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# *Ab initio* calculations of pressure-induced structural phase transitions of GeTe

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Structural phase transitions of GeTe are studied with the use of the *ab initio* pseudopotential density-functional method. Transition pathways and pressures for NaCl-to-CsCl structures are investigated considering three different paths, namely, the Watanabe, Tolédano, and modified Buerger pathways. Structural and electronic properties of the phases are also studied near the transition pressures. Our calculations show that GeTe exhibits very complex transition behaviors at intermediate pressures around 20 GPa, implying the existence of mixed phases in this pressure range. It is found that the Te 4*d* orbitals require careful treatment to properly describe the structural and electronic properties of GeTe.

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## I. INTRODUCTION

Recently there is a renewal of interest in chalcogenide compounds because they are actively used or are candidate materials for optical storages, nonvolatile memory devices, and photonic integrated circuits. They are also used for radiation detectors and thermoelectric devices. This class of materials is known to exhibit a variety of structural and physical properties such as glassy semiconducting states, superconductivity, and ferroelectricity.[1,2] As exotic topological insulating states are observed in binary chalcogen compounds,[3] these materials are attracting great attention from various fields of condensed-matter physics. First-principles calculations of atomic and electronic structures of bulk and surface states of the materials have significant importance to such studies. GeTe which is a representative material in this class is known to crystallize in the distorted rocksalt (rhombohedral) structure with a displacement along a [111] direction at room temperatures. At elevated temperatures above 720 K, GeTe transforms into a NaCl structure and becomes a small gap semiconductor. GeTe moreover undergoes a series of structural phase transitions under pressure from the rhombohedral to NaCl to *Cmcm* and to the CsCl structure as pressure increases.[4–10] Despite the rich nature of underlying physics and potential applications, its structural phase transition is not comprehensively understood. This is in part due to the complexity of intermediate structures, internal atomic distortion, and the bonding nature of *p*-*d* electrons under pressure. While the transition behavior at low pressures is relatively well known, the nature of the crystal structures at intermediate and high pressures is less clear. Reported transition pressures and structures show variations depending on measurement techniques and sample preparations.[8–11] For the rhombohedral-NaCl transition, Kabalkina *et al.*[7] obtained a 3.5 GPa transition pressure accompanied by a 3% decrease in volume. Onodera *et al.*[8] found that the transition occurs at around 3 GPa without a volume discontinuity, and similar results were also reported by Leger and Redon.[9] As pressure is increased further, GeTe was shown to exhibit very complex structural characteristics including orthorhombic or even amorphous phases. Onodera *et al.*[8] reported that NaCl-structure GeTe transforms to another structure with orthorhombic symmetry at about 18 GPa. At higher pressures, the NaCl-CsCl transition occurs at about 43 GPa as measured by Serebryanaya *et al.*[10] As the complexity in measured structural and electronic properties of GeTe (particularly at intermediate pressures) increases, first-principles calculations of transition paths, atomic structures, and energetics can provide detailed information of GeTe under pressure. In addition, study of this kind can help explore atomic, structural, and electronic properties of other chalcogen compounds and alloys such as Ge-Sb-Te.

In this paper, we study the structural phase transition of GeTe under pressure with the use of *ab initio* pseudopotential density-functional method and the electronic band structure with the GW approach. While several theoretical studies of GeTe under pressure for specific transitions have been reported,[11–13] a comprehensive study of structural phase transitions of GeTe through potentially accessible paths is not available. Here we investigate possible transition paths of GeTe as well as their electronic structures under pressure up to 50 GPa. We considered three different transition paths of GeTe from rhombohedral to CsCl structures, namely, the Watanabe, Tolédano, and the modified Buerger pathways.[14–16]

