Crystal and electronic structure of BiTeI, AuTeI, and PdTeI compounds: A dispersion-corrected density-functional study

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Semilocal and dispersion-corrected density-functional calculations have been performed to study the crystal structure, equation of state, and electronic structure of metal tellurohalides with chemical formula MeTeI where Me=Bi, Au, or Pd. A comparative investigation of the results of these calculations is conducted, which reveals the role of van der Waals attraction. It is shown that the prediction of crystal structure of metal tellurohalides is systematically improved thanks to the inclusion of van der Waals dispersion. It is found for BiTeI and AuTeI that the energy versus volume curve is anomalously flat in the vicinity of equilibrium volume and the calculated equation of state has an excessively steep slope in the low-pressure region, which are also fixed in the dispersion-corrected calculations. Analysis based on the computation of the volume and axial compressibilities shows that predicting the anisotropy of BiTeI via the semilocal calculations yields an unrealistic result whereas the results of dispersion-corrected calculations agree with the experimental compressibility data. Our calculations render that BiTeI (AuTeI) is a narrow band gap semiconductor with Rashba-type spin-splitting at the band edges (with an indirect band gap) while PdTeI is a metal with relatively low density of states at the Fermi level. The band gaps of BiTeI and AuTeI obtained via semilocal (dispersion-corrected) calculations are found to be greater (smaller) than the respective experimental values, which is against (in line with) the expected trend. Similarly, the Rashba parameters of BiTeI are bracketed by the respective values obtained via semilocal and dispersion-corrected calculations, e.g., a larger value for the Rashba parameter αR is obtained in association with the reduction of the band gap caused by modification of the crystal structure owing to van der Waals attraction. Excellent agreement with the experimental Rashba parameters is obtained via interpolation of the calculated (semilocal and dispersion-corrected) values.

I. INTRODUCTION

Bismuth tellurohalide (BiTeI) has recently been attracting a great deal of interest as a potential spintronnic material due to emergence of giant Rashba-type spin-splittings in its band structure and of a pressure-induced topological insulating phase, albeit it has also been pointed out that the latter would probably be hindered by a structural phase transition. Prompted by the discovery of Rashba splittings in the band structure of BiTeI, density-functional calculations have increasingly been employed to explore the electronic and crystal structure of this semiconductor. Curiously, although BiTeI is often described to have a layered structure where the triple Bi–Te–I layers are stacked along an axis perpendicular to the layers, the van der Waals attractions were not explicitly included in these studies. The lattice parameters of BiTeI were therefore needed to be fixed to their experimental values in most density-functional calculations. In order to provide a more complete description, we adopt here the dispersion-corrected density-functional (DFT-D2) approach, where the van der Waals forces are incorporated by means of a semiempirical force field. We employ the DFT-D2 calculations for not only BiTeI but also AuTeI and PdTeI as far as we are aware of few experimental studies on the structure and properties of the latter, which have not been explored via first-principles methods before.

In order to reveal the effect of the dispersion correction on the crystal and electronic structure of MeTeI (Me=Bi, Au, or Pd) compounds, we carried out our calculations at two levels of approximations: the density-functional calculations performed within the generalized gradient approximation (GGA) using the functional of Perdew, Burke, and Ernzerhof (PBE) without and with the semiempirical dispersion correction. Hence, we compare the results of the PBE (semilocal) and PBE-D2 (dispersion-corrected) calculations to each other and to the experimental data. The total energy calculations performed for compressed and dilated systems are used to derive equation of state for metal tellurohalides under consideration. Our results show that inclusion of van der Waals interactions is necessary for an adequate physical description of these compounds. In particular, predicting the anisotropy of BiTeI via the PBE calculations yields an unrealistic result whereas the results of the PBE-D2 calculations agree with the experimental compressibility data.

Although oxidation state of Bi, Au, and Pd atoms is the same (+3) in the BiTeI, AuTeI, and PdTeI compounds, the crystal structures of the latter are quite different as shown in Figs. 1(a)-(c). BiTeI, AuTeI, and PdTeI crystallize in trigonal, monoclinic, and tetragonal structures with space groups P3m1 (No. 156), P21/c (No. 14), and P42/mmc (No. 131), respectively. The crystal structure of BiTeI could be 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, cf. Ref. 15. As shown in Figure 1(a), adjacent trigonal layers formed by Bi, Te, and I atoms stack along the $c$-axis of the hexagonal lattice in BiTeI. The crystal structure of AuTeI could be characterized by the monoclinic lattice parameters $a$, $b$, $c$, and $\beta$, and nine internal parameters since Au, Te, and I atoms occupy the $1a$, $3j$, and $4j$ positions with fractional coordinates $(0,y_{Au},z_{Au})$, $(x_{Te},y_{Te},z_{Te})$, $(x_{I},y_{I},z_{I})$, respectively, cf. Ref. 18. As shown in Fig. 1(b), the atoms form corrugated layers parallel to the $bc$-plane, which stack along the $a$-axis in AuTeI. The crystal structure of PdTeI could be characterized by the tetragonal lattice parameters $a$ and $c$, and three internal parameters since Pd, Te, and I atoms occupy the $4m$, $4l$, and $4j$ positions with fractional coordinates $(x_{Pd},y_{Pd},0)$, $(x_{Te},0,0)$, and $(x_{I},2/3,0)$, respectively, cf. Ref. 19. As shown in Fig. 1(c), ladder chains made of Te$_2$Pd$_2$ units running along the $a$- and $b$-axes stack along the $c$-axis in PdTeI. Note that the Te and I atoms are mixed in the layers or ladder chains of AuTeI or PdTeI, respectively, whereas the layers of BiTeI are umary, consisting of Bi, Te or I atoms. Accordingly, the space group of the BiTeI crystal is noncentrosymmetric while the crystal structures of AuTeI and PdTeI are centrosymmetric. This puts BiTeI in a unique position in terms of spintronic material properties,\(^{4}\) which lacks inversion symmetry in the crystal structure.

The rest of the paper is organized as follows: Sec. II is devoted to the method of calculation, giving also a summary of the computational details. We focus on the crystal structure, equation of state, and electronic band structure in Sec. III where we discuss the results of our semilocal (PBE) or dispersion-corrected (PBE-D2) density-functional calculations. A summary of our findings is given in Sec. IV. Lastly, the spin-orbit coupling (SOC) effects on the BiTeI band structure are described in further details in the Appendix.

