Bismuth tellurohalide (BiTeI) is a narrow-band-gap semiconductor at ambient pressure. Under compression, the BiTe band gap decreases with increasing pressure, and diminishes at a critical pressure $P_c$. Recent studies show that an inversion of valence band maximum (VBM) and conduction band minimum (CBM) states occurs when the applied pressure $P$ exceeds $P_c$, which marks a transition to the topological insulating phase.\(^1\)\(^2\)\(^3\)\(^4\)\(^5\)\(^6\)\(^7\) This means that the band gap reopens and increases at pressures higher than $P_c$. Furthermore, analysis presented in Ref.\(^5\) indicates that an intermediate Weyl semimetal phase is present over a narrow pressure interval around $P_c$. The evolution of the electronic structure of BiTe under compression has been experimentally explored in two optical spectroscopy studies.\(^2\)\(^6\) Tran et al. (Ref.\(^6\)) reported no evidence for the band-gap reopening, whereas the infrared spectral weight of the charge carriers measured in Ref.\(^2\) exhibited a maximum, which implies the reopening of the band gap with increased pressure. On the other hand, both studies reveal that BiTe undergoes a structural transformation at pressure $P_t \sim 8$ GPa (Ref.\(^2\)) or $\sim 9$ GPa (Ref.\(^6\)). It was therefore suggested that the topological phase transition is hindered by a structural phase transition.\(^1\)\(^2\) On the theoretical side, density-functional calculations have been employed to estimate $P_c$, the reported values of which range from 1.7 to $\sim 10$ GPa owing to various types of approximations.\(^1\)\(^2\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\) It is crucial to have a reliable estimate of $P_c$ to see if the topological phase transition takes place before the structural phase transition occurs, which clearly depends critically on the accuracy of the equation of state (EOS). Our recent investigation revealed that the inclusion of van der Waals (vdW) interactions is necessary for a reliable and truly \textit{ab initio} computation of the EOS of BiTeI, which was not taken into account in the aforementioned calculations. Thus, we examine here the variation of the BiTe band gap with pressure with the aid of dispersion-corrected density-functional (PBE-D2) calculations using the functional of Perdew, Burke, and Ernzerhof (PBE\(^\footnote{Ref. [10]}\)) together with a semiempirical force field.\(^10\) In addition, we employ semilocal density-functional calculations using the PBEsol\(^\footnote{Ref. [11]}\) functional for the purpose of comparison. It was curious to see whether the PBEsol and PBE-D2 approaches result in \textit{consistent} predictions concerning the interlayer metallic bonding in BiTeI under compression. It is consequently shown that the calculated band-gap energies follow \textit{qualitatively} and \textit{quantitatively} the same trend within the two approximations employed here, and the transition to the zero-gap state occurs at the same critical width of the van der Waals gap.

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BiTeI crystallizes in a layered trigonal structure with noncentrosymmetric space group $P3m1$ (No. 156). Its crystal structure is characterized by the hexagonal lattice parameters $a$ and $c$, and two internal parameters since Bi, Te, and I atoms occupy the $1a$, $1c$, and $1b$ positions with fractional coordinates $(0,0,0)$, $(2/3,1/3,z_{Te})$, and $(1/3,2/3,z_I)$, respectively.\(^10\)\(^13\) cf. Ref.\(^8\). In this structure, adjacent (unary) layers formed by Bi, Te, and I atoms stack along the $c$-axis, and the \textit{van der Waals} (vdW) gap exists in the vacuum region between the Te and I layers. As will be clear below, our findings reveal the importance of the width of the vdw gap. Thus we investigate the effect of pressure not only on the BiTeI band structure but also on the vdw gap. To this end, we carried out crystal-structure optimizations, for which the total energy was

Pressure dependence of the band-gap energy in BiTeI

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FIG. 1. The band structure of BiTeI in the vicinity of the band edges for (a) $V = V_0$, (b) $V = 0.94V_0$, and (c) $V = 0.9V_0$.

