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Electronic topological transition and semiconductor-to-metal conversion of Bi$_2$Te$_3$ under high pressure
Lattice dynamics and chemical bonding in Sb$_2$Te$_3$
from first-principles calculations

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Pressure effects on the lattice dynamics and the chemical bonding of the three-dimensional topological insulator, Sb$_2$Te$_3$, have been studied from a first-principles perspective in its rhombohedral phase. Where it is possible to compare, theory agrees with most of the measured phonon dispersions. We find that the inclusion of relativistic effects, in terms of the spin-orbit interaction, affects the vibrational features to some extend and creates large fluctuations on phonon density of state in high frequency zone. By investigations of structure and electronic structure, we analyze in detail the semiconductor to metal transition at $\sim$2 GPa followed by an electronic topological transition at a pressure of $\sim$4.25 GPa. © 2015 AIP Publishing LLC.

I. INTRODUCTION

Topological insulators (TIs) are novel materials that have a bulk energy gap that coexists with gapless Dirac fermion states on the surface, due to the effects of spin-orbit interaction (SOI).$^{1–5}$ Among the three-dimensional (3D) TIs discovered, the group V chalcogenides Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ have spurred tremendous interests by virtue of offering physical properties suitable for future spintronic devices, quantum computing, and photonic.$^{6–9}$ For example, Zhang et al. have confirmed pressure-induced superconductivity in Bi$_2$Te$_3$ by resistance measurements.$^{10}$ Jiang et al. have experimentally found that the Fermi level of Sb$_2$Te$_3$ can be tuned over the entire range of the bulk band gap by regulating intrinsic defects and substrate transfer doping.$^{11}$ Furthermore, these compounds are also well known for harboring substantial thermoelastic effects at ambient conditions.$^{12}$

The study of physical properties in these materials under compression is receiving increasing attention especially due to continuous experimental and theoretical developments.$^{13–22}$ The high-pressure phases II, III, and IV of Bi$_2$Te$_3$ were recognized by x-ray diffraction experiments with the additional help from the particle swarm optimization algorithm.$^{13–15}$ The same type of phases was observed in Bi$_2$Se$_3$ and Sb$_2$Te$_3$ by the experiment group of Vilaplana et al.$^{16,17}$ Here, the phase transition from the $\alpha$ phase I to the $\beta$ phase II was between the rhombohedral $R\bar{3}m$ crystal structure to the monoclinic $C2/m$ structure at 10 GPa for Bi$_2$Se$_3$, 7.4 GPa for Bi$_2$Te$_3$, and 7.7 GPa for Sb$_2$Te$_3$.

In a recent work,$^{23}$ the phonon dispersions of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ at zero pressure were calculated from first-principles theory. In the present study, however, we take a step further and focus on Sb$_2$Te$_3$ in order to exemplify how pressure influences the dynamical stability and chemical bonding of a typical 3D TI. Our present calculations are only concerned with the low-pressure $\alpha$ phase. From previous experimental work, the phonon dispersion along $\Gamma$–$Z$ direction in the Brillouin zone (BZ)$^{24,25}$ and the pressure dependence of Raman-active modes$^{17}$ have been obtained for Sb$_2$Te$_3$. However, the full dispersions of the phonons along different directions in reciprocal space have not yet been either calculated nor measured, and this is the main topic of the present investigation. The effect of pressure on the phonon spectrum and chemical bonding has also not been studied before and is presented here.

II. METHODS

All calculations were performed by first-principles density functional theory (DFT). Here, the frozen-core projector augmented wave (PAW) method was used, as is implemented in the Vienna $ab$ initio simulation package (VASP),$^{26}$ mainly within the context of the local density approximation (LDA).$^{27}$ We also have used the Perdew–Burke–Ernzerhof (PBE)$^{28}$ form of the generalized gradient approximation. Furthermore, since PBE nor LDA hardly can treat the weak van der Waals (vdW) type interaction in this layered material, we also used the density functional theory approach including dispersion corrections (DFT-D2) of Grimme$^{29}$ to correct the description. Relativistic effects are included in the calculations in terms of the SOI. To obtain an accurate total energy, a cutoff energy of 300 eV is used for the plane-wave basis-set with a $10 \times 10 \times 10$ $k$-point mesh in the BZ for the rhombohedral crystal structure. All atoms were fully relaxed until the Hellmann-Feynman forces became less than 0.001 eV/Å. The Sb 5$s^25p^3$ and the Te 5$s^25p^4$ orbitals are included as valence electrons. In order to study the dynamical stability of this typical 3D TI under finite pressure, phonon spectrum calculations were carried out by using the direct force method.$^{30,31}$ In these phonon calculations, 3 $\times$ 4 $\times$ 4 rhombohedral supercells were used together with a $2 \times 2 \times 2$ $k$-point mesh. An amplitude of the direct force displacements around 0.04 Å was used.

