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Citation for published version:

Digital Object Identifier (DOI):
10.1103/PhysRevB.93.224109

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Physical Review B

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Atomic Ordering in Cubic Bismuth Telluride Alloy Phases at High Pressure

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(Dated: June 8, 2016)

Pressure-induced transitions from ordered intermetallic phases to substitutional alloys to semi-ordered phases were studied in a series of bismuth tellurides. Using angle-dispersive x-ray diffraction, the compounds Bi4Te3, Bi3Te4, and Bi2Te5 were observed to form alloys with the disordered body-centered cubic (bcc) crystal structure upon compression to above 14–19 GPa at room temperature. The BiTe and Bi2Te3 alloys and the previously discovered high-pressure alloys of Bi3Te5 and Bi4Te3 were all found to show atomic ordering after gentle annealing at very moderate temperatures of ∼100°C. Upon annealing, BiTe transforms from the bcc to the B2 (CsCl) crystal structure type, and the other phases adopt semi-disordered variants thereof, featuring substitutional disorder on one of the two crystallographic sites. The transition pressures and atomic volumes of the alloy phases show systematic variations across the BiₙTeₙ series including the end members Bi and Te. First-principles calculations were performed to characterize the electronic structure and chemical bonding properties of B2-type BiTe and to identify the driving forces of the ordering transition. The calculated Fermi surface of B2-type BiTe has an intricate structure and is predicted to undergo three topological changes between 20 and 60 GPa.

PACS numbers: 61.50.Ks, 61.66.Dk, 62.50.-p, 71.20.Lp

I. INTRODUCTION

Bismuth tellurides, BiₙTeₙ, are a class of intermetallic compounds with intriguing physical properties. Bi₃Te₅ is one of the best bulk thermoelectric materials for operation near room temperature; it becomes superconducting under pressure, 2-6 it has been reported to undergo a pressure-induced electronic topological (Lifshitz) transition, 7-10 and it has recently attracted much interest in the context of topological insulators. 11-13 Like Bi₃Te₅, the compound Bi₄Te₃ also becomes superconducting under pressure after turning from a narrow-bandgap semiconductor into a metal. The structural changes in Bi₃Te₅ and Bi₄Te₃ under compression have been studied previously, and both intermetallic compounds were observed to transform to alloys with a disordered body-centered-cubic (bcc) crystal structure above ∼15 GPa at room temperature. 14-16 The two materials are members of the infinitely adaptive series of compounds with compositions (Bi₂)ₚ · (Bi₄Te₃)y, and their crystal structures at ambient conditions are all superlattice structures consisting of hexagonal Bi₂ and Bi₄Te₃ blocks. 13,17,18 The materials with compositions near μ'ν = 2:1 (e.g. Bi₄Te₃) are promising p-type thermoelectrics. 17,18

Here we show that the existence of high-pressure bcc alloy phases is a common feature across the BiₙTeₙ series, and that these phases are thermally rather unstable — they have a propensity for atomic ordering upon gentle annealing at only ∼100°C under pressure. During annealing, the BiTe compound adopts the fully-ordered B2 (CsCl-type) structure, and the other compounds semi-disordered variants thereof. First-principles electronic structure calculations are used to investigate the chemical bonding and electronic structure of B2-type BiTe and to gain insight on the driving forces for the ordering transition.

The compounds Bi₄Te₅, Bi₅Te₆, Bi₄Te₇, and Bi₃Te₅ were synthesized as polycrystalline pellets by solid-state reaction from the elements as described previously. 17,18 A single crystal of Bi₄Te₃ was provided by D. L. Sun and C. T. Lin (Max-Planck-Institut für Festkörperforschung, Stuttgart). Each material was manually ground to a fine powder and loaded into diamond anvil cells (DACs) for high-pressure generation. In the majority of the experiments, condensed helium was used as the pressure transmitting medium; some additional experiments that focussed on the effect of annealing the samples at ∼100°C were performed with nitrogen or a 4:1 methanol-ethanol mixture as the pressure transmitting medium. Pressures where determined with the ruby fluorescence method using the calibration of Ref. 19.