## II. COMPUTATIONAL METHODS

For given structures, we performed a series of *ab initio* pseudopotential density-functional calculations with a plane-wave basis by changing volumes while keeping the crystal symmetry of the structures. We used norm-conserving pseudopotentials as generated by following the scheme of Troullier-Martins.[17] In generating pseudopoentials, Te 4*d* orbitals were treated as valence states, which were found to be very critical in obtaining accurate transition pressures and equilibrium structures. The explicit treatment of semicore *d* orbitals is necessary particularly when the interaction between them and the valence states is non-negligible.[18,19] In-

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cluding Te 4*d* orbitals into the valence states produced correct lattice constant and bulk modulus of Telluride compounds compared to experiment and all-electron calculations.[19,20] For example, the calculated lattice constant for the NaCl structure is smaller than the experimental value by more than 5% without the Te *d* orbitals included. The exchange-correlation energy functional was implemented using the generalized gradient approximation (GGA) in the form of Perdew-Burke-Enzelhof parametrization.[21] It is found that GGA calculations provide better agreement with experiment than the local-density approximation (LDA). *k*-point sampling is done with the Monkhorst-Pack special *k*-point method with $8\times8\times8$ grid points or an equivalent number of points in the irreducible part of the Brillouin zone. A large cutoff energy of 150 Ry for the plane wave basis is needed to correctly represent the deep Te *d* potential. Atomic positions in the unit cell are relaxed until the Hellmann-Feynman forces are less than 0.01 eV/Å at each step of total-energy calculations. Once the total energy of each structure is calculated as a function of unit-cell volume, the data are fit with the Birch-Murnaghan's equation of state[22] to obtain the equilibrium volume, the bulk modulus and its derivative with respect to volume. The transition pressure is calculated by comparing the enthalpy between competing structures, and the transition pressure is calculated from the slope of the common tangent to the energy-volume curves. To obtain accurate electronic structure, we employed the GW method[23] to correct the energy gaps obtained within GGA.

## III. RESULTS AND DISCUSSIONS

We adopt the transition paths and intermediate structures discussed in Ref. 24. The Watanabe path describes a transition from NaCl (B1) to CsCl (B2) structures by a displacive movement of a layer in (001) plane along [110] direction, having *Pmmn* phase as an intermediate. The modified Buerger path involves a lattice distortion without a change in (relative) atomic positions. It has the *Cmcm* structure as an intermediate phase and also a metastable phase of monoclinic $P2_1/m$ between NaCl and *Cmcm*.[24] On the other hand, for the Tolédano path, the transition is characterized by a coupled motion of tensile and shear deformation with an intermediate phase of *Pbnm* structure. This transition path is frequently observed for IV-VI compounds such as GeS, SnS, and GeSe.[13,25–27]

TABLE I. Calculated (calc) and measured (exp) structural parameters of low- and high-pressure phases of GeTe. The angle of lattice distortion of the rhombohedral structure is also shown in parenthesis.

| | Lattice constant (Å) | | Bulk moulus (GPa) | |
|---|---|---|---|---|
| Structure | Calc | Exp | Calc | Exp |
| Rhombohedral | 6.002<br>(88.9°) | 5.98[a]<br>(88.35° [a]) | 49.4 | 49.9[b] |
| NaCl | 5.974 | 5.986[c] | 49.4 | 49.9[b] |
| CsCl | 3.663 (3.270)[d] | 3.268[a,d] | 49.6 | |

[a] Reference 10

[b] Reference 8.

[c] Reference 7.

[d] The experimental value in Ref. 10 is obtained at pressure of 38 GPa. Our calculated value at the same pressure is also given in the parenthesis.