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### III. RESULTS

#### A. Structure and electronic structure

The rhombohedral crystal structure of Sb₂Te₃ belongs to space group $R\bar{3}m$, which has the Sb atoms situated at $2c(\mu,\mu,\mu)$, the type 1 Te atoms (Te1) at $2c(\nu,\nu,\nu)$, and type 2 Te atoms (Te2) at $1a(0,0,0)$ Wyckoff positions (see Table I). The theoretical equilibrium structural parameters and insulating band gap ($E_g$) within LDA, LDA+SOI, PBE+SOI, DFT-D2, and DFT-D2 with SOI are listed in Table I, together with the corresponding experimental values.\(^{11,24,32}\) Clearly, one can find that the PBE+SOI overestimates the lattice constant $a$ of about 2% compared with experiment. After including vdW modification, the DFT-D2 gives a value of $a$ that is almost identical with the experimental lattice constants. For the lattice constant $c$, LDA or LDA+SOI underestimates its value with 3.3%, PBE+SOI overestimates it with 2.8%, and DFT-D2 with or without SOI overestimates it with 1.7%. SOI effects on the structural parameters are not as important as the vdW correction. Including vdW interaction results in the best agreement between theory and experiment, as far as the lattice constants are concerned. However, SOI effects on the electronic structure are more prominent than the vdW correction (see Fig. 1). While the LDA predicts metallic bulk character, the LDA+SOI opens the band gap and inverts the occupation character of the valence-band maximum (VBM) and conduction-band minimum (CBM) states, reflecting the topological nature of this material. Direct semiconductor features described by DFT-D2 are modified by LDA+SOI and DFT-D2 with SOI to features of an indirect semiconductor, with the VBM located halfway in the $Z$–$F$ direction and the CBM in the $\Gamma$–$Z$ direction. However, as shown in Table I, the underestimation of $E_g$ compared with the experimental value of around 0.3 eV\(^{11,24}\) is clear. This fact is due to the limitation of the approximations used in the exchange-correlation functional. LDA and PBE are known to underestimate the band gaps and might change the band inversion energy $\Delta_i = \epsilon_x - \epsilon_{p,d}$ of the TI transition.\(^{33}\)

![Fig. 1. Band structure for Sb₂Te₃ at 0 GPa calculated by (a) LDA, (b) LDA+SOI, (c) DFT-D2, (d) PBE+SOI and DFT-D2 with SOI. The Fermi energy level is set at zero.](image-url)
B. Phonons

We show in Fig. 2(a) the phonon dispersion along \( \Gamma - Z - F - \Gamma \) directions and the phonon density of state (DOS) of \( \text{Sb}_2\text{Te}_3 \) at 0 GPa by LDA and LDA+SOI, together with experimental phonon frequencies\(^{24} \) along the \( \Gamma - Z \) symmetry line and phonon DOS\(^{25,26} \) for comparison. Pressure dependence of the phonon frequencies at \( \Gamma \) point obtained from LDA+SOI calculations is presented in Fig. 2(b), in comparing with recent Raman scattering values.\(^{17} \) High symmetry points in the BZ are illustrated in Fig. 2(c).

The \( R3\bar{m} \) structure possesses the point group symmetry of \( D_{3d} \). By analyzing the sites symmetry, we list in Table II the Wyckoff positions of the \( \text{Sb}, \text{Te} \) atoms and the corresponding vibration modes. Here, one \( E_u \) and one \( A_{2u} \) modes are acoustic. Due to the fact that \( E \) and \( A \) modes represent displacement in the \( a - b \) plane and along the \( c \) axis, respectively, all the five vibration \( E \) modes along \( \Gamma - Z \) direction are double degenerate.