TABLE I. The calculated (PBEsol and PBE-D2) and experimental values of the bulk modulus $K_0$ (in GPa) and its pressure derivatives $K_0''$, $K_0'''$ (in GPa$^{-1}$), and $K_0'''$ (in GPa$^{-2}$) of BiTeI.

|       | $K_0$ | $K_0''$ | $K_0'''$ | $K_0'''$ |
|-------|-------|---------|----------|----------|
| PBE-D2| 28.1  | 6.8     | -2.9     | 2.3      |
| PBEsol| 17.0  | 12.4    | -7.2     |          |
| Expt. | 20.5  | 7.6     |          |          |
notes the width of the pressure interval corresponding to the Weyl semimetal phase. Analysis presented in Ref. [5] reveals also that one finds $\Delta P_c = 0$ if $E_g$ is deduced only from the band dispersions along the $A-H$ line in the irreducible wedge of the Brillouin zone. Thus, we conducted a search over the whole Brillouin zone for a set of pressure values around the critical pressure. Although we had not attempted to deduce a precise value for $\Delta P_c$, in this way we estimated upper and lower bounds for it: $0.04$ GPa $< \Delta P_c < 0.13$ GPa (PBE-D2) and $0.03$ GPa $< \Delta P_c < 0.09$ GPa (PBEsol). Clearly, the experimental observation of the Weyl semimetal phase[2] as well as the closure of the band gap would be obstructed, cf. Ref. [6] unless the applied pressure is fine tuned to this extremely narrow pressure range. We shall defer the discussion of the Weyl semimetal phase in the rest of this paper, due to the diminutiveness of $\Delta P_c$.

Figure 2(b) displays a plot of the band-gap energy $E_g$ versus the normalized pressure $P/K_0$, which shows that the band gap diminishes at $P = P_c$ and reopens for $P > P_c$. The predicted band gap takes the values $0.167$ eV (PBEsol) and $0.206$ eV (PBE-D2) at zero pressure, compared to the experimental[23] value of $0.36$ eV at ambient pressure. This shows that the band-gap underestimation is relatively more (less) severe within the PBEsol (PBE-D2) description. The solid symbols (blue squares and red circles) in Fig. 2(b) represent the calculated (PBEsol and PBE-D2) points. The blue and red curves passing through these points satisfy the relation $E_g(P) = C_1 \left( \frac{P}{K_0} - \frac{P_c}{K_0} \right) + C_2 \left( \frac{P}{K_0} - \frac{P_c}{K_0} \right)^2$,

$$E_g(P) = C_1 \left( \frac{P}{K_0} - \frac{P_c}{K_0} \right) + C_2 \left( \frac{P}{K_0} - \frac{P_c}{K_0} \right)^2,$$ (2)

where the coefficients $C_1$ and $C_2$ take different values for the cases $P < P_c$ and $P_c < P$. The values of these coefficients are given in Table I which were obtained via fitting. It is noteworthy to observe that the $P < P_c$ portions of blue (PBEsol) and red (PBE-D2) curves in Fig. 2(b) are almost parallel to each other, especially in the vicinity of the critical pressure $P_c$. This implies that this portion of the dispersion-corrected (PBE-D2) curve could be qualitatively reproduced by adding a constant shift to the PBEsol-calculated band-gap energies, which is known as the “scissors” correction. Encouraged by the latter, we apply the “scissors” correction to the dispersion-corrected (PBE-D2) band-gap energies by using a constant shift of $154$ meV that is equal to the difference between the experimental[23] and predicted values of the band gap. In Fig. 2(b) the magenta curve represents the “scissors”-corrected (PBE-D2+SC) band-gap energy as a function of the normalized pressure. It is seen that the predicted value of the critical pressure increases from $P_c = 3.8$ to $P_c = 4.8$ GPa as a result of applying the “scissors” correction. Thus, underestimation of the band gap by $154$ meV translates to underestimating $P_c$ by $1$ GPa. It should be emphasized that all of our estimates for $P_c$ are substantially smaller than $P_t$, cf. Fig. 2(b). It is thus clear that the closure of the band gap would not be hindered by the structural transformation of BiTeI at $P = P_t$.