First, the structural and electronic properties are investigated for the rhombohedral, NaCl, and CsCl structures, where the first two are the structures at ambient conditions and the last is the high-pressure phase. The rhombohedral structure, which is the distorted NaCl structure and the equilibrium phase at low temperatures, has two internal parameters, the angle and the displacement, that characterize the distortion from the NaCl phase. Calculated structural parameters are summarized in Table I together with experimental data for comparison. Our results are in excellent agreement with experiment for both the lattice constants and the bulk modulus. It was found that the rhombohedral phase is more stable than NaCl structure by about 12 meV per Ge-Te pair in cohesive energy with a distorted angle of 88.9° and a displacement of 0.02 Å. The calculated cohesive-energy difference is well above the precision ($<1$ meV per unit cell) in our total-energy calculations. We also note that GGA (or LDA) usually overestimates the cohesive energy but the difference in cohesive energy between two different structures is considerably more reliable than the cohesive energy itself. As mentioned above, the inclusion of the Te 4*d* orbital is crucial to obtain the correct values of the structural parameters. Without Te 4*d* orbitals included, for example, the lattice constant of the NaCl structure was calculated to be 5.701 Å, which is much smaller (by about 5%) than the one calculated with the Te 4*d* orbitals. And the relative cohesive energies of NaCl and rhombohedral structures were not correctly reproduced. Furthermore, the NaCl structure was found to be metallic, which is not consistent with measurements. This indicates that the *p*-*d* coupling is playing a significant role for electronic and structural properties of GeTe. The role of Ge 3*d* is found to be relatively insignificant (the lattice constant of the NaCl structure with both Ge 3*d* and Te 4*d* orbitals included is 6.091 Å, about 2% larger than that without Ge 3*d* but with Te 4*d* included).

Figure 1 shows the electronic band structures of NaCl and rhombohedral phases at equilibrium conditions. The NaCl phase is calculated to be a small-gap semiconductor with a direct band gap of 0.24 eV at the L point whereas the rhombohedral structure has an indirect gap of 0.51 eV from the L to T point. The direct gaps at the L and T points are 0.52 eV and 0.56 eV, respectively. Similar results were reported in a previous study.[12] At elevated pressure, the band gap of the NaCl phase decreases and is closed at about 3.5 GPa. We note that the GGA (or LDA) for electron exchange-correlation interactions in density-functional theory (DFT) does not properly describe the band gap of semiconductors and usually underestimates it. This shortcoming should be addressed carefully with more accurate methods such as the GW method.[23] The band gap of NaCl structure, for example, is corrected to 0.5 eV using GW calculations, and its pressure dependence is estimated to be about 0.08 eV/GPa, which is compared to the GGA value of about 0.07 eV/GPa.

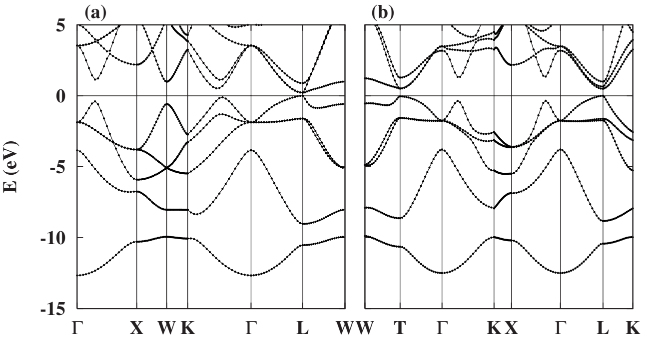

FIG. 1. Calculated band structures within GGA of (a) NaCl and (b) rhombohedral GeTe, respectively. The minimum energy gap of NaCl structure is calculated to be about 0.24 eV with GGA, which is compared to 0.5 eV from the GW calculations.

Our GW calculations indicate that GeTe in the NaCl structure will undergo a semiconductor-metal transition at a pressure of around ~6 GPa and its transport and optical properties will show significant changes.