At 0 GPa, Fig. 2(a) displays a good agreement between the calculated phonon dispersion and the corresponding experimental frequencies along \( \Gamma - Z \). Also in Fig. 2(a), it can be observed that the calculated phonon DOSs and the DOSs from inelastic neutron scattering\(^{24} \) as well as nuclear resonant inelastic scattering (NIS) data\(^{25} \) show a large overlap. We note that a theoretical work\(^{25} \), where the Plane-Wave Self-Consistent Field code (PWSCF) was used, also reproduced the experimental phonon frequencies along \( \Gamma - Z \) direction. Furthermore, different with the previous study of \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \), where the two lowest acoustic branches obtained by LDA+SOI exhibit imaginary frequencies along the \( \Gamma - F \) and/or \( Z - F \) directions, our present phonon spectra of \( \text{Sb}_2\text{Te}_3 \) by LDA and LDA+SOI are all positive. Actually, when we using the same supercell of \( 3 \times 3 \times 3 \) as previous study,\(^{23} \) either within LDA+SOI or DFT-D2 with SOI, imaginary frequencies along \( \Gamma - U \), \( \Gamma - F \), and \( Z - F \) directions were observed. Only after increasing the supercell to \( 3 \times 4 \times 4 \), the imaginary frequencies along the two lowest acoustic branches disappear.

The unphysical errors of our previous study are mainly due to the limitation of the computational resource. Inclusion of SOI and increasing size of the supercell result in great requirement of the computer memory which was not satisfied at that moment. Anyway, our present results indicate that inclusion of SOI, although not changes phonon spectra and phonon DOSs that much, does impact them in some places. The acoustic \( E_u \) mode shows uplift along the \( \Gamma - F \) direction and also near the \( U, F, \) and \( L \) points. This makes the phonon DOS near 1.5 THz smoother and closer to experimental observations\(^{24,25} \) than pure LDA. In range of 3.8-5.4 THz, the phonon DOS by LDA+SOI exhibits larger fluctuations than that by LDA. While the result by LDA shows a good agreement with the old neutron data, the phonon DOS curve by LDA+SOI is consistent with the new NIS results which also show large fluctuations in the high frequency zone.

By employing the LDA+SOI, we study carefully the pressure effects on the phonon spectra of this typical 3D TI. Under pressure up to 7 GPa, no unstable phonon branches have been observed. Thus, the rhombohedral phase in \( \text{Sb}_2\text{Te}_3 \) can be expected to remain dynamically stable at pressures exceeding 7 GPa. Similar with studies in other systems,\(^{36,37} \) pressure only pushes the vibrational spectra even harder. In Fig. 2(b), we show the pressure dependence of the phonon frequencies at the \( \Gamma \) point. We choose to perform this investigation with a LDA functional, due to the computational efficiency over DFT-D2.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Atom} & \textbf{Wyckoff position} & \textbf{Raman active} & \textbf{Infrared active} \\
\hline
\text{Sb} & 2c & \( A_{1g} + E_g \) & \( A_{2u} + E_u \) \\
\text{Te} & 2c & \( A_{1g} + E_g \) & \( A_{2u} + E_u \) \\
\text{Te} & 1a & \( A_{2u} \) & \( A_{2u} + E_u \) \\
\hline
\textbf{Modes} & \textbf{LDA+SOI} & \textbf{Expt.}\(^{6} \) & \textbf{LDA+SOI} & \textbf{Expt.}\(^{6} \) \\
\hline
\text{Symmetry} & \text{Atoms} & \text{(THz)} & \text{(THz)} & \text{(THz)} & \text{(THz)} \\
\text{E}^1_1 & \text{Sb,Te} & 1.56 & 1.41 & \text{Sb,Te} & 1.56 & 1.41 \\
\text{A}^1_1 & \text{Sb,Te} & 2.18 & 2.17 & \text{Sb,Te} & 2.18 & 2.17 \\
\text{E}^1_1 & \text{Sb,Te,Te} & 2.21 & 1.95 & \text{Sb,Te,Te} & 2.21 & 1.95 \\
\text{E}^1_1 & \text{Te,Te} & 2.97 & 2.30 & \text{Te,Te} & 2.97 & 2.30 \\
\text{A}^2_1 & \text{Sb,Te} & 3.30 & 3.18 & \text{Sb,Te} & 3.30 & 3.18 \\
\text{A}^3_1 & \text{Sb,Te,Te} & 3.50 & 3.33 & \text{Sb,Te,Te} & 3.50 & 3.33 \\
\text{A}^1_1 & \text{Sb,Te} & 4.40 & 4.98 & \text{Sb,Te} & 4.40 & 4.98 \\
\hline
\end{tabular}
\end{table}