II. METHOD

All calculated properties reported here were obtained via semilocal\(^{20}\) (PBE) or dispersion-corrected\(^{16}\) (PBE-D2) density-functional calculations performed by employing the projector augmented-wave (PAW) method,\(^{23}\) as implemented\(^{24}\) in the Vienna \textit{ab initio} simulation package\(^{25}\) (VASP). The calculations for BiTeI and AuTeI were performed in the noncollinear mode\(^{26,27}\) of VASP in order to take spin-orbit coupling into account. The $4d$ and $5s$, $5p$ and $5d$, $6p$ and $6d$, and $6s$ and $6p$ states are treated as valence states for palladium, tellurium, iodine, gold, and bismuth, respectively. Plane wave basis sets were used to represent the electronic states, which were determined by imposing a kinetic energy cutoff of 325 eV. The long-range dispersion corrections\(^{16}\) for periodic systems were treated as described in Ref. 28. The values of the dispersion coefficient $C_6$ and van der Waals radius $R_0$ used in this study are given in Table I. The global scaling factor $s_6$ was set to 0.75, which is the adequate value for the PBE functional.\(^{28}\)

We first carried out full optimization of the crystal structures where concurrent relaxations of the unit cell volume and shape as well as the ionic positions were performed with no symmetry constraints, until the maximum value of residual forces on atoms was reduced to be smaller than 0.01 eV/Å. Convergence criterion for the electronic self-consistency was set up to $10^{-6}$ eV. In these

**TABLE I.** Dispersion coefficients $C_6$ (in J nm$^6$ mol$^{-1}$) and van der Waals radii $R_0$ (in Å) employed in the present PBE-D2 calculations. These values are taken from the references given in the rightmost column.

| Element | $C_6$ | $R_0$ | Reference |
|---------|-------|-------|-----------|
| Pd      | 24.67 | 1.639 | 16        |
| Te      | 31.74 | 1.892 | 16        |
| I       | 31.50 | 1.892 | 16        |
| Au      | 40.62 | 1.772 | 21        |
| Bi      | 63.55 | 1.900 | 22        |
optimizations, we used the primitive unit cells of BiTeI, AuTeI, and PdTeI, whose Brillouin zones were sampled by 20 × 20 × 16, 8 × 8 × 8, and 21 × 21 × 29 k-point meshes, respectively, which were generated according to Monkhorst-Pack scheme.29 Using the optimized crystal structures, we then carried out band-structure and (projected) density-of-states calculations. Besides, we performed geometry optimizations for the elemental solids of bismuth, gold, palladium, tellurium, and iodine, and employed the respective equilibrium energies per atom $E_{\text{Me}}$ (Me=Bi, Au, Pd), $E_{\text{Te}}$, and $E_1$ in the computation of the formation energy $\Delta H_f$. It should be reminded that the form of the electronic Hamiltonian used in dispersion-corrected (PBE-D2) calculations is the same as in the calculations employing the PBE functional alone. In other words, the effect of dispersion correction on the electronic structure is indirectly through modification of the crystal structure since the van der Waals interactions are treated as semiempirical force fields in the DFT-D2 approach.16

Secondly, we carried out constant-volume optimization of the crystal structures where the unit cell shape and the ionic positions were allowed to relax. Hence, we obtained the energy $E$ per formula unit as a function of the volume $V$ per formula unit, which was used to derive equation of state (EOS) at zero temperature. We found that the energy-volume curve is not accurately reproduced as semiempirical force fields in the DFT-D2 approach.16, 8

Thus, we performed forth- and fifth-order BM fits by a third-order Birch-Murnaghan (BM) fit that is in widespread use, which is further discussed in Section III. Thus, we performed forth- and fifth-order BM fits as a function of the Eulerian strain $f = [(V_0/V)^{2/3} - 1]/2$ that is defined from $V$ and the zero-pressure volume $V_0$, employing

$$E = E_0 + \sum_{k=2}^{k_{\text{max}}} C_{k-1} f^k$$

with $k_{\text{max}} = 4$ and 5, respectively. Here $C_k$s are the fitting coefficients, and $E_0$ denotes the equilibrium energy (per formula unit). Note that $\Delta H_f = E_0 - (E_{\text{Me}} + E_{\text{Te}} + E_1)$. The pressure $P$ was computed by using

$$P = \left(1 + 2f/3V_0\right)^2 \sum_{k=1}^{k_{\text{max}}-1} (k + 1)C_k f^k.$$  \hspace{1cm} (2)

The isothermal bulk modulus $K_0$ and its pressure derivatives $K_0'$, $K_0''$, and $K_0'''$ (all evaluated at $V_0$) were obtained via

$$K_0 = \frac{2C_1}{9V_0},$$

$$K_0' = \frac{C_2}{C_1} + 4,$

$$K_0'' = \frac{1}{K_0} \left(\frac{4C_3}{3C_1} - K_0'(K_0 - 7) - \frac{143}{9}\right),$$

$$K_0''' = \frac{1}{9K_0^2} \left(\frac{20C_4}{C_1} - 12K_0(3K_0' - 8)K_0'' - K_0'(3K_0' - 16)^2 + 118 + \frac{1888}{3}\right).$$  \hspace{1cm} (3)

respectively.

The volume compressibility $\kappa_v$ was obtained as the inverse of the bulk modulus, i.e., $\kappa_v = 1/K_0$. The axial (linear) compressibilities $\kappa_l = -(d\ln l/dP)_{P=0}$, with $l$ denoting the lattice constant along one of the crystal axes, were computed by dividing $-\frac{1}{l} \frac{d(l/V)}{dP}$ by $\left(\frac{dV}{dP}\right)_{V=V_0}$, where the former [latter] was obtained via cubic spline interpolation of the lattice parameter $l$ as a function of the volume $V$ [via Eq. (2)]. The reliability of this procedure was tested by checking whether $\kappa_v = \kappa_n + \kappa_s + \kappa_c$ holds or not. The latter equality was satisfied in the cases of BiTeI and PdTeI, but not in the case of AuTeI. As discussed in Section III, the variation of the lattice parameter $c$ with the pressure is nonmonotonic in the case of AuTeI, which results in a substantial error in estimating derivatives via spline interpolation. The linear compressibilities of AuTeI are therefore not reported.