In order to investigate the structural transition of GeTe along the three different paths from NaCl to CsCl structure, the total energy-volume curves were obtained by calculating the total energy at various volumes while keeping the symmetry of the structure of interest. Our calculated results are shown in Fig. 2. The transition pressure for rhombohderal to NaCl was obtained to be about 3.1 GPa in excellent agreement with experimental value of about 3.5 GPa.[6] The gap closing at 3.5 GPa of NaCl structure may affect the pressure of rhombohedral-NaCl structural transition (3.1 GPa), and a more comprehensive comparison to the results with highly correlated functionals going beyond the GGA is desired. The volume change in the transition was negligible (less than about 1%), and the energy-volume curves for the two structures merge together above the transition pressure, implying a second-order phase transition. There have been several experimental and theoretical reports on this transition, but its nature remains unclear.[7,8] A recent DFT calculation estimated the transition pressure to be about 5.3 GPa (8.4 GPa) within LDA (GGA).[28] Other structural parameters in Ref. 28 show some deviations from measurements and our calculations, which is likely due to the treatment of Te 4*d* orbitals as core states. The pressure for the direct NaCl-CsCl transition is calculated to be 42.9 GPa, again in excellent agreement with measurement by Serebryanaya *et al.*[10] of about 43 GPa. The nearly exact numeric agreement with experiment in the transition pressure should be taken with caution since both experiment and calculation have error bars. For the *Pmmn* phase along the Watanabe path, the transition pressures were obtained to be about 34.5 and 48.8 GPa for NaCl-*Pmmn* and *Pmmn*-CsCl transitions, respectively.

The Tolédano model is visualized as a slipping of double layers simultaneously in the (001) plane generating *Cmcm* structure (B33) and CsCl phase at a subsequent slip of another two layers.[24] The space group between NaCl and *Cmcm* structures corresponds to *Pbnm*, which is the layered orthorhombic. Other IV-VI compounds are also known to follow the Tolédano transition path under pressure.[8,13,25–27] The lattice constants of *Pbnm* structure are obtained to be $a=4.633$ Å, $b=12.621$ Å, and $c=4.027$ Å. The internal parameters of atomic positions, given as $\pm(u,v,0.25)$ and $\pm(0.5-u,v+0.5,0.25)$, are $u_{\mathrm{Ge}}=0.177$, $v_{\mathrm{Ge}}=0.038$, $u_{\mathrm{Te}}=0.510$, and $v_{\mathrm{Te}}=-0.140$. The *Cmcm* is also orthorhombic with lattice constants of $a=4.633$ Å, $b=12.621$ Å, and $c=4.027$ Å and atomic internal parameters of $w_{\mathrm{Ge}}=0.356$ and $w_{\mathrm{Te}}=0.136$ in $\pm(0,w,0.25)$ and $\pm(0.5,w+0.5,0.25)$. From the energy-volume curves, the transition pressure for NaCl-*Pbnm* is calculated to be 15.7 with a volume change of about 3.74%. We note that our calculated transition pressure of 15.7 GPa for the NaCl-*Pbnm* transition is close to the observed value of 18 GPa in the experiment of Onodera *et al.*[8] This implies that the structure in the measurement is likely to have the *Pbnm* symmetry. The direct transition from NaCl to *Cmcm* without going though the *Pbnm* phase is also estimated to be about 23.7 GPa with a volume change of about 6.3%. For the *Pbnm*-*Cmcm* transition, the error bar in the pressure obtained from the energy-volume curve is some-