Monochromatic powder x-ray diffraction patterns were measured in the Debye-Scherrer geometry on beamline ID09a of the European Synchrotron Radiation Facility (ESRF) and beamline I15 of Diamond Light Source (DLS), UK. Monochromatic x-rays of wavelength λ ≈ 0.415 Å were focused to a spot size of ∼20 µm at the sample, and the two-dimensional diffraction images were recorded with a mar555 and a Perkin Elmer XRD1621 flat panel detector at the ESRF and DLS, respectively. The DACs were rotated by ±3–5° during the exposure to improve the powder averaging. The diffraction images were integrated azimuthally with the Fit2D software to yield conventional intensity vs 2θ diffraction diagrams, and then analyzed with the Rietveld method using the program Jana2006. 21

Electronic structure calculations of BiTe were performed in the framework of density functional theory (DFT) and the full-potential augmented-plane-wave + local orbital (APW+lo) approach as implemented in the Wien2k 22 and ELK 23 codes.
The 5d, 6s, and 6p orbitals of Bi and the 4d, 5s, and 5p orbitals of Te were treated as valence states. Exchange and correlation effects were treated with the revised generalized gradient approximation for solids (PBEsol). Spin-orbit coupling was previously found to have a significant effect on the electronic structure of Bi₂Te₃ and was therefore included in the present calculations. Regular Monkhorst-Pack grids of k-points, typically 20 × 20 × 20, were used for the Brillouin-zone sampling. The electronic band structure and density of states obtained with the two codes were in complete agreement. To quantify the charge transfer between Bi and Te in BiTe, the ELK code was used to perform Bader analyses of the charge density distribution obtained with Wien2k. The electron localization function (ELF) was calculated using the ELK code.

### III. RESULTS AND DISCUSSION

#### A. Disordered bcc Phases

All five compounds were compressed at room temperature, and after one or more phase transitions, each of them was found to transform to a phase with the diffraction pattern characteristic of a bcc crystal, as illustrated in Figure 1. This suggests that disordered bcc alloy phases at high pressure are a general feature of the compounds across the Bi-Te system. With the exception of the Bi₂Te pattern, the diffraction patterns show a very weak feature at the position of the (100) reflection, which is forbidden for a monatomic or ideal bcc phase. In the alloy phases, the presence of this reflection indicates a slight deviation from a completely random distribution of the Bi and Te atoms, i.e., the occurrence of some short-range correlations. Overall, however, Rietveld analysis of the diffraction patterns confirms them to be consistent with the model of disordered Bi-Te alloys as reported previously for Bi₂Te₃ and Bi₄Te₅ (Refs. 14 and 15).

Figure 2 shows the average atomic volumes for the alloy phases at 20 GPa as a function of composition. The atomic volumes of Bi and Te at the same pressure are shown for comparison. Note that Bi adopts the bcc structure at this pressure, whereas Te has an incommensurately-modulated body-centered monoclinic (Te-III). The straight line indicates a linear variation of the volume with composition according to Vegard’s law.
Overall, we see little evidence for a significant deviation from Vegard’s law. The nature of the bonding in the Bi-Te alloys at high pressure, on the other hand, remains a pertinent question, to which we will return later.

Figure 3 illustrates that the pressure at which the transition to the bcc phase occurs varies continuously across the series of compositions — with the notable exception of Bi$_2$Te for which the transition pressure is ~9 GPa higher than expected from the overall trend. The determination of the crystal structures that precede bcc Bi$_2$Te at lower pressure is in progress, and the results, that may shed some light on this anomaly, will be reported elsewhere.

