the starting and ending pressure points gives that, the volume of crystal unit cell is contracted by ~18.3% and ~14.2% for the cotunnite-type and Fe2P-type, with the GW band gaps changed by ~+0.14 eV and ~−0.14 eV, respectively. As a contrast, at a volume contraction of ~15%, the GW band gap of rutile TiO2 is increased by ~0.59 eV (figure S1). The plateau-like behavior (figures 2(a), (b)) suggests that a step-like jump of the band gaps of TiO2 can be observed when the applied pressure is increased gradually from 50 to

1 Comparison of the key parameters employed in DFT calculations: (a) electron–ion core interactions: PAW potentials (this work) versus ultrasoft pseudopotentials [33]; (b) exchange–correlation functional: PBE-type GGA (this work) versus PBE-type GGA [33]; (c) energy cut-off for plane waves: 600 eV (this work) versus 100 Ry ([33]); (d) k-mesh for integral in BZ: 6 x 10 x 5 for the cotunnite-type and 6 x 6 x 10 for the Fe2P-type (this work) versus 4 x 6 x 2 for the cotunnite-type and 6 x 6 x 8 for the Fe2P-type ([33]).
260 GPa, across the phase transition pressure point (∼115 GPa). On the other hand, the GW band gaps (2.989 and 1.876 eV) of the cotunnite-type and Fe₂P-type at 160 GPa are comparable with the values (3.0 and 1.9 eV) estimated by previous work [33], and rationalize the empirical corrections therein.

3.3. Origin of the robustness of band gaps upon compression
To understand the robustness of the band gaps upon compression, we studied the pressure dependence of the valence band maximum (VBM) and conduction band minimum (CBM), the difference of which gives the value of band gap. The results by GGA and GW calculations are shown in figures 2(e) and (f), for the cotunnite-type and Fe₂P-type TiO₂. The VBM and CBM of both phases increase almost linearly with pressure. From the GW

Figure 2. Pressure dependence of the band gaps (panels (a) and (b)), pressure coefficients (panels (c) and (d)), the region $|\epsilon_p| \leq 0.5$ meV GPa$^{-1}$ is highlighted, and the valence band maximum (VBM) and conduction band minimum (CBM) (panels (e) and (f)) of the two TiO₂ phases. The left panels (a), (c), (e) are for the cotunnite-type and the right panels (b), (d), (f) are for the Fe₂P-type. The solid lines in panels (a) and (b) represent the least-squares fits to the GGA and GW data points of band gaps.
It is interesting to note that the wave function of VBM for the Fe₂P-type TiO₂ is mainly composed of the orbitals of Ti atoms, while for the cotunnite-type TiO₂, the wave function of VBM is mainly composed of the orbitals of O atoms. The wave function of CBM for the Fe₂P-type TiO₂ is mainly composed of the orbitals of O atoms, and for the cotunnite-type TiO₂, it is mainly composed of the orbitals of Ti atoms.

The nearly identical rates of change explain the slow variations of band gaps with pressure. By contrast, the rates of change of VBM and CBM are of approximately the same value. The nearly identical rates of change indicate that the calculated band gaps are likely to be reliable.

### 3.4. Comparison of the structural and electronic properties of the two phases

We have further studied the atomic and electronic properties of the two high-pressure phases. The local atomic bonding structures of the cotunnite-type and Fe₂P-type TiO₂ at P ≈ 115 GPa (phase transition point), are schematically shown in the left panels of figures 3(a) and (c). The corresponding radial distribution functions (RDFs) \( g_{TiO} \) and \( g_{O4c} \), which describe the spatial arrangement of O atoms around Ti, are shown in the right panels of figures 3(b) and (d). In both phases, each Ti atom is bonded with nine O atoms, i.e., nine-coordinated, which is readily deduced by doing integral within the first coordination shells as defined by the RDFs in figures 3(b) and (d): 1.82 Å ≤ \( R \) ≤ 2.12 Å for the cotunnite-type and 1.82 Å ≤ \( R \) ≤ 2.06 Å for the Fe₂P-type. On the other hand, from their first coordination numbers, the surrounding O atoms can be classified into two types: the ones which are coordinated by four Ti atoms (O₄c) and that coordinated by five Ti atoms (O₅c), as schematically marked in figures 3(a) and (c).