### III. RESULTS AND DISCUSSION

#### A. Crystal Structure

The crystal structure optimizations result in the experimentally determined ground-state structures, i.e., a noncentrosymmetric (centrosymmetric) crystal for BiTeI (AuTeI and PdTeI) that are shown in Fig. 1(a)-(c) where color contour plots of computed electronic charge density are also displayed. Inspection of the charge-density plot in Fig. 1(a) reveals that the most electron-rich (electron-poor) regions in BiTeI are around I (Bi) atoms. This reflects the fact that bismuth is less electronegative than both iodine and tellurium.32 It is also interesting to note that the electronegativity difference $\chi_{\text{Te}} - \chi_{\text{Bi}}$ is positive and comparatively small whereas $\chi_\text{I} - \chi_{\text{Bi}}$ is also positive but comparatively large.32,33 Accordingly, the electronic charge distribution around Bi–Te (Bi–I) bonds in Fig. 1(a) is rather of a covalent (ionic) character, which introduces an asymmetry between Bi–Te and Bi–I bonds. On the other hand, we have $\chi_{\text{Te}} - \chi_{\text{Me}} < 0 < \chi_\text{I} - \chi_{\text{Me}} < \chi_\text{I} - \chi_{\text{Te}}$ for both Me=Au and Pd, i.e., the differences $\chi_{\text{Te}} - \chi_{\text{Me}}$ and $\chi_\text{I} - \chi_{\text{Me}}$ are both relatively small, which are of the opposite sign.32,33 In agreement with the latter, the electronic charge distribution around not only Me–Te bonds and but also Me–I bonds in Fig. 1(b)-(c) look more like those of covalent bonds. Thus, the tellurium and iodine atoms prefer to coordinate with the metal atoms almost equally, and therefore tend to mix (as opposed to form unary layers) in the AuTeI and PdTeI compounds, rendering the crystal structures of the latter centrosymmetric.

A comparison of the results of the crystal structure optimizations (PBE and PBE-D2) to the experimental data is given in Tables II and S1 (Ref. 34). It is seen in Table II that the improvement due to the dispersion correction is mostly on the lattice parameters ($a$, $b$, $c$)
whereas the PBE and PBE-D2 calculations yield errors of similar magnitude in the prediction of the internal parameters ($x$, $y$, $z$). It is thus notable that the prediction of unit cell volume and shape is substantially improved: Figure 2(a) displays a plot of the calculated (PBE and PBE-D2) versus experimental values for the equilibrium volume per formula unit. Although it is well known the unit cell volume is overestimated within the GGA, the error in the PBE-optimized volume is clearly greater than expected, which is 13.4, 16.7, and 8.3 % for BiTeI, AuTeI, and PdTeI, respectively. As evident from the trend of the empty symbols in Fig. 2(a) this anomalous overestimation is widespread. Since the lattice parameters ($a$, $b$, $c$) obtained in the PBE-D2 optimizations are smaller than those in the PBE-D2 optimizations, cf. Table II, the prediction of equilibrium volume is systematically improved thanks to the dispersion correction, as evident from the trend of the filled symbols in Fig. 2(a). Moreover, a comparison of the empty (PBE) and filled (PBE-D2) symbols of the same shape to each other in Fig. 2(b) shows that the errors in the prediction of $b/a$ and $c/a$ ratios are, at the same time, significantly reduced thanks to the dispersion correction.

As for the prediction of the internal parameters of the BiTel crystal, it is interesting to compare our results to the results of Bahramy et al.\textsuperscript{5} (Sklyadneva et al.\textsuperscript{8}) who predicted $z_{Te} = 0.7482$ and $z_1 = 0.3076$ ($z_{Te} = 0.758$ and $z_1 = 0.299$). Note that our PBE-D2 and PBE values for $z_{Te}$ and $z_1$ are in close agreement with those given by Bahramy et al.\textsuperscript{5} and Sklyadneva et al.\textsuperscript{8} respectively - albeit in both Refs. 5 and 8 the PBE functional was employed with no additional terms for the dispersion correction. This is so because the lattice parameters $a$ and $c$ were fixed to their experimental values (that are close to our PBE-D2 values) in Ref. 5, which was not done in Ref. 8.

The predictions of Ref. 5 and 8 show that the computed values of the equilibrium Bi–Te and Bi–I distances correspond to the Bi–I and Bi–Te distances in the experimentally determined structure,\textsuperscript{15} respectively, which is supported by our PBE-D2 values, cf. Table S1 (Ref. 34). Note that in Ref. 15 the bond lengths given in Table S3 are not consistent with the internal parameters given Table 2. It is therefore problematic to perform a direct comparison of experimental and optimized values of the internal lattice parameters $z_{Te}$ and $z_1$. Thereupon, we considered a second “phase” for BiTel, which was generated by exchanging the positions of Te and I atoms so that

### Table II. Calculated (PBE and PBE-D2) and measured lattice parameters of the MeTeI crystals. The experimental values are taken from Ref. 15, Ref. 18, and Ref. 19 for BiTeI, AuTeI, and PdTeI, respectively.

|          | PBE   | PBE-D2 | Exptl. |
|----------|-------|--------|--------|
| BiTeI    |       |        |        |
| $a$ (Å)  | 4.4371| 4.2843 | 4.3392 |
| $c$ (Å)  | 7.433 | 7.021  | 6.854  |
| $z_{Te}$ | 0.7692| 0.7479 | 0.6928 |
| $z_1$    | 0.2828| 0.3115 | 0.2510 |
| AuTeI    |       |        |        |
| $a$ (Å)  | 8.0057| 7.2579 | 7.3130 |
| $b$ (Å)  | 7.8918| 7.3654 | 7.6242 |
| $c$ (Å)  | 7.4208| 7.3483 | 7.2550 |
| $\beta$  | 104.81| 103.95 | 106.26 |
| $x_{Au}$ | 0.4589| 0.4746 | 0.4654 |
| $y_{Au}$ | 0.1333| 0.1370 | 0.1395 |
| $z_{Au}$ | 0.2308| 0.2405 | 0.2370 |
| $x_{Te}$ | 0.6481| 0.6868 | 0.6720 |
| $y_{Te}$ | 0.1433| 0.1331 | 0.1301 |
| $z_{Te}$ | 0.9821| 0.9908 | 0.9910 |
| $x_1$    | 0.1954| 0.1626 | 0.1758 |
| $y_1$    | 0.0659| 0.1059 | 0.0857 |
| $z_1$    | 0.3895| 0.3799 | 0.3892 |
| PdTeI    |       |        |        |
| $a$ (Å)  | 8.095 | 7.806  | 7.821  |
| $c$ (Å)  | 5.722 | 5.652  | 5.659  |
| $y_{Pd}$ | 0.2500| 0.2495 | 0.2525 |
| $x_{Te}$ | 0.2086| 0.2262 | 0.2164 |
| $x_1$    | 0.2321| 0.2462 | 0.2435 |

![Figure 2](image-url)

FIG. 2. (Color online) The plots of calculated versus experimental equilibrium volume (a), and error in $b/a$ or $c/a$ ratios (b).
the Te and I atoms occupy the 1b and 1c positions with fractional coordinates (1/3,2/3,znTe), and (2/3,1/3,zi), respectively. The crystal structure optimization performed for this second phase yielded znTe = 0.2520 and zi = 0.6884, and the total energy the same as that of the BiTe phase described in Sec. I and Table II. In line with the latter, comparison performed with the aid of the COMP- STRU program35 proved that this second BiTe phase (Te atoms residing at 1b positions with znTe = 0.2520 and I atoms residing at 1b positions with zi = 0.6884) is indeed identical to the first one (Te atoms residing at 1c positions with znTe = 0.7479 and I atoms residing at 1b positions with zi = 0.3115). It is interesting to point out that excellent agreement between experimental data and our computed values (znTe = 0.2520 and zi = 0.6884) is obtained once the positions of Te and I atoms are exchanged in the experimental15 crystal structure of BiTeI. As long as the x-ray diffraction fails to distinguish the Te and I layers in BiTeI,5 we anticipate that a full-fledged experimental characterization would render the values of znTe and zi in agreement with our optimized (PBE-D2) values given in Table II.