### B. Semi-disordered B2-Type Phases

In our initial experiments on Bi$_2$Te$_3$ we attempted to sharpen the diffraction pattern of a phase at 17 GPa (phase III in the notation of Refs. 15, 16, and 35) by annealing the sample in the DAC gently at 120°C. During this treatment, the sample transformed to a cubic phase, but not the bcc alloy phase discussed above. Rather, a closely-related phase with superstructure reflections in the diffraction pattern was observed, as illustrated in Fig. 4. Evidently, the thermal treatment induced some atomic ordering, and the same effect was subsequently observed also for BiTe, Bi$_2$Te$_3$, and Bi$_2$Te. (Bi$_3$Te$_5$ has not yet been tested for this effect.) The diffraction patterns with the superstructure reflections can be indexed using a simple cubic unit cell and lattice parameters similar to those of the corresponding bcc phases.

As it is not possible to obtain an ordered structure of Bi$_2$Te$_3$ on the basis of a cubic unit cell containing only two atoms, we considered superstructures that are compatible with the given stoichiometry, such as the cubic Pr$_2$C$_3$ structure type, but none of these was consistent with the observed diffraction pattern. We also considered the monoclinic structure “nine/ten-fold C2/m” proposed by Zhu et al.\(^{16}\) which they identified in their structure search calculations as the stable phase above 16 GPa. This structure model produces a diffraction pattern similar to that observed for Bi$_2$Te$_3$ after annealing, but with the large monoclinic unit cell containing 20 atoms, it produces also a large number of low-intensity reflections that are not observed experimentally. Zhu et al. interpreted this structure as an approximation of the disordered bcc alloy structure. Careful inspection of the “nine/ten-fold C2/m” structure reveals it to be actually more closely related to the B2 (CsCl) structure type, with 1/5 of the rows of Bi atoms along the cubic (110) direction being replaced with rows of Te atoms (in an ordered fashion). Building on this realization and taking into account the substitutional disorder before annealing, we determined the structures of the annealed Bi$_m$Te$_n$ phases to be semi-disordered variants of the B2 structure type. In each case, one crystallographic site of the B2 unit cell is essentially occupied by the majority element only, whereas the other site is randomly occupied by either element under the constraint of the overall stoichiometry. For Bi$_2$Te$_3$, one site is then, ideally, fully occupied by Te and the other site has a mixed occupancy by Bi and Te at a ratio of 80:20 as illustrated in Fig. 5.

Figure 6 shows the result of a Rietveld refinement for the diffraction pattern of annealed Bi$_2$Te$_3$ at 20 GPa on the basis of the semi-disordered B2 structure, which yields an excellent fit with residuals of $R_p = 1.5\%$ and $R_{wp} = 2.5\%$. One site is mostly occupied by the majority Te with a Bi:Te ratio of 6:94(1) and the other site consequently with a Bi:Te ratio of 74:26(1). This sample was annealed for 26 h at 120°C, but we found that much shorter annealing can already induce significant ordering. This is illustrated in Fig. 7 which shows
the result of a Rietveld refinement for Bi$_2$Te at 14.8 GPa after only 2 h of annealing at 100°C. The Rietveld fit (with residuals of $R_p = 2.2\%$ and $R_wp = 3.0\%$) yields Bi:Te ratios of 90:10(2) and 41:59(2) for the two sites. This figure illustrates furthermore that we found Bi$_2$Te to precipitate a small amount of Bi (~6%) into a second phase. The bcc Bi phase has a lattice parameter slightly larger than that of B2-type Bi$_2$Te at this pressure, so that it produces shoulders on the lower-angle sides of some peaks as highlighted in the inset. The dots and the solid line in the upper part show the measured and fitted diffraction intensities, respectively. The tick marks show the calculated peak positions, and the bottom curve the difference between measured and fitted intensities.

The semi-disordered B2-type phases observed after thermal annealing. The temperature, duration and final pressure of the thermal treatment are indicated by $T$, $\Delta t$, and $P$, respectively. The Bi:Te ratios or relative occupancies of the two sites were determined with Rietveld refinements. Site 1 is the site of the majority element, and its Bi:Te ratio represents the degree of ordering. The BiTe sample was annealed three times in succession, with each step as indicated.