The sharp and discrete RDFs peaks shown in figures 3(b) and (d) are the characteristics of crystalline structures [63], in which the Ti–O bond lengths (\( R_{TiO} \)) show a distribution instead of a single value. The averaged Ti–O bond lengths for Ti, O₄c, and O₅c are listed in table 2. The difference of O₄c and O₅c is clearly reflected: the averaged value of \( R_{TiO} \) is ~1.89 Å for the O₄c of both phases, while the averaged \( R_{TiO} \) of O₅c is ~2.07 Å for the cotunnite-type and ~2.06 Å for the Fe₂P-type TiO₂. Moreover, judging from the averaged values of \( R_{TiO} \) in table 2, the Ti atoms in the Fe₂P-type structure can be divided into two types: Type A (\( R_{TiO} \) ~ 2.00 Å) and Type B (\( R_{TiO} \) ~ 1.95 Å). The classification agrees with previous work [33].

The electron densities associated with the wave function of VBM and CBM, i.e., \( |\psi_{VBM}|^2 \) and \( |\psi_{CBM}|^2 \), are displayed in figure 4, for the two high-pressure phases of TiO₂ at \( P = 115 \) GPa. Clearly, the electronic states of VBM come mainly from the 2p orbitals of O atoms and that of CBM come mainly from the 3d orbitals of Ti atoms (see also figure S2). Using the Bader charge analysis [64, 65], we are able to assign the number of electrons intuitively to each atom. The results are tabulated in table 2. It is interesting to find that, for both phases, different types of atoms (e.g., O₄c versus O₅c and Ti₁₄ versus Ti₈ in the Fe₂P-type) are distinguished by the different number of Bader charges. We go on to study the characteristics of VBM and CBM by projecting the corresponding wave functions on spherical harmonics. The obtained \( lm \)-components of VBM and CBM are summarized in table 3. For the cotunnite-type TiO₂, the wave function of VBM mainly consists of the \( p_x \) and \( p_y \) orbitals of O atoms, and the wave function of CBM comes mainly from the superposition of the \( d_{x^2} \) and \( d_{y^2} \) orbitals of Ti atoms. For the Fe₂P-type TiO₂, major component of the wave function of VBM is the \( p_z \) orbitals of O, and the wave function of CBM involves mainly the \( d_{z^2} \) orbitals of Ti, together with minor hybridization with the \( s \) and \( p \) orbitals of O. Within the pressure range under investigation, only minor modifications are found for

| Method  | \( E_g(P_{0}) \) (eV) | \( E_F(P_{0}) \) (eV) | \( \alpha \) (meV GPa⁻¹) | \( \beta \) (meV GPa⁻²) |
|---------|---------------------|---------------------|------------------|------------------|
| GGA     | 1.626               | 1.637               | 0.117            | -2.601 × 10⁻³    |
| GW      | 2.842               | 2.867               | 1.831            | -7.035 × 10⁻³    |
| TiO₂, Cotunnite-type | GGA | 0.574               | 0.548             | -0.813           | 5.260 × 10⁻³     |
|        | GW                  | 1.893               | 1.880            | 0.489            | -8.153 × 10⁻³    |
| TiO₂, Rutile       | GGA | 1.664               | 1.653             | 4.583            | 9.989 × 10⁻³     |
|        | GW                  | 2.920 (3.03)        | 2.914            | 12.876           | -0.035           |

* Experimental value [28–30]. (GGA) calculations, the linear rate of change (\( dE/dP \)) of VBM and CBM is ~0.0171 eV GPa⁻¹ (0.0176 eV GPa⁻¹) and ~0.0179 eV GPa⁻¹ (0.0173 eV GPa⁻¹), for the cotunnite-type TiO₂; and ~0.0139 eV GPa⁻¹ (0.0144 eV GPa⁻¹) and ~0.0132 eV GPa⁻¹ (0.0127 eV GPa⁻¹) for the Fe₂P-type TiO₂.