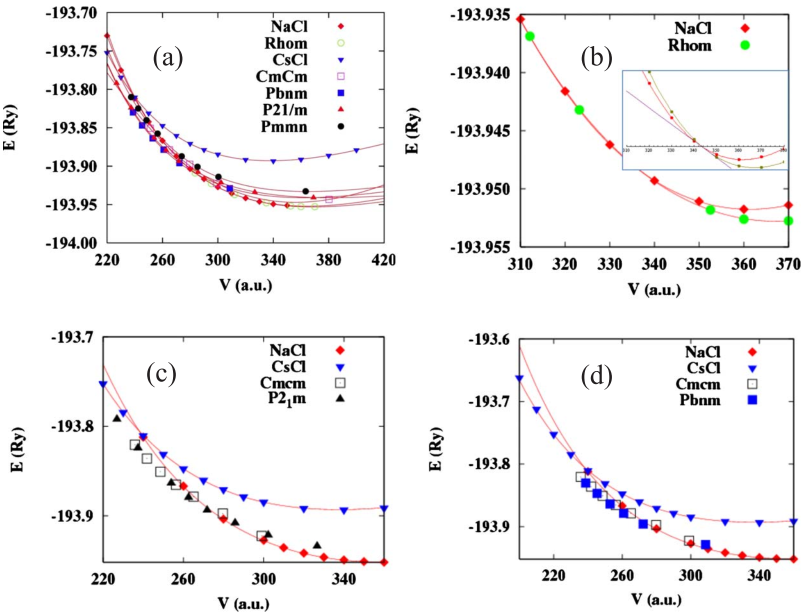

FIG. 2. (Color online) (a) Calculated total energy-volume curves of GeTe for various crystal structures. The volumes and energies are given per Ge-Te pair. The CsCl phase is stable at high pressures above ~50 GPa and NaCl and rhombohedral (Rhom) are the stable structures found at ambient conditions. (b)–(d)] Details of total energy-volume curves for Rhombohedral-NaCl transition, Toledano path, and modified Buerger path, respectively. The inset in (b) depicts near the transition point and the common tangent.

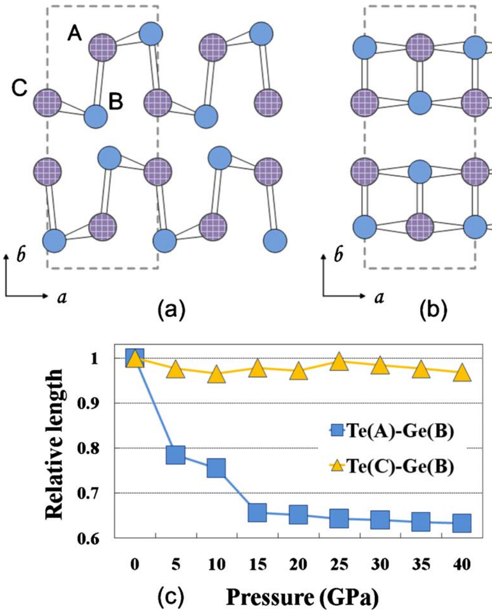

FIG. 3. (Color online) Atomic structure of (a) *Pbnm* and (b) *Cmcm* phases. Filled blue (small gray) and striped purple (large gray) circles denote Ge and Te atoms, respectively. Both are layered orthorhombic structure with the crystal axis shown in the corner (*c* axis is perpendicular to *ab* plane). As pressure increases, one of two inequivalent Ge-Te bonds in *Pbnm* phase decreases much faster than the other as their relative scale shows in (c). At pressure of about ~25 GPa, the two bonds have almost the same length and the coordination number increases from 3 to 5.

what large, and we investigated the Ge-Te bond length to estimate the transition pressure, which is about 25 GPa as described below.

During the structural transition, Ge-Te bond exhibits characteristic deformations. There are two inequivalent Ge-Te bonds in the *Pbnm* phase with one along the *b* axis and another lying in the *a-c* plane as shown in Fig. 3. In the *Cmcm* structure, the two Ge-Te bonds have the same length. It is found that the difference in the Ge-Te bond length becomes less than 0.01 Å around the pressure of 25 GPa, which is close to the calculated transition pressure of 23.7 GPa for the change to *Cmcm* from NaCl. It is interesting to observe that the bond length of Ge-Te in the *a-c* plane remains almost the same while the bond along the *b* axis decreases significantly at increasing pressures. This means that the relative motion of Ge and Te atoms is depicted as a rotation of Ge around Te in the *a-c* plane. The shrink of the lattice constant along the *b* axis is caused by the decrease in the nonbonding Ge-Te distance. To put together these observations, the transition of *Pbnm-Cmcm* is visualized as the decrease in the *b*-axis lattice constant and the change in bond angle at elevated pressures. At the transition pressure, new bonds are formed between the second nearest neighbors, as also observed in other chalcogenides such as GeS.[13]