It should be noted that the band-gap pressure coefficients $\alpha_1 = dE_g/dP|_{P=0}$ and $\alpha_2 = d^2E_g/dP^2|_{P=0}$ are related to the coefficients introduced in Eq. (2) through $\alpha_1 = C_1/K_0 - 2C_2P_c/K_0^2$ and $\alpha_2 = C_2/K_0^2$. The calculated values of $\alpha_1$ and $\alpha_2$ are given in Table III. Replacing Eq. (2) as $E_g(P) = E_g + \alpha_1P + (1/2)\alpha_2P^2$ (for $P \leq P_c$) yields the following expression for the critical

\[
E_g(P) = \frac{1}{2} \alpha_2 P^2 + \frac{1}{2} \alpha_1 P + C_1 + C_2 P_c.
\]
TABLE II. The calculated (PBEsol and PBE-D2) values of the equilibrium band gap $E_g$ (in meV), the critical pressure $P_c$ (in GPa), and the coefficients $C_1$ and $C_2$ introduced in Eq. (2).

|        | $E_g$ | $P_c$ | $C_1$  | $C_2$  |
|--------|-------|-------|--------|--------|
| PBE-D2 | 206   | 3.8   | -1.565 | -0.407 |
|        |       |       | for $P < P_c$ |        |
|        |       |       | 1.926  | -2.057 |
|        |       |       | for $P > P_c$ |        |
| PBEsol | 167   | 1.6   | -1.127 | 6.245  |
|        |       |       | for $P < P_c$ |        |
|        |       |       | 1.176  | -1.160 |
|        |       |       | for $P > P_c$ |        |

TABLE III. The calculated (PBEsol and PBE-D2) values of the band-gap pressure coefficients $\alpha_1$ (in meV/GPa) and $\alpha_2$ (in meV/GPa$^2$).

|        | $\alpha_1$ | $\alpha_2$ |
|--------|-------------|-------------|
| PBE-D2 | -51.8       | -1.0        |
| PBEsol | -135.4      | 43.2        |

The relationship given in Eq. (3) implies that the value of $P_c$ could be obtained from the equilibrium band gap $E_g$ (for which the experimental value is available) and the band-gap pressure coefficients $\alpha_1$ and $\alpha_2$ (for which the experimental values are lacking). Thus, experimental determination of $\alpha_1$ and $\alpha_2$ is called for.

It was proposed that an observed minimum in $c/a$ in the pressure range of 2.0–2.9 GPa is an indicator of the topological phase transition. It is thus interesting to explore how the lattice parameter ratio $c/a$ varies with pressure. The plots of $c/a$ versus the normalized pressure are therefore given in Fig. 2(c) where the experimental values (the green diamonds) are seemingly bracketed by the blue and red curves passing through the PBEsol-calculated and dispersion-corrected (PBE-D2) points, respectively. As a matter of fact the results of PBEsol and PBE-D2 calculations are in better agreement with the experimental data in regard to the pressure variation of the lattice parameters $c$ and $a$, respectively, cf. Fig. S2 (Ref. 22). It should be remarked that the PBEsol-calculated points (the blue squares) form a curve that lies virtually parallel to the experimental points, and accordingly possess a minimum. On contrary, the curve passing through the dispersion-corrected (PBE-D2) points (the red circles) shows no minimum. It is thus clear that the results of the PBEsol (PBE-D2) calculations are in line (conflict) with the experimental trend in regard to the pressure variation of the lattice parameter ratio $c/a$. Despite this disagreement between the PBEsol and PBE-D2 results, the closure of the band gap at the critical pressure occurs within not only the PBEsol but also PBE-D2 description, which reveals that the pressure variation