For each high-pressure phase, the rates of change of VBM and CBM are of approximately the same value. The nearly identical rates of change explain the slow variations of band gaps with pressure. By contrast, the rates of change of VBM and CBM are of approximately the same value. The nearly identical rates of change explain the slow variations of band gaps with pressure.
the electron density of states (DOS) and the energy band structures near the Fermi level (figures S2–S4). Slight shifts to higher energies are observed at the edges of the conduction bands (figures S2 and S3). For geometrically the same type of atoms, Ti or O, the difference between their partial DOS is negligible. For the valence states near the VBM, the contributions from different types of O (and Ti in the case of Fe₂P-type) atoms are nearly the same. For the conduction states near the CBM, Ti atoms (Ti_A in the case of Fe₂P-type) show dominant contributions (figure S3).

3.5. Understanding the difference of band gaps
As mentioned above, at pressure $P \sim 115$ GPa, the two high-pressure phases of TiO₂ have equal enthalpy, the same coordination numbers of Ti and O in the first coordination shells, and similar averaged value of Ti–O

Table 2. At $P = 115$ GPa, the averaged Ti–O bond lengths ($R_{\text{TiO}}$), the first coordination numbers of the Ti (CNO) and O (CNTi) atoms, and the Bader charges associated with the valence band maximum (VBM) and the conduction band minimum (CBM), which are assigned to each type of atoms of the two TiO₂ phases. For both VBM and CBM, the total number of electronic states is 2 (spin-degenerate).

|                      | $R_{\text{TiO}}$ (Å) | CNO | CNTi | Bader_VBM$^a$ | Bader_CBM$^a$ |
|----------------------|----------------------|-----|------|---------------|---------------|
| TiO₂ Cotunnite-type  | Ti 1.987             | 9   | —    | 0.0195 $\times$ 4 | 0.4450 $\times$ 4 |
|                      | O₄c 1.887            | —   | 4    | 0.2286 $\times$ 4 | 0.0427 $\times$ 4 |
|                      | O₅c 2.066            | —   | 5    | 0.2502 $\times$ 4 | 0.0115 $\times$ 4 |
| TiO₂ Fe₂P-type       | Ti_A 2.003           | 9   | —    | 0.0016 $\times$ 2 | 0.6699 $\times$ 2 |
|                      | Ti_B 1.948           | 9   | —    | 0.0126 $\times$ 1 | 0.4383 $\times$ 1 |
|                      | O₄c 1.893            | 4   |      | 0.3349 $\times$ 3 | 0.0216 $\times$ 3 |
|                      | O₅c 2.058            | 5   |      | 0.3226 $\times$ 3 | 0.0517 $\times$ 3 |