B. Equation of State

A plot of the energy difference ΔE = E − (Em + ETe + EI) with respect to the volume V is given in Figs. 3(a), (b), and (c) for BiTeI, AuTeI, and PdTeI, respectively. The calculated values are represented by the blue (PBE) and red (PBE-D2) circles. The solid-line curves connecting the symbols show the forth- and fifth-order BM fits, whose equation is given by ΔE = ΔHf + Σk=2 Ck−1f[k]/k, cf. Eq. (1). Although we first performed the BM fits with kmax = 3, we found it necessary to increase kmax to 4 for AuTeI and PdTeI and to 5 for BiTeI in order to ensure a satisfactory level of accuracy in the fitting procedure, as mentioned in Section II. It is discernible in Fig. S1 (Ref. 34) that a good fit is not obtained when kmax is reduced to 4 for BiTeI, and 3 for AuTeI and PdTeI.

The values of Ck parameters obtained via fitting as well as the formation energies ΔHf are given in Table III. Note that while ΔHf is significantly (AuTeI) or slightly (PdTeI) reduced due to addition of the dispersion terms to the PBE functional, both PBE and dispersion-corrected (PBE-D2) calculations yield a similar degree of overbinding for BiTeI since the experimental value36 of the enthalpy of formation for BiTeI is ΔHf°(298 K) = 0.856 eV per formula unit. On the other hand, the interlayer binding energy of BiTeI was computed to be 24 and 332 meV per formula unit in our PBE and PBE-D2 calculations, respectively. Thus, the dispersion-corrected (PBE-D2) calculations yield a substantially stronger interlayer binding for BiTeI, compared to the PBE calculations. It is also notable that the PBE-calculated binding curves of BiTeI [Fig. 3(a)] and AuTeI [Fig. 3(b)] are anomalously flat in the vicinity of equilib-
FIG. 3. (Color online) The plot of the energy difference $\Delta E = E - (E_{Me} + E_{Te} + E_{I})$, cf. Eq. (1), versus the volume for BiTeI (a), AuTeI (b), and PdTeI (c). Here $k_{\text{max}}$ is set to 4 for BiTeI, and 3 for AuTeI and PdTeI. The respective pressure-volume curves are plotted in (d), (e), and (f). The variation of the lattice parameters ($a$, $b$, $c$) with the pressure is shown in (g)-(m). The PBE-calculated and dispersion-corrected (PBE-D2) curves are in blue and red, respectively. The filled symbols mark the experimental values of the equilibrium volumes [(d)-(f)] and lattice parameters [(g)-(m)] measured by Shevelkov et al. (Ref. 15), Fenner et al. (Ref. 18), and Seo et al. (Ref. 19) for BiTeI, AuTeI, and PdTeI, respectively. The empty circles in (d), (g), and (h) represent the experimental compressibility data of Xi et al. (Ref. 3) for BiTeI.

TABLE III. The values of the formation energy $\Delta H_f$, the equilibrium volume $V_0$, and the fitting coefficients $C_k$ in Eq. (1) for MeTeI ($Me=\text{Bi,Au,Pd}$) compounds.

|        | $k_{\text{max}}$ | $\Delta H_f$ (eV) | $V_0(Å^3)$ | $C_1$ (eV) | $C_2$ (eV) | $C_3$ (eV) | $C_4$ (eV) |
|--------|------------------|------------------|-------------|------------|------------|------------|------------|
| BiTeI  | PBE 5            | -0.958           | 127.039     | 15.357     | 278.613    | 1091.512   | -8932.044  |
|        | PBE-D2 5         | -0.978           | 111.626     | 88.806     | 228.317    | -4645.020  | 30756.053  |
| AuTeI  | PBE 4            | -0.404           | 113.317     | 13.558     | 172.994    | -444.287   |            |
|        | PBE-D2 4         | -0.337           | 95.308      | 58.526     | 244.128    | -1103.027  |            |
| PdTeI  | PBE 4            | -0.973           | 93.742      | 61.728     | -11.560    | 506.408    |            |
|        | PBE-D2 4         | -0.961           | 86.101      | 90.574     | 103.902    | -695.661   |            |
TABLE IV. The bulk modulus $K_0$ (in GPa) and its pressure derivatives $K_0'$, $K_0''$ (in GPa$^{-1}$), and $K_0'''$ (in GPa$^{-2}$).

|        | $k_{\text{max}}$ | $K_0$  | $K_0'$ | $K_0''$ | $K_0'''$ |
|--------|------------------|--------|--------|---------|----------|
| BiTeI  | PBE              | 5      | 4.3    | 22.1    | -59.6    | 658.8    |
|        | PBE-D2           | 5      | 28.3   | 6.6     | -2.9     | 2.5      |
|        | Experimental     | 3      | 20.5   | 7.6     |          |          |
| AuTeI  | PBE              | 4      | 4.3    | 16.8    | -52.4    |          |
|        | PBE-D2           | 4      | 21.9   | 8.2     | -2.3     |          |
|        | PBE              | 4      | 23.4   | 3.8     | 0.3      |          |
|        | PBE-D2           | 4      | 37.5   | 5.1     | -0.4     |          |

The behavior of negative linear compressibility has nevertheless been observed in a number of systems recently.

The bulk modulus $K_0$ and its pressure derivatives $K_0'$, $K_0''$, and $K_0'''$ computed via Eq. (3) with $C_k$ coefficients listed in Table III are given in Table IV where the experimental values for BiTeI are also included. The latter were obtained by performing a third-order BM fit, cf. the black solid curve in Fig. 4, to the experimental compressibility data. It is seen that the PBE calculation yields a substantially underestimated (overestimated) value for $K_0$ ($K_0''$) of BiTeI. Recalling that (i) the PBE-calculated binding energy curve anomalously flat in the vicinity of equilibrium volume, cf. Fig. 3(a), and (ii) the PBE-calculated equation of state has an excessively steep slope in the low-pressure region, cf. Fig. 3(d), it is no surprise that the bulk modulus is substantially underestimated in the PBE calculations. The PBE-calculated first pressure derivative $K_0'$ is consequently greatly overestimated, balancing this underestimation of $K_0$. On the contrary, the dispersion-corrected (PBE-D2) calculations, albeit in much better agreement with the experimental values, result in overestimation (underestimation) for $K_0$ ($K_0''$). Hence, the experimental values of $K_0$ and $K_0''$ are bracketed by the PBE-calculated and dispersion-corrected (PBE-D2) values.