FIG. 3. (a) The layer thickness $t_l$ and the width $t_v$ of the van der Waals gap, which are depicted in the inset, are plotted with respect to the normalized pressure $P/K_0$. The vertical and horizontal dashed lines mark the values of $P_c/K_0$ and $t_c$, respectively. (b) The $ab$ planar average $\langle \rho \rangle$ of the charge density is plotted as a function of the position $z$ along the $c$-axis for zero pressure [the orange solid (PBE-D2) and green dashed (PBEsol) curves] and for $P = P_c$ [the red solid (PBE-D2) and blue dashed (PBEsol) curves]. (c) The band-gap energy versus the difference $t_v - t_c$. 
of the band gap is not in correlation with that of c/a. A comparative inspection of Figs. 2(b) and 2(c) indeed shows that the transition to the zero-gap state does not correspond to the minimum of c/a.

We find that the width of the vdW gap, viz. the thickness $t_v$ of the vacuum region, rather than the lattice parameter ratio $c/a$, serves as an adequate structural parameter for studying the variation of the BiTeI band-gap energy with pressure, as will be explained now. Figure 3(a) shows the variation of $t_v$ and the layer thickness $t_l$ with the normalized pressure, where the inset displays the division of the lattice parameter $c$ into $t_v$ and $t_l$. While the pressure increases, $t_l$(PBE-D2) remains virtually constant whereas $t_v$(PBEsol) tends to increase slowly. The slight increase of the layer thickness as a result of compression was observed in TiS$_2$, viz. a layered material with a vdW gap, which is associated with an increase of the electronic charge in the interlayer region, indicating enhanced metallic rather than van der Waals bonding between the layers.$^{23}$ In accordance with this, we think that the qualitative description of the pressure variation of $t_l$ within the PBEsol, rather than PBE-D2, approach is realistic (in the low-pressure regime). The latter is also supported by the fact that the results of PBEsol, rather than PBE-D2, calculations are in excellent agreement with the measured pressure variation of the lattice parameter $c$, cf. Fig. S2 (Ref. 22). As long as $c = t_l + t_v$, the effect of pressure on $c$ is manifested primarily (solely) as the compression of the vdW gap according to the PBEsol (PBE-D2) calculations. While $t_v$ is getting reduced, the electronic charge density $\rho(r)$ in the vdW gap region increases, as illustrated in Fig. 3(b) where the $ab$ planar average $\langle \rho \rangle$ of the charge density is plotted for zero pressure and for $P = P_c$. This means that the interlayer metallic bonding becomes stronger as $t_v$ decreases. The decrease in $t_v$(PBEsol), compared to that in $t_v$(PBE-D2), is more pronounced in the low-pressure regime, as seen in Fig. 3(a). Accordingly, the transition to the zero-gap state occurs at a relatively lower (higher) pressure within the PBEsol (PBE-D2) approach. This explains why $P_c^{\text{PBEsol}}$ is smaller than $P_c^{\text{PBE-D2}}$.

The band gap diminishes when the width $t_v$ of the vdW gap is reduced to a critical value $t_{v_c}$, which is marked by the horizontal dashed lines in Fig. 3(a). It is remarkable that $t_{v_c}$ takes practically the same value in both PBEsol and PBE-D2 approaches, i.e., $t_{v_c} = 2.76$ Å. Hence the transition to the zero-gap state occurs at the same critical thickness $t_v$ according to the two approximations (PBEsol and PBE-D2) employed in this study. It is also striking that the PBEsol and PBE-D2 calculations yield almost identical $\langle \rho \rangle$ in the vdW gap region for zero pressure as well as for $P = P_c$, which is discernible in Fig. 3(b); compare the orange solid ($P = 0$; PBE-D2) curve to the green dashed ($P = 0$; PBEsol) curve, and the red solid ($P = P_c$; PBE-D2) curve to the blue dashed ($P = P_c$; PBEsol) curve. Thus the PBEsol and PBE-D2 approaches that in conflict to some degree (as pointed out above) yield consistent predictions concerning the electronic structure and the interlayer metallic bonding in BiTeI under pressure. This is further evidenced in Fig. 3(c) where the band-gap energy is plotted with respect to the difference $t_v - t_{v_c}$. It is seen that the calculated (PBEsol and PBE-D2) values of the band gap follow not only qualitatively but also quantitatively the same trend. Thus the difference between the predictions of the PBEsol and PBE-D2 approaches does not pertain to the variation of the electronic structure of BiTeI under pressure, which actually pertains only to the overestimation (PBEsol) and underestimation (PBE-D2) of the compressibility of BiTeI.