$^a$ The format of Bader charges of each type of atoms: Bader charge (e) $\times$ the number of atoms.
bond lengths (table 2). Besides, the volume per formula unit is also very close, which is $\sim 20.253 \text{Å}^3/\text{TiO}_2$ for the cotunnite-type and $\sim 20.197 \text{Å}^3/\text{TiO}_2$ for the Fe$_2$P-type. Both have a direct band gap at varying high pressures (figure S4). Despite these similarities, their band gaps differ by $\sim 1.06$ eV. Such difference should originate from the different crystal structures (supplementary table I): an orthogonal unit cell with four formula units ($Z = 4$) for the cotunnite-type and a hexagonal unit cell with $Z = 3$ for the Fe$_2$P-type. The positional difference of RDFs peaks (figures 3(b), (d)) beyond the first coordination shell is a consequence of different O–Ti–O and Ti–O–Ti angles. This leads to different ion-electron interaction potential $V_{\text{ext}}$ and consequently the changes of the quasiparticle energies and wave functions (table 3). To the first-order perturbation of correction [58], the quasiparticle energies within the GW method is given by: $E_{\text{q}} \approx \varepsilon_n + \langle \psi_{\text{CBM}} | \sum E_n - V_{\text{xc}} | \psi_{\text{CBM}} \rangle$, where $\varepsilon_n$ is the eigenvalue of the corresponding Kohn–Sham orbital $\psi_n$, and $V_{\text{xc}}$ is the exchange-correlation potential. At $P = 115$ GPa, the VBM given by GGA (GW) calculations for the cotunnite-type TiO$_2$ is $\sim 0.31$ eV (0.18 eV) lower than the Fe$_2$P-type. Consequently, the different band gaps are mainly attributed to the values of CBM: $E_{\text{CBM}} \approx \varepsilon_{\text{CBM}} + \langle \psi_{\text{CBM}} | \sum E_n - V_{\text{xc}} | \psi_{\text{CBM}} \rangle$. Our calculations find that, both terms $\varepsilon_{\text{CBM}}$ and $\langle \psi_{\text{CBM}} | \sum E_n - V_{\text{xc}} | \psi_{\text{CBM}} \rangle$ of the cotunnite-type are larger than that of the Fe$_2$P-type, differing by a value of $\sim 0.74$ eV for the first term and $\sim 0.15$ eV for the second. Addition of the differences between VBM and CBM results in a value of $\sim 1.07$ eV, compares well with the value (1.06 eV) obtained by solving equation (2).

### Table 3. Calculated $lm$-components of the wave function of the valence band maximum (VBM) and the conduction band minimum (CBM) of the two TiO$_2$ phases at $P = 115$ GPa.

|       | s  | $p_x$ | $p_y$ | $p_z$ | $d_{xy}$ | $d_{yz}$ | $d_{xz}$ | $d_{2,3}^2$ |
|-------|----|-------|-------|-------|----------|----------|----------|-----------|
| TiO$_2$ Cotunnite-type | VBM | 0.002 | 0.454 | 0.019 | 0.446 | 0.004 | 0.013 | 0.007 | 0.000 | 0.026 |
|     | CBM | 0.067 | 0.000 | 0.033 | 0.017 | 0.000 | 0.000 | 0.232 | 0.032 | 0.537 |
| TiO$_2$ Fe$_2$P-type | VBM | 0.000 | 0.000 | 0.962 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
|     | CBM | 0.064 | 0.016 | 0.000 | 0.016 | 0.000 | 0.000 | 0.820 | 0.000 | 0.000 |

### 4. Conclusions and outlook

In conclusion, we have studied the large-pressure-scale behavior of the structural and electronic properties of TiO$_2$, a wide band gap semiconductor. Calculation of enthalpies suggests the coexistence of two high-pressure phases across a wide range of pressures. For pressures that span over an interval of $\sim 150$ GPa, the band gaps ($E_g$) of both phases are rather robust to compression. The related pressure coefficients are found to be significantly smaller than that of diamond and SiC, which has the smallest pressure coefficient ever reported by experiments. For both phases of TiO$_2$, the variation of $E_g$ with pressure is well described by a quadratic polynomial. The
robustness of $E_g$ is due to the nearly identical rates of changes of the VBM and CBM with pressure. Such unusual properties may have potential applications for optical devices operate at extreme conditions such as high-pressure and/or high-temperature environment. Detailed analysis on crystal structures and the wave function characteristics of VBM and CBM helps to understand the difference in $E_g$ of the two structures. Finally, the pressure dependence of the optical properties, and the expected gap closure and metallization with further increasing pressures, will be the subject of a forthcoming work.

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