The volume (bulk) and axial (linear) compressibilities and their ratios are given in Table V for BiTeI and PdTeI. Note that $\kappa_a = \kappa_c$ for these systems. For BiTeI (PdTeI), the PBE and PBE-D2 values for the $a$-axis (c-axis) compressibility are close to each other. In contrast, $\kappa_a^{\text{PBE}} < \kappa_c^{\text{PBE-D2}}$ for BiTeI, and $\kappa_a^{\text{PBE}} > \kappa_c^{\text{PBE-D2}}$ for PdTeI. Thus, the c-axis compressibility of BiTeI is greatly overestimated in the PBE calculations (which reflects lacking van der Waals binding). We have furthermore $\kappa_a/\kappa_c \ll 1$ (PBE) while $\kappa_a/\kappa_c \sim 1$ (PBE-D2), and $\kappa_a/\kappa_c < 1/3$ and $\kappa_c/\kappa_a > 1/3$ (PBE) while $\kappa_a/\kappa_c \sim 1/3$ and $\kappa_c/\kappa_a \sim 1/3$ (PBE-D2) for BiTeI. Note that the ratio $\kappa_a/\kappa_c$ should be unity, and both $\kappa_a/\kappa_c$ and $\kappa_c/\kappa_a$ need to be equal to 1/3 for isotropic materials. For layered materials, on the other hand, one would expect to have the ratio $\kappa_a/\kappa_c$ ($\kappa_a/\kappa_c$) significantly smaller (larger) than 1/3 and the ratio $\kappa_a/\kappa_c$ much smaller than unity (e.g., $\kappa_a/\kappa_c = 0.028$, $\kappa_c/\kappa_a = 0.943$, $\kappa_a/\kappa_c = 0.03$ for graphite, a known layered material). Thus, the PBE calculations predict BiTeI to be an extremely layered material whereas the PBE-D2 calculations indicate a layered, but substantially less anisotropic material. In other words, predicting the anisotropy of BiTeI via the PBE calculations yields an unrealistic result, given that the PBE-D2 calculations are in much better agreement with the experimental compressibility data. It appears that the inclusion of van der Waals attraction, which was motivated by the quasi-layered structure of BiTeI, leads to a much less anisotropic crystal structure. Note that this issue does not raise in the case of PdTeI where van der Waals binding plays a much less prominent role and therefore the PBE and PBE-D2 calculations qualitatively yield similar results, cf. Table V.

TABLE V. The volume ($\kappa_v$) and axial ($\kappa_a$ and $\kappa_c$) compressibilities (in GPa$^{-1}$), and their ratios.

|        | $\kappa_v$ | $\kappa_a$ | $\kappa_c$ | $\kappa_a/\kappa_v$ | $\kappa_c/\kappa_v$ | $\kappa_a/\kappa_c$ |
|--------|------------|------------|------------|----------------------|----------------------|----------------------|
| BiTeI  | PBE        | 0.232      | 0.010      | 0.212                | 0.043                | 0.914                | 0.047                |
|        | PBE-D2     | 0.035      | 0.011      | 0.013                | 0.314                | 0.371                | 0.846                |
| PdTeI  | PBE        | 0.043      | 0.017      | 0.008                | 0.395                | 0.186                | 2.125                |
|        | PBE-D2     | 0.027      | 0.010      | 0.007                | 0.370                | 0.259                | 1.429                |
C. Electronic Structure

Figure 5(a)-(c) displays the calculated band structure (left panels in each subplot) and projected density of states (right panels in each subplot) of the MeTeI compounds under consideration, obtained by using the optimized (PBE-D2) lattice parameters given in Table II. BiTeI and AuTeI appear to be narrow band gap semiconductors whereas PdTeI is predicted to be a metal with relatively low density of states at the Fermi level $E_F$. In Fig. 5(a), Rashba-type splitting near the Brillouin zone point $A$ is visible, which is in agreement with the former studies.\textsuperscript{1,5} This is important because the emergence of the bulk Rashba-type splittings in the calculated band structure depends on the reliable prediction of the BiTeI lattice parameters, cf. Fig. 4 of Ref. 13. We present a comparison of the BiTeI band structures with and without SOC in the Appendix, which confirms that splitting near the point $A$ in Fig. 5(a) manifests SOC-induced modification of the band edges. It is further shown that the gradient of the crystal potential $\nabla V(r)$ leads predominantly to an asymmetric electric field along the $c$-axis that facilitates the spin-orbit coupling. As long as the latter gives rise to an effective magnetic field\textsuperscript{43} $\vec{H}_{\text{eff}}$, a simple understanding is that Rashba-type splitting in Fig. 5(a) originates from the interaction of the crystal electrons with $\vec{H}_{\text{eff}}$ that is proportional to $\vec{V}(r) \times \vec{p}$, where $\vec{p}$ denotes the momentum operator. It is to be noted that a comprehensive analysis has already been given by Bahramy et al. in Ref. 5, revealing the origin of (giant) Rashba-type splitting in BiTeI.

We see in Fig. 5(a) that the lower valence band consists of the Bi, Te, and $I$ $s$ orbitals whereas the upper valence band as well as lower conduction band are derived from the Bi, Te, and $I$ $p$ orbitals. Fig. 5(b) shows that the bands of AuTeI are relatively flat (nondispersive), which are derived primarily from Te and I $s$ orbitals (lower valence band), and Te and $I$ $s$ and Au $d$ orbitals (upper valence band as well as lower conduction band). An d states dominate the bottom of the upper valence band. Fig. 5(c) shows that the bands of PdTeI around the Fermi level are quite dispersive along not only perpendicular $\Gamma-Z$ direction but also parallel $\Gamma-M$ and $X-M$ directions. Thus our calculations indicate that opening a band gap owing to a possible $c$-axis-doubling distortion\textsuperscript{19} would probably not render PdTeI a semiconductor. We see in Fig. 5(c) that the deep-lying bands consists mainly of the Te $s$ and I $s$ orbitals while the vicinity of the Fermi level are derived from the Te $p$, I $p$ and Pd $d$ orbitals.

Table VI gives some characteristic band structure parameters for BiTeI and AuTeI semiconductors, for which experimental data is available: the band gap $E_g$ and the Rashba energy $E_R$ and momentum offset $k_R$ for the conduction band minimum. As for the BiTeI band gap, it is interesting to point out that our PBE-D2 value is close the PBE value (0.242 eV) of Rusinov et al.\textsuperscript{10} who employed the experimental\textsuperscript{15} lattice parameters $a$ and $c$ and PBE-optimized\textsuperscript{6} internal parameters $z_{Te}$ and $z_{I}$ in their calculations. Similarly, our PBE-D2 values for the Rashba energy and momentum offset are in close agreement with the respective PBE values reported in Ref. 10 (where $E_R = 0.122$ eV and $k_R = 0.050$ Å\textsuperscript{-1}).