The predictions of the PBEsol and PBE-D2 approaches are further compared to each other in the matter of the inversion of the character of the VBM and CBM states, which was mentioned in the beginning of this article, cf. Refs. 1–4. The angular-momentum-resolved (s, p$_x$, p$_y$, p$_z$) contributions from Bi, Te, and I atoms are computed by projecting the VBM and CBM wave functions onto spherical harmonics within a sphere around each atom. Figure 4 shows plots of the $s$+$p_x$+$p_y$+$p_z$ (the left panels), $p_x$+$p_y$+$p_z$ (the center panels) and $p_z$ (the right panels) contributions from Bi (the upper panels), Te (the middle panels) and I (the lower panels) atoms to the VBM and CBM wave functions as a function of $t_v$, viz. the degree of compression. The total p contribution from the Bi atom is also roughly constant, as seen in Fig. 4(b). On the other hand, Figs. 4(a), 4(c), 4(f) show some variation. For example, Fig. 4(a), 4(d) shows that the overall contribution from Bi [Te] atoms is slightly increasing [decreasing] as the degree of compression increases. The contribution from Bi-$p_z$ [Te-$p_z$] decreases [increases] at the expense of increasing contributions from Bi-$p_x$ and Bi-$p_y$ [Te-$p_x$ and Te-$p_y$], cf. Figs. 4(a) and 4(b) [Figs. 4(e) and 4(f)], while $t_v$ is getting reduced. Accordingly, the character of the CBM (VBM) wave function is mostly of Bi-$p$ (Te-$p_z$+$I_p$) for $t_v - t_{v_c} > 0$, which is of Te-$p_z$+$I_p$ (Bi-$p$) for $t_v - t_{v_c} < 0$. This demonstrates clearly the inversion of the VBM and CBM states that occurs at $t_v - t_{v_c} = 0$. As a matter of fact the inversion of the character of the VBM and CBM wave functions is easily noticed in any panel of Fig. 4 if the smoothing effect of the plots at $t_v - t_{v_c} = 0$. It is also readily noticeable that the PBEsol-calculated and dispersion-corrected (PBE-D2) curves follow qualitatively and quantitatively (within a few percent) the same trend in all panels of Fig. 4. Hence the results of the PBEsol and PBE-D2 calculations are in agreement as regards the inversion of the character of the VBM and CBM wave functions.

In conclusion, the evolution of the electronic structure of BiTeI under compression is studied by employing semilocal (PBEsol) and dispersion-corrected (PBE-D2) density-functional calculations. A comparative investigation of the results of these calculations confirms that the band-gap energy of BiTeI decreases till it attains a min-
FIG. 4. The variation of the \( s + p_x + p_y + p_z \) [(a), (d) and (g)], \( p_x + p_y + p_z \) [(b), (e) and (h)] and \( p_z \) [(c), (f) and (i)] contributions from Bi [(a)-(c)], Te [(d)-(f)] and I [(g)-(i)] atoms to the VBM and CBM wave functions with the difference \( t_v - t_c \). Note that the latter is positive (negative) for pressures lower (higher) than \( P_c \), which is zero for \( P = P_c \).