Table I summarizes the conditions under which four Bi$_n$Te$_m$ phases were annealed to transform them from their alloys to the semi-disordered B2 phases, together with the relative occupancies of the two sites as a measure of the ordering. The BiTe sample was annealed three times in succession. The first treatment at a relatively high pressure of 25 GPa (11 GPa above the transition pressure to bcc) produced only rather limited ordering. Two subsequent annealing steps at lower pressures of 17–18 GPa eventually produced almost complete (97%) ordering. Altogether, we found that thermal treatment at moderate temperatures of 100–120°C causes the high-pressure Bi-Te bcc alloy phases to transform readily to semi-ordered phases of the B2 structure type. Prolonged annealing of BiTe led to nearly complete ordering, and it appears likely that for the other phases a higher degree of ordering could also be obtained with prolonged annealing.

The phases with compositions other than 1:1 BiTe could potentially order further by adopting superlattice structures of the B2 type, e.g. partially disordered variants of the structures of Heusler compounds. However, careful inspection of the patterns in Fig. 4 yields no evidence for $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ superlattice reflections that would be indicative of structure types such as L2$_1$, D0$_3$ or Y (Ref. 36 and 37).

Intermetallic compounds are well known to exhibit widely varying degrees of atomic order — from completely disordered alloys to fully ordered compound phases — depending on stoichiometry, temperature, and thermal and mechanical treatment. The semi-disordered B2-type phases observed...
here are reminiscent of semi-disordered B2-type phases observed in some X<sub>2</sub>YZ Heusler compounds, e.g. Co<sub>2</sub>FeAl at high temperature, where the X atoms occupy one site of the B2 structure and the Y and Z atoms randomly occupy the other site. Intermetallic phases generally have a tendency to long-range order. To obtain an alloy, atomic ordering must be prevented, typically by quenching a high-temperature disordered phase, or destroyed, e.g. by cold working. Although it is therefore to be expected to observe ordering in the Bi-Te phases at elevated temperatures, it is surprising to observe it at such relatively low temperatures of only ~100°C. It is therefore possible that atomic ordering will occur already at room temperature on a longer time scale. In other words, the Bi-Te alloy phases may show signs of aging.

Atomic disorder in intermetallic compounds is well documented to affect their physical properties, e.g. the magnetism in Heusler compounds, the mechanical properties of structural alloys, or the superconductivity in A15 intermetallics. Superconductivity in Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>4</sub>Te<sub>3</sub> has been observed in the pressure range where their cubic alloy phases exist. The existence of both alloy and semi-ordered Bi-Te phases therefore needs to be taken into account in investigations of their physical properties, in particular in electronic structure calculations.

### C. Electronic Structure and Chemical Bonding in BiTe

The fully-ordered B2-type BiTe phase provides an ideal starting point for electronic structure calculations, which allow us to gain insight on the nature of its chemical bonding and the forces that drive the atomic ordering. Figure 8(a) shows the calculated band structure of B2-type BiTe at the experimental density of bcc BiTe at 20 GPa. Spin-orbit coupling was included in all calculation and was found to produce significant band splittings, in agreement with earlier studies on Bi<sub>2</sub>Te<sub>3</sub>. In the calculation, BiTe is metallic at this pressure, which is in line with the observation that the band gap in Bi<sub>2</sub>Te<sub>3</sub> closes at pressures of 2–5 GPa, depending on the sample and pressure/stress conditions. The BiTe band structure is similar to that of bcc Bi at the same atomic density [Fig. 8(b)]. The most notable difference is the occurrence...
of additional band splittings for BiTe, as indicated by arrows in Fig. 8(a). This reduces the number of bands crossing the Fermi level and produces a suppression in the electronic density of states — a pseudogap — near the Fermi level as illustrated in Fig. 9. This suppression is absent for bcc Bi and, more importantly, for an approximant of the BiTe alloy, which we modeled as a $2 \times 2 \times 2$ supercell of B2-type BiTe with a random distribution of the eight Bi and eight Te atoms. The result is a slightly reduced band structure contribution to the total energy of the ordered phase in comparison to the alloy. This illustrates at a fundamental level the discussion in the previous section on the effect of atomic disordering on the electronic properties.