It is clear from the entries of Table VI that the calculations with the PBE functional yield band gaps that are greater than the respective experimental values, which is against the expected trend inasmuch as the band gap is known to be underestimated within the GGA. Contrary to this, the calculated band gaps corresponding to the PBE-D2 optimized crystal structures are smaller than the respective experimental values, in line with the expected trend. Hence, the experimental band gaps are bracketed by the respective PBE and PBE-D2 values, i.e.,

$$E_{g}^{\text{PBE-D2}} < E_g < E_{g}^{\text{PBE}}.$$

Similarly, the experimental values of $E_R$ and $k_R$ are also bracketed by the respective PBE and PBE-D2 values (cf. Table VI) since

$$E_{R}^{\text{PBE}} < E_R < E_{R}^{\text{PBE-D2}},$$
$$k_{R}^{\text{PBE-D2}} < k_R < k_{R}^{\text{PBE}}.$$ We accordingly anticipate that comparative usage of the PBE and PBE-D2 calculations would be a useful strategy for predicting the band structure of layered polar semiconductors, which eliminates the need to employ the experimental lattice parameters.

As for the Rashba parameter $\alpha_R = 2E_R/k_R$ of BiTeI, which represents the strength of Rashba splitting, the PBE-calculated and dispersion-corrected (PBE-D2) values are $\alpha_R = 3.06$ and 4.82 eVÅ, respectively, bracketing the experimental value\textsuperscript{4} of $\alpha_R = 3.85$ eVÅ. It is shown in the Appendix that ending up with a larger Rashba parameter within the dispersion-corrected (PBE-D2) description is due to the enhancement of the asymmetric electric field $\langle -\nabla V \rangle$ along the $c$-axis [Fig. A2(b)].

Given that the experimental values of $k_R$, $E_R$, and $\alpha_R$ are bracketed by their calculated (PBE and PBE-D2) values, one might attempt to interpolate their PBE-calculated and dispersion-corrected (PBE-D2) values in

|       | PBE     | PBE-D2  | Experimental |
|-------|---------|---------|--------------|
| BiTeI | $E_g$   | 0.432   | 0.207, 0.36$^a$, 0.26$^c$ |
|       | $E_R$   | 0.081   | 0.1$^a$      |
|       | $k_R$   | 0.0529  | 0.0514, 0.052$^a$ |
| AuTeI | $E_g$(indirect) | 0.938 | 0.623        |
|       | $E_g$(direct) | 0.938  | 0.803, 0.9$^d$ |

$^a$Ref. 1  $^b$Ref. 44  $^c$Ref. 45  $^d$Ref. 17
with the band gap values, as shown in Figs. 6(a) and (b), in each subplots) of BiTeI (a), AuTeI (b), and PdTeI (c). The crystal structures optimized via dispersion-corrected (PBE-D2) calculations are assumed, cf. Table II.

FIG. 5. (Color online) The calculated band structure (left panels in each subplots) and projected density of states (right panels in each subplots) of BiTeI (a), AuTeI (b), and PdTeI (c). The crystal structures optimized via dispersion-corrected (PBE-D2) calculations are assumed, cf. Table II.

FIG. 6. (Color online) The momentum offset \( k_R \) (a), Rashba energy \( E_R \) (b), and Rashba parameter \( \alpha_R \) (c) for the conduction band minimum of BiTeI versus the band gap \( E_g \).

In order to obtain better estimates. The band gap \( E_g \) can be used as an interpolation variable for this purpose since the values of \( k_R \) and \( E_R \) are in almost linear correlation with the band gap values, as shown in Figs. 6(a) and (b), respectively. Note that the error due to the underestimation (PBE-D2) or overestimation (PBE) of \( E_g \) could then be corrected by using the experimental value of the band gap (i.e., \( E_g = 0.36 \) eV) in the interpolation. The dashed lines in Figs. 6(a) and (b) passes though the calculated points, whose equations are given by

\[
k_R = 0.05002 + 0.00667E_g,
\]

\[
E_R = 0.16356 - 0.19111E_g,
\]

respectively. Combining the latter two equations, \( \alpha_R \) could be obtained as a function of \( E_g \), which is shown by the dashed line in Fig. 6(c). Substituting the experimental value of \( E_g \) in Eq. (4) yields the interpolated values of \( k_R = 0.0524 \) Å\(^{-1}\), \( E_R = 0.995 \) eV, and \( \alpha_R = 3.62 \) eVÅ [which are marked by the black circles in Figs. 6(a), (b) and (c), respectively] in close agreement with the respective experimental values [marked by the green circles in Figs. 6(a)-(c)], cf. Table VI.

Finally, forasmuch as the pressure-induced closure of the BiTeI band gap has been explored in a number of recent studies,\(^2\) we estimated the critical pressure \( P_c \) at which the band gap disappears (the latter being a signature of the topological phase transition). We obtain \( P_c = 3.73 \) GPa using our dispersion-corrected (PBE-D2) equation of state, cf. Section III.B, together with a series of band structure calculations (not shown), which confirms the refined value \( P_c = 3.5 \) GPa) of Bahramy et al. (Refs. 2 and 46). Our investigation of the variation of the BiTeI band gap and Rashba parameters with pressure will be reported in detail in a separate publication.
IV. CONCLUSION

In summary, our comparative investigation of the results of semilocal (PBE) and dispersion-corrected (PBE-D2) calculations reveals the effect of van der Waals attractions on the crystal and electronic structure of metal tellurohalides BiTeI, AuTeI, and PdTeI. We find that the prediction of crystal structure is systematically improved thanks to the inclusion of van der Waals dispersion. It is shown for the compounds with a quasi-layered crystal structure, viz. BiTeI and AuTeI, that (i) the PBE-calculated energy versus volume curve is anomalously flat in the vicinity of equilibrium volume, and especially for volumes larger than the equilibrium volume, and (ii) the PBE-calculated equation of state has an excessively steep slope in the low-pressure region, which are also fixed in the dispersion-corrected (PBE-D2) calculations. Our analysis based on the computation of the volume and axial compressibilities shows that predicting the anisotropy of BiTeI via the semilocal calculations yields an unrealistic result whereas the results of the PBE-D2 calculations agree with the experimental compressibility data. Our calculations render that BiTeI and AuTeI are narrow band gap semiconductors with Rashba-type spin-splitting at the band edges and with an indirect band gap, respectively. PdTeI, on the other hand, is predicted to be a metal with relatively low density of states at the Fermi level. It is notable that the band gaps computed by using the optimized crystal structures from the PBE (PBE-D2) calculations are found to be greater (smaller) than the respective experimental values, which is against (in line with) the expected trend inasmuch as the band gap is known to be underestimated within the GGA. We also find that the Rashba parameter, Rashba energy and momentum offset of BiTeI are bracketed by the respective values obtained via the semilocal (PBE) and dispersion-corrected (PBE-D2) calculations. Specifically, a larger value for the Rashba parameter is obtained in the PBE-D2 calculations, which could be attributed to the reduction of the band gap caused by modification of the crystal structure owing to the inclusion of van der Waals dispersion terms. Excellent agreement with the experimental data for the Rashba parameter, Rashba energy and momentum offset of BiTeI is obtained via interpolation of the calculated (PBE and PBE-D2) values.