Finally, we studied the transition along the modified Buerger path, which is similar to that along the Tolédano path. Both have *Cmcm* structure as an intermediate phase, but the modified Buerger path requires a larger shear deformation than the transition along the Tolédano path. In the middle of the B1-B33 transition, the structure has a space group of $P2_1/m$, which is monoclinic with internal parameters specified by $\pm(u,0.25,v)$. The lattice constants of $P2_1/m$ structure are calculated to be $a$=4.716 Å, $b$=4.122 Å, and $c$=6.079 Å with a monoclinic angle of 67.74°. Internal parameters are obtained to be $u(\text{Ge})=0.771$, $v(\text{Ge})=0.810$, $u(\text{Te})=0.655$, and $v(\text{Te})=0.297$. The $P2_1/m$ structure is found to be an indirect-gap semiconductor with GGA energy gap of 0.18 eV and becomes metallic above about 10 GPa. The transition pressure for NaCl-$P2_1/m$ is calculated to be 18.6 GPa with a volume change $\Delta V/V$=4.88%. The $P2_1/m$ structure transforms to the *Cmcm* structure at about 30 GPa as estimated by comparing the Ge-Te bond length as was done for the Tolédano path.

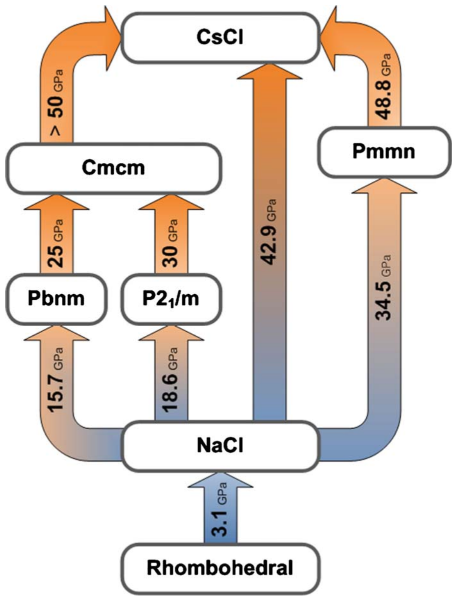

FIG. 4. (Color online) Calculated transition paths and pressures of GeTe. Three different pathways were considered in this work. Toledano and modified Buerger paths: left two paths with *Cmcm* as intermediate structure; Watanabe path: the path on the right with *Pmmm* as intermediate structure. The direct transition from NaCl to CsCl was also shown for comparison in the middle

Figure 4 summarizes our calculations for the three transition paths considered together with associated transition pressures. It is interesting to observe that the transition pressures in the modified Buerger and Tolédano paths are very similar. This implies that, at an intermediate pressure of around 15–30 GPa, GeTe is expected to exist in a mixture of several phases and structural domains. The kinetic barriers from NaCl to the intermediate phases, *Pbnm*, $P2_1/m$, and *Pmmn* are calculated to be about 6 meV, 6 meV, and 8 meV, respectively. This energy barrier was obtained by evaluating the difference between the value at the point of the common tangent at the lower of the two enthalpy curves and that at the crossing point of these two curves. These small values of kinetic barriers again support the finding that all three phase can coexist at intermediate pressures.

## IV. SUMMARY

We studied the structural phase transitions of GeTe under pressure along three different paths using first-principles methods. While the transition at low pressure is relatively simple, it is found that GeTe can exist in several phases at intermediate pressures of about 20–30 GPa. Our GW calculations show that the low-pressure phase (NaCl structure) undergoes a semiconductor-metal transition at a pressure of about 6 GPa.

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