Analysis of the partial charges from the individual band states shows that the lower-energy components of the split bands near the Fermi level have predominantly Te character, and the higher-energy components predominantly Bi character [Fig. 8(c,d)]. This indicates a charge transfer from Bi to Te, which is in keeping with Te having a slightly higher electronegativity than Bi (2.1 vs 2.02 on the revised Pauling scale$^{41}$). To quantify the charge transfer, we performed a Bader (“Atoms in Molecules”) analysis$^{42,43}$ of the charge density distribution. In this analysis, the unit cell is divided into regions whose boundaries are defined by minima in the charge density. More precisely, at any point on the dividing boundaries, the gradient of the charge density is parallel to the boundary or zero. This provides an unambiguous partitioning of the unit cell into atomic basins, and by integrating the charge within these basins one can quantify the charge transfer between atoms. For BiTe at $\sim 20$ GPa, the Bader analysis indicates a significant charge transfer from Bi to Te of approximately 0.44 e. The charge transfer depends only weakly on the pressure and decreases with increasing pressure to 0.40 e at 100 GPa.

The chemical bonding and charge transfer between Bi and Te have been analyzed in several studies on Bi$_2$Te$_3$ at normal pressure.$^{16,23,44,45}$ The Bi$_2$Te$_3$ crystal structure can be regarded as a repeating sequence of “quintuple layers” that comprise five atomic layers, Te(1)–Bi–Te(2)–Bi–Te(1), where Te(1) and Te(2) denote the two crystallographic sites occupied by Te. The bonding within the quintuple layers is of mixed covalent-ionic type, whereas the bonding between the quintuple layers of van-der-Waals type. The degree of ionicity is generally difficult to quantify, and model-dependent, and the results of several studies vary correspondingly. The combined DFT and tight-binding calculations by Mishra et al.$^{35}$ gave ionic charges of Bi$^{3+}$, Te(1)$^{2-}$, Te(2)$^{2-}$, and Bi$^{+}$. An earlier tight-binding model by Pecheur and Toussaint$^{46}$ had indicated ionic charges about 50% lower than those obtained by Mishra et al. On the other hand, Zhu et al.$^{16}$ recently reported ionic charges of Bi$^{3+}$, Te(1)$^{2-}$, Te(2)$^{2-}$ (on the basis of DFT calculations and Bader analysis), which suggested a strong charge disproportionation between the two Te sites. They furthermore reported the charge transfer from Bi to Te to increase with increasing pressure. It is therefore interesting to note that the charge transfer obtained here for cubic BiTe is significantly lower than those reported by Zhu et al. for the layered ambient-pressure and three high-pressure phases of Bi$_2$Te$_3$, and their pressure dependences are also at variance.

To further address the question whether any significant covalent contribution to the chemical bonding is still present at high pressure in the cubic phases (as suggested in Refs 15 and 16), we have calculated the electron localization function (ELF)$^{30,39}$ for BiTe. The results for B2-type BiTe are shown in Fig. 10. The upper panel shows the ELF in the (110) plane that passes through four Te atoms at the corners of the unit cell and the Bi atom in the center. There is no indication of a local maximum of the ELF along the Bi–Te line, and hence no indication of directional, covalent bonding between Bi and Te. The oscillations in the ELF in Fig. 10(b) represent merely the electronic shell structure of Bi and Te.