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Appendix: Spin-Orbit-Induced Modification of the BiTeI Band Edges

A comparison of the calculated band structures with and without SOC has already been presented by Bahramy et al. in Ref. 5 where the PBE-optimized values for \( z_T \) and \( z_i \) were employed together with the experimental values for \( a \) and \( c \). Here we present a similar comparison in Fig. A1 where no experimental data are used. The lower conduction (upper valence) band states are marked as CBM and CBM+1 (VBM and VBM−1) by the solid circles.

FIG. A1. (Color online) The band structure of BiTeI in the vicinity of the band edges, calculated with and without SOC and dispersion correction. The lower conduction (upper valence) band states labeled as CBM and CBM+1 (VBM and VBM−1) are marked by the solid circles.

The numerical calculations reported here were carried out at the High Performance and Grid Computing Center (TRUBA Resources) of TUBITAK ULAKBIM.
TABLE A. The projected wave function character of the lower conduction (CBM and CBM+1) and upper valence (VBM and VBM−1) band states, cf. Fig. A1. The entry values represent, in %, the angular-momentum-resolved (s, px, py, pz) contributions from all (Bi, Te, or I) atoms. The latter are rounded within 1%, and the contributions less than 1% are ignored.

| State | Bi | pₓ | pᵧ | pₓ | s | pₓ | pᵧ | pₓ | pₓ | pᵧ | pₓ |
|-------|----|----|----|----|---|----|----|----|----|----|----|
| CBM+1 |    | 2  | 13 | 10 | 22| 2  | 14 | 15 | 4  | 1  | 14 |
|       |    | 11 | 9  | 30 | 3 | 14 | 17 | 1  | 2  | 1  | 9  |
|       |    |    |    |    |   |    |    |    |    |    |    |
|       |    | 69 | 12 | 6  | 11|
|       |    | 12 | 16 | 28 | 5 | 14 | 10 | 2  | 2  | 3  | 6  |
|       |    | 10 | 13 | 35 | 5 | 13 | 8  | 2  | 2  | 5  | 4  |
|       |    | 72 | 10 | 6  | 11|
| CBM   |    | 16 | 1  | 3  | 9 | 44 | 24 |
|       |    | 14 | 2  | 6  | 12 | 37 | 1  | 1  | 23 |
|       |    | 11 | 4  | 9  | 18 | 34 | 1  | 1  | 16 |
|       |    | 13 | 5  | 8  | 17 | 33 | 2  | 4  | 16 |
|       |    |    |    |    |   |    |    |    |    |    |    |
| VBM   |    | 13 | 4  | 2  | 1 | 7  | 10 | 35 | 1  | 6  | 3  | 14 |
|       |    | 10 | 4  | 2  | 13| 14 | 32 | 5  | 4  | 13 |

FIG. A2. (Color online) The ab planar average of |ψₓ(r)|²(a) and 〈−∇V(r)〉(b) as a function of distance z along the c-axis of BiTeI, obtained via semilocal (PBE) and dispersion-corrected (PBE-D2) calculations. The location of the unary Bi, Te, and I layers are marked by the vertical dashed lines.

Going back to Fig. A1, it is interesting to point out that BiTeI turns out to be an indirect semiconductor in all calculations presented in Fig. A1, which is in line with the former studies.44,45,49 The difference k_{CBM} − k_{VBM} is largest [0.181 Å⁻¹ for PBE w/o SOC] when SOC and dispersion correction are both ignored, which is reduced to 0.044 Å⁻¹ (0.077 Å⁻¹) via inclusion of SOC (dispersion correction). Taking SOC and dispersion correction into account together yields the smallest difference k_{CBM} − k_{VBM} = 0.010 Å⁻¹ (PBE-D2). Similarly the band gap E₉ is reduced from 1.313 eV (PBE w/o SOC) to 1.246 eV (PBE-D2 w/o SOC) owing to the dispersion correction, which is further reduced to 0.207 eV (PBE-D2) via inclusion of SOC. Thus, the reduction in the value of E₉ is largely due to SOC (rather than the dispersion correction). Accordingly, strong (weak) SOC implies a smaller (larger) band gap, which corresponds to a greater (smaller) value of the Rashba parameter. Hence E₉ and α_R are roughly inversely proportional to each other, which is also noted in a recent study on the (BiTeI)m(Bi₂Te₃)n heterostructures.
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One obtains \( \chi_{\text{Te}} - \chi_{\text{Au}} = -0.30, \chi_{\text{Te}} - \chi_{\text{Pd}} = -0.10, \chi_{\text{Te}} - \chi_{\text{Bi}} = 0.20, \chi_{\text{I}} - \chi_{\text{Au}} = 0.26, \chi_{\text{I}} - \chi_{\text{Pd}} = 0.46, \chi_{\text{I}} - \chi_{\text{Te}} = 0.56, \text{and } \chi_{\text{I}} - \chi_{\text{Bi}} = 0.76, \) using the elemental electronegativities\(^\text{22}\) (on Pauling’s scale).

See Supplemental Material for (i) Table S1 that contains the calculated and experimental bond lengths and bond angles in the MeTeI (Me=Bi, Au, Pd) crystals, (ii) Figure S1 that displays the BM fits with \( k_{\text{max}} = 4 \) for BiTeI and 3 for AuTeI and PdTeI, (iii) Figure S2 that shows a comparison of the calculated and experimental pressure-volume curves for BiTeI. (iv) Figure S3 that displays the \( bc \) planar average of the gradient of the BiTeI crystal potential as a function of distance \( x \) along the \( a \)-axis.

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SUPPLEMENTAL MATERIAL

• Table S1 lists the calculated and experimental bond lengths and bond angles in the MeTeI (Me=Bi, Au, Pd) crystals.

• Figure S1 displays a plot of the energy difference $\Delta E$ versus the volume, and the BM fits with $k_{\text{max}} = 4$ for BiTeI and $k_{\text{max}} = 3$ for AuTeI and PdTeI.

• Figure S2 shows a comparison of the calculated and experimental pressure-volume curves for BiTeI.