\(^{6}\text{Reference 24.}\)
These two methods give similar results and motivating the more efficient methodology. Good agreement with recent Raman scattering data\(^{17}\) of \(A_{1g}^1\), \(E_g^1\), and \(A_{2g}^1\) modes can be found. This guarantees the correctness of our calculation results. Gomis et al. have revealed that both frequency and linewidth of their observed Raman modes show different behaviors above 3.5 GPa,\(^{17}\) where experimentally the effects of an electronic topological transition (ETT) are observed.

### C. Topology of Fermi surface

Our calculations show that a semiconductor to metal transition occurs at around 2 GPa and an ETT happens just above 4 GPa. Here, the ETT has been suggested experimentally\(^{17,38}\) in Sb\(_2\)Te\(_3\) by the change in the compressibility. However, it is possible that the observed change in compressibility is caused by the semiconductor to metal transition. Nevertheless, we now proceed with a detailed analysis of the pressure dependence of the ETT.

In Fig. 3, the calculated Fermi surfaces of Sb\(_2\)Te\(_3\) at 3 GPa and 7 GPa are displayed. At the higher pressure the topology has drastically changed as compared to the lower pressure Fermi surface, with the emergence of ellipsoidal surfaces radiating out from the \(\Gamma\)-point (blue surface sheets in Fig. 3(b)) and extra blobs (green surface sheets in Fig. 3) appearing at the Brillouin zone boundaries. The ETT represented by the occurrence of ellipsoidal surfaces will give rise to Van Hove singularity in the electronic density of states \(N(E) \sim \sqrt{|E - E_c|}\), close to the critical energy \(E_c\) where the topological transition occurs.\(^{39}\) Furthermore, close to the Van Hove singularity, the band contribution to the compressibility, \(B\), will be dominated by \(B \sim |E_F - E_c|^{-1/2}\), which is singular whenever the Fermi energy, \(E_F\), equals the critical energy and will thus induce drastic changes in the compressibility.

By shifting the Fermi level continuously until the topology of the Fermi Surface changed by the appearance of the above mentioned ellipsoidal surfaces, the energy difference \(E_F - E_c\) was estimated to 35 meV at 3 GPa and to \(-77\) meV at 7 GPa. Furthermore, by assuming that \(E_F - E_c\) depends linearly upon pressure, we were able to estimate the pressure at which the ETT will occur at \(-4.25\) GPa.

Similar ETTs have been observed in Bi\(_2\)Se\(_3\) around 5 GPa\(^{16}\) and Bi\(_2\)Te\(_3\) around 3.2 GPa.\(^{10}\) Furthermore, in Bi\(_2\)Te\(_3\) at pressures between 3 and 6 GPa, a superconductive transition with a transition temperature, \(T_c\), of \(-3\) K has been observed.\(^{10}\) Similar phenomena have also been reported for Sb\(_2\)Te\(_3\)\(^{20}\) at its ETT pressures.

### IV. DISCUSSION

In order to explore the effects of the pressure-induced ETT in Sb\(_2\)Te\(_3\) in detail, we show in Fig. 4 the pressure dependences of structural parameters, bond lengths, line charge density at the corresponding bond points (CD\(_a\)), electron transfer from the Sb atoms to the Te atoms, and the value of the energy difference \((E_d)\) between the bottom of the conduction and the top of the valence band. Here, positive value of \(E_d\) stands for the indirect energy gap \((E_g)\). In Fig. 4(e), the number of electrons of each atom is obtained through Bader analysis.\(^{40}\)

When comparing with the experimental structural parameters,\(^{8,41}\) a good agreement is found for the calculated lattice constant \(a\) while the \(c\) lattice parameter is slightly underestimated by the present calculations. However, the pressure dependency of the calculated lattice parameters is in qualitative agreement with the experimentally observed parameters. For instance, the experimentally observed minimum in the \(c/a\) parameter at about 2-4 GPa is also found in the presently calculated \(c/a\) ratio.