minimum value of zero at a critical pressure, after which it increases again, which was reported in a number of recent studies.\(^{1-4}\) The critical pressure is found to be lower than the pressure at which BiTeI undergoes a structural phase transition, implying that the closure of the band gap would not be hindered by a structural transformation. In addition, the band-gap pressure coefficients of BiTeI are computed, and an expression of the critical pressure is devised in terms of these coefficients, cf. Eq. (3). It is to be emphasized that the latter enables one to estimate the critical pressure from the equilibrium band gap and its pressure coefficients. It is exposed that the essential difference between the results of PBEsol and PBE-D2 calculations pertains to the prediction of the compressibility of BiTeI. Nevertheless, the effect of pressure on the atomic structure of BiTeI is found to be manifested primarily as the reduction of the width of the van der Waals gap according to both types of calculations. It is further revealed that the PBEsol and PBE-D2 approaches yield consistent predictions concerning the variation of band-gap energy with respect to the width of the van der Waals gap. Consequently, it is shown that the calculated (PBEsol and PBE-D2) band-gap energies follow qualitatively and quantitatively the same trend within the two approximations employed here, and the transition to the zero-gap state occurs at the same critical width of the van der Waals gap.

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Appendix: Crystal structure calculations using the optB86b-vdW functional

We computed the total energy \( E \) as a function of the lattice parameters \( a \) and \( c \) using the optB86b-vdW functional and determined the energy minimum \( E_{\text{min}} \). A colored contour plot of the energy difference \( \Delta E = E - E_{\text{min}} \) versus \( a/a_{\text{exp}} \) and \( c/c_{\text{exp}} \) is given in Fig. A1 where \( a_{\text{exp}} \) and \( c_{\text{exp}} \) denote the experimental values of
FIG. A1. Colored contour plot of the energy difference $\Delta E$ computed using the optB86b-vdW functional as a function of $a/a_{\text{exp}}$ and $c/c_{\text{exp}}$. The solid black circles mark the values of the ratios $a/a_{\text{exp}}$ and $c/c_{\text{exp}}$ obtained via various approximations, i.e., PBE, PBE-D2, PBEsol, and optB86b-vdW.

\[ \Delta E (\text{eV}) \]

the equilibrium lattice parameters of $a_0$ and $c_0$, respectively. There appears to exist an anomalously flat energy plateau that is the red portion of the plot in Fig. A1. Within this plateau, the optB86b-vdW functional results in a great overestimation in $c_0$ ($a_0$) by 66% (5%). In other words, crystal structure calculations using the optB86b-vdW functional yield an unacceptably unrealistic (unexpectedly inaccurate) prediction for $c_0$ ($a_0$), cf. the solid black circles in Fig. A1, which is clearly not the case with the other calculation (PBE, PBE-D2, PBEsol) results. Owing to this difficulty, the resolution of which is beyond the scope of this paper, we avoid employing the optB86b-vdW functional in electronic structure calculations.
SUPPLEMENTAL MATERIAL

- Figure S1 displays the fourth- and fifth-order Birch-Murnaghan fits for the PBEsol-calculated and dispersion-corrected (PBE-D2) energy-volume curves, respectively.

- Figure S2 shows the plots of $a/a_0$ and $c/c_0$ versus the normalized pressure $P/K_0$, where $a_0$ and $c_0$ denote the equilibrium values of the lattice parameters $a$ and $c$, respectively.
FIG. S1. The energy-volume curves obtained via the PBEsol and PBE-D2 calculations. It is discernible that the PBEsol-calculated and dispersion-corrected (PBE-D2) curves are reproduced well by fourth- and fifth-order Birch-Murnaghan (BM) fits, respectively.
FIG. S2. The plots of $a/a_0$ (top panel) and $c/c_0$ (bottom panel) versus the normalized pressure $P/K_0$, where $a_0$ and $c_0$ denote the equilibrium values of the lattice parameters $a$ and $c$, respectively.