• Figure S3 displays the $bc$ planar average of the gradient of the BiTeI crystal potential as a function of distance $x$ along the $a$-axis.
TABLE S1. The calculated (PBE and PBE-D2) and experimental bond lengths \(d\) (in Å) and bond angles \(\theta\) (in °) of the MeTeI crystals. The experimental values are taken from Refs. 15, 18, and 19 for BiTeI, AuTeI, and PdTeI, respectively. The labeling of bond lengths and angles are therefore the same as in the latter references.

|          | PBE   | PBE-D2 | Experimental |
|----------|-------|--------|--------------|
| BiTeI    |       |        |              |
| \(d_{\text{Bi}-\text{Te}}\) | 3.08  | 3.04   | 3.27\(^a\)   |
| \(d_{\text{Bi}-\text{I}}\)  | 3.31  | 3.30   | 3.04\(^a\)   |
| \(\theta_{\text{Te}-\text{Bi}-\text{Te}}\) | 92.03 | 89.55  | 83.05\(^b\)  |
| \(\theta_{\text{Te}-\text{Bi}-\text{I}}\)  | 174.45| 174.10 | 174.43\(^b\) |
| \(\theta_{\text{I}-\text{Bi}-\text{I}}\)   | 91.82 | 94.63  | 92.79\(^b\)  |
| \(\theta_{\text{I}-\text{Bi}-\text{I}}\)   | 84.06 | 80.90  | 91.11\(^b\)  |
| AuTeI    |       |        |              |
| \(d_{\text{Au}-\text{I}}\)  | 2.719 | 2.711  | 2.680        |
| \(d_{\text{Au}-\text{Te}}\)  | 2.671 | 2.665  | 2.642        |
| \(d_{\text{Au}-\text{Te}(\text{I})}\) | 2.702 | 2.694  | 2.654        |
| \(d_{\text{Au}-\text{Te}(\text{II})}\) | 2.727 | 2.694  | 2.684        |
| \(d_{\text{Te}-\text{Te}(\text{I})}\)  | 3.337 | 3.375  | 3.325        |
| \(d_{\text{Te}-\text{Te}(\text{II})}\) | 3.711 | 3.584  | 3.500        |
| \(d_{\text{Au}-\text{I}(\text{I})}\)  | 3.753 | 3.791  | 3.633        |
| \(d_{\text{Au}-\text{I}(\text{II})}\) | 4.212 | 4.163  | 4.193        |
| \(d_{\text{Au}-\text{II}(\text{I})}\) | 4.143 | 4.034  | 4.000        |
| \(d_{\text{Au}-\text{II}(\text{II})}\) | 3.998 | 3.700  | 3.843        |
| \(\theta_{\text{I}-\text{Au}-\text{Te}}\) | 160.89| 158.97 | 160.26       |
| \(\theta_{\text{I}-\text{Au}-\text{Te}(\text{I})}\) | 85.99 | 84.27  | 86.17        |
| \(\theta_{\text{I}-\text{Au}-\text{Te}(\text{II})}\) | 100.78| 100.79 | 100.09       |
| \(\theta_{\text{Te}-\text{Au}-\text{Te}(\text{I})}\) | 76.77 | 78.07  | 75.29        |
| \(\theta_{\text{Te}-\text{Au}-\text{Te}(\text{II})}\) | 98.02 | 98.44  | 99.40        |
| \(\theta_{\text{Te}(\text{I})}-\text{Au}-\text{Te}(\text{II})}\) | 163.69| 170.06 | 167.71       |
| \(\theta_{\text{Te}(\text{I})}-\text{Au}-\text{Te}(\text{I})}\) | 103.23| 101.93 | 104.71       |
| \(\theta_{\text{Te}(\text{II})}-\text{Au}-\text{Te}(\text{II})}\) | 100.25| 97.65  | 97.34        |
| \(\theta_{\text{Te}(\text{I})}-\text{Te}(\text{II})}\)  | 94.86 | 86.75  | 92.12        |
| PdTeI    |       |        |              |
| \(d_{\text{Pd}-\text{Te}_{\parallel}}\) | 2.636 | 2.629  | 2.601        |
| \(d_{\text{Pd}-\text{Te}_{\perp}}\)  | 2.281 | 2.832  | 2.844        |
| \(d_{\text{Pd}-\text{I}}\)   | 2.762 | 2.742  | 2.715        |
| \(d_{\text{Pd}-\cdots-\text{Pd}}\) | 4.047 | 3.946  | 3.952        |
| \(d_{\text{Te}_{\parallel}-\text{Te}_{\parallel}}\) | 4.048 | 3.910  | 3.873        |
| \(d_{\text{Te}_{\parallel}-\text{Te}_{\perp}}\)  | 3.377 | 3.532  | 3.385        |
| \(d_{\text{Te}_{\perp}-\text{Te}_{\perp}}\)  | 3.727 | 3.772  | 3.706        |
| \(d_{\text{I}-\cdot-\cdot-\text{I}}\)   | 3.758 | 3.844  | 3.809        |
| \(\theta_{\text{Te}_{\parallel}-\text{Pd}-\text{Te}_{\parallel}}\) | 79.7  | 84.4   | 81.2         |
| \(\theta_{\text{I}-\text{Pd}-\text{I}}\)  | 85.74 | 89.02  | 89.06        |
| \(\theta_{\text{Te}_{\perp}-\text{Pd}-\text{Te}_{\perp}}\) | 166.64| 172.64 | 168.62       |

\(^a\)Computed by using the lattice parameters given in Tables 1 and 2 of Ref. 15 since in Ref. 15 the bond lengths given in Table 3 are not consistent with Tables 1 and 2, as noted by Bahramy et al. (Ref. 5).

\(^b\)Note that in Ref. 15 the bond angles given in Table 3 are consistent with Tables 1 and 2.
FIG. S1. (Color online) The plot of the energy difference $\Delta E = E - (E_{Me} + E_{Te} + E_{I})$, cf. Eq. (1), versus the volume for BiTeI (a), AuTeI (b), and PdTeI (c). Note that $k_{max}$ is reduced to 4 for BiTeI, and 3 for AuTeI and PdTeI. It is discernible that a good BM fit is achieved with these values of $k_{max}$.
FIG. S2. (Color online) The calculated and experimental pressure-volume curves for BiTeI. The PBE-calculated and dispersion-corrected (PBE-D2) curves are in blue and red, respectively. The empty circles and triangles represent the experimental data provided by X. Xi (Ref. 3) and Y. Chen (Ref. 14), respectively. The filled square marks the experimental value of the equilibrium volume measured by Shevelkov et al. (Ref. 15).
FIG. S3. (Color online) The $bc$ planar average of the gradient of the BiTeI crystal potential as a function of distance $x$ along the $a$-axis, obtained via semilocal (PBE) and dispersion-corrected (PBE-D2) calculations.