As shown in Figs. 4(c)-4(e), when viewed separately at around 3.5 GPa, the bond lengths and electron transfer from Sb atom to Te decrease while the CD\(_a\) increases nearly linearly with elevated pressure. The decreasing or increasing rates, obtained by performing first-order linear fitting on these curves, are reminiscent of the pressure dependent transition characteristic of an ETT at around 3.5 GPa. These characteristics are not evident for the pressure dependency of the Te1–Sb and Te2–Sb bonds due to their covalent bonding character. But, for the Te1–Te1 bond, the characteristics of a pressure-induced transition can be clearly seen with a slow down about 41% and 26% for decreasing rate of bond length and increasing rate of CD\(_a\), respectively. Furthermore, the effect of pressure upon the Te1–Te1 bond is more prominent than on the Te1–Sb and Te2–Sb bonds in the whole pressure zone, which is mainly due to relative strong compression effect on the weak vdW type bonding of Te1–Te1. Specifically, the decreasing rate of Te1–Te1 bond length is about 4 times that of the other two types of bonds before 3.5 GPa, and a factor of 2 larger after 3.5 GPa; the increasing rate of CD\(_a\) for Te1–Te1 bond is about 2 times that of the of Te1–Sb and Te2–Sb bonds in the whole pressure zone considered. Transition at around
3.5 GPa for electrons transfer from the Sb atoms to the Te atoms is also evident with a slowdown of the decreasing rate about 31%. Therefore, the covalent and ionic bonding nature of this typical 3D TI also occurs transition at around 3–4 GPa. This kind of transition behavior supplies more theoretical understanding of the semiconductor to metal transition as well as the ETT.

The pressure dependence of $E_d$ [see Fig. 4(f)] obtained from LDA+SOI clearly shows a transition from semiconductor to metal at around 2 GPa. This transition coincides well with the emergence of superconductivity in this material.\textsuperscript{20} Besides, the slope of the pressure dependent $E_d$ shows a change at around 3 GPa, which should also possess potential correlation with aforementioned ETT as well as the changes in slope of the Te1–Te1 distance and charge transfer at 3–4 GPa.

To investigate the pressure effect of electronic structures in more detail, we compare in Fig. 5 the band structures of Sb$_2$Te$_3$ at 0 and 7 GPa calculated from LDA+SOI. At 7 GPa, curves near CBM, $F$, and $L$ points have already passed across the Fermi level which clearly indicates the semiconductor to metal transition. However, the gap at the $\Gamma$ point ($E^\Gamma_d$) shows no evident change upon compression. Recent experimental work found that the $E^\Gamma_d$ of Bi$_2$Se$_3$ increases with pressure.\textsuperscript{42} Since DFT studies of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ have not been able to find a semiconductor to metal transitions and the experiments\textsuperscript{10,18,20,22} exist controversy, further experimental and theoretical studies are needed before any general conclusions can be drawn about how pressure affects the semiconductor to conductor transitions in the group V chalcogenides.

\section*{V. CONCLUSION}

In summary, through the investigation of the lattice dynamics of one of the typical 3D, TI Sb$_2$Te$_3$, we have found that the SOI has some effects on the phonon spectra in the group V chalcogenides, although not that visible. Concerning the use of different functionals, we find that the inclusion of vdW interaction gives slightly improved lattice parameters when compared to experiment. The calculated pressure-induced behavior of the phonon frequencies at the $\Gamma$ point is in an excellent agreement with experiment. Furthermore, the different pressure dependencies of phonon frequencies, the $c/a$ ratio, bond lengths, and electron transfer together with our Fermi surface calculations support the experimental suggestion of an ETT.\textsuperscript{17,38}

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4M. Hasan and C. Kane, Rev. Mod. Phys. 82, 3045 (2010).