The overall picture emerging from these calculations is thus one where the mixed covalent-ionic plus van-der-Waals bonding found in the bismuth tellurides at ambient conditions gives way to metallic bonding with a significant ionic component at high pressures of $\sim 20$ GPa. The charge transfer from Bi to Te is rather insensitive to further increase in pressure. We consider the charge transfer to be the driving force behind the thermally-induced atomic ordering. Firstly, ordering of the Bi and Te ions reduces the Madelung energy. The semi-ordered phases for the compositions other than BiTe represent the most-ordered configurations that can be achieved within
the bcc/B2 structure type under the constraint of the given stoichiometry. Secondly, the ion ordering in BiTe causes a suppression of the electronic density of states near the Fermi level, and hence a lowering of the band structure contribution to the total energy. It is not clear at present to what extent this second effect contributes to the formation of the semi-ordered phases.

D. Fermi Surface of BiTe and Topological Changes

Figure 8(a) shows that several electronic bands cross the Fermi level in B2-type BiTe and that there are three band extrema in close proximity to the Fermi level. These extrema arise from the band splittings marked by arrows in Fig. 8(a), which are due to the ionicity in BiTe as discussed above. The Fermi surface thus comprises several sheets, and its topology can be expected to change with pressure when band extrema cross the Fermi level. Figure 11(a) shows the calculated Fermi surface of B2-type BiTe at the same density as for the band structure in Fig. 8(a). It consists of three electron pockets nested inside one another and centered around the R point as well as a tube-like feature with necks at the X points. With increasing pressure, the band minimum along Γ–M, the maximum along Γ–R, and the maximum at M cross the Fermi level at calculated pressures of 29, 38, and 47 GPa, respectively. The associated changes in the topology of the Fermi surface are illustrated in Fig. 11(b). The tube-like feature breaks up into pockets centered on the X points, and additional pockets appear upon further compression. We expect these Fermi surface features to be sensitive not only to changes in pressure but also to atomic displacements, which may give rise to interesting electron-phonon coupling effects.

We should note that although we did not investigate the stability of cubic bcc/B2-type BiTe at pressures above 25 GPa, we expect it to be stable over a wide pressure range. B2-type phases are generally rather stable under compression, and bcc Bi has been reported to be stable to at least 222 GPa (Ref. 31), bcc Te to 97 GPa (Ref. 46), and the Bi$_2$Te$_3$ bcc alloy phase to at least 52 GPa (Ref. 16).

IV. CONCLUSIONS

We have shown that the formation of alloy phases at high pressure appears to be a common feature across the series of Bi$_m$Te$_n$ compounds. The alloy phases were found to be thermally unstable and to adopt semi-disordered B2/CsCl-type structures after gentle annealing, but not the superlattice structures known from Heusler compounds. The atomic ordering must be expected to affect the physical properties of the alloy phases, e.g. superconductivity. Electronic structure calculations indicate a significant charge transfer of ∼0.4 e from Bi to Te in B2-type BiTe. The ionic contribution to the bonding favors atomic ordering and thus the transition from alloy to ordered compound. Another contribution is the lowering of the band structure contribution to the total energy due to a suppression of the electronic density of states near the Fermi level that results from the charge transfer. The calculated electron localization function for BiTe provides no evidence for any remaining covalent bonding. The chemical bonding thus changes from mixed covalent-ionic (plus van-der-Waals interactions between the layers) at normal conditions to mixed metallic-ionic at pressure of 20 GPa and above. The Fermi surface of BiTe has an intricate structure, which may give rise to interesting electron-phonon coupling effects, and it has been calculated to undergo three topological changes in the 20–60 GPa range.

Note added. After submission of the manuscript, Stillwell et al. reported the observation of a bcc alloy phase in Bi$_2$Te under high pressure and that this phase is superconducting. The Fermi surface of BiTe has an intricate structure, which may give rise to interesting electron-phonon coupling effects, and it has been calculated to undergo three topological changes in the 20–60 GPa range.

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ACKNOWLEDGMENTS

We thank D. L. Sun and C. T. Lin (Max-Planck-Institut für Festkörperforschung, Stuttgart) for providing the Bi₈Te₈ single crystal as well as M. Hanfland (ESRF) and A. Kleppe (DLS) for their support during the diffraction experiments. Facilities were made available by the European Synchrotron Radiation Facility and Diamond Light Source.