

## Atomic Ordering and Gap Formation in Ag-Sb-Based Ternary Chalcogenides

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Novel semiconductors with tailored properties can be designed theoretically based on our understanding of the interplay of atomic and electronic structures and the nature of the electronic states near the band-gap region. We discuss here the realization of this idea in Ag-Sb-based ternary chalcogenides, which are important optical phase change and thermoelectric materials. Based on our studies we propose new systems for high-performance thermoelectrics.

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Over the past 10 years, *ab initio* studies have had an increasingly important impact on materials science, not only in fundamental understanding but also with a strong emphasis toward materials design. Density functional based calculations, in spite of their limitations, can be quite helpful in this regard [1]. For example, in semiconductors, where it is well known that their transport and optical properties are dominated by the states near the band gap, it is essential to understand the underlying physics of the band-gap formation and the nature of the electronic states in its neighborhood before being able to tailor the properties of these systems. Although the origin of band gaps in elemental and binary semiconductors and their alloys is well understood in terms of covalency and ionicity concepts, first proposed by Pauling [2] and later extended by Phillips [3], the physics of gap formation in valence-compensated ternary semiconductors, particularly in narrow band-gap systems, generally is not. In this Letter, we address these issues in a class of ternary chalcogenides  $\text{AgSbQ}_2$  ( $Q = \text{S, Se, Te}$ ). The measured temperature dependence of electrical conductivity for  $Q = \text{Te}$  and available low temperature heat capacity and magnetic susceptibility data are used to critically examine the calculated electronic structure.

Ag-Sb-based ternary chalcogenides have been studied mainly in connection with optical phase change [4] and thermoelectric applications [5].  $\text{AgSbTe}_2$  is itself not only a good thermoelectric but is the end compound of several high-temperature high-performance thermoelectrics [5–8]. Although it was synthesized almost 50 years ago and was thought to be a semiconductor [9], the ordering of Ag and Sb on a face-centered cubic (fcc) lattice has been confirmed only recently [10]. Furthermore, the electronic properties of these systems are quite intriguing and show anomalies. Diffuse reflectance measurements [11] in  $\text{AgSbTe}_2$  give an apparent band gap ( $\sim 0.35$  eV), whereas electrical conductivity [12] suggests a metallic behavior. A similar observation in the diffuse reflectance spectrum of  $\text{AgSbSe}_2$  has also been made [11].

To understand the origin of the intriguing physical properties of these chalcogenides, we have carried out extensive

*ab initio* electronic structure calculations within the density functional theory (DFT) formalism (see Ref. [11] for the computational details). The energetics of different types of ordering of Ag and Sb atoms and how they impact the electronic properties have been investigated. Our theoretical calculations for  $\text{AgSbTe}_2$  give a low-energy structure similar to the one observed in x-ray diffraction (XRD) refinements [10]. The observed electronic properties of  $\text{AgSbTe}_2$  can be understood in terms of a small gap in the single-particle density of states (DOS) whereas our theoretical calculations give a pseudogap. The other two chalcogenides,  $\text{AgSbSe}_2$  and  $\text{AgSbS}_2$ , are found to be indirect narrow band-gap semiconductors. The connectivity of the Ag-Sb- $Q$  network plays an important role in controlling the DOS near the Fermi energy ( $E_F$ ) and hence the physical properties governed by low-energy excitations. Our calculations suggest how to modify the ternary tellurides by replacing the Ag atoms such that the DOS shows an actual gap, thereby making new narrow band-gap semiconductors for thermoelectric and photovoltaic applications.

For electronic structure calculations we need to know the ordering of Ag and Sb atoms. Although earlier XRD measurements of  $\text{AgSbQ}_2$  indicated that Ag and Sb were disordered on the Na site of the NaCl-type structure [9], recent careful single-crystal XRD studies of  $\text{AgSbTe}_2$  have found evidence of Ag-Sb order;  $Pm\bar{3}m$  (cubic),  $P4/mmm$  (tetragonal), and  $R\bar{3}m$  (rhombohedral) space groups were used successfully in diffraction refinement [10]. Also, Monte Carlo (MC) simulation of an ionic or Coulomb lattice gas (CLG) model gave a body-centered tetragonal (bct) structure with a  $c$  parameter double that of the NaCl-type cubic lattice [13]. We have calculated the total energies of various ordered structures to find the one(s) with the lowest energy.

Before presenting our energy calculations, we describe the different types of ordering of Ag and Sb ions using the standard nomenclature of antiferromagnetic (AF) orderings [14], i.e., identify Ag(Sb) ions as spin-up(down) occupying the sites of the fcc lattice. The simplest structure is AF-I [Fig. 1(a)] with alternating Ag- $Q$  and Sb- $Q$  planes

normal to the [100] direction. AF-III [Fig. 1(c)] can be obtained from AF-I by doubling the unit cell along the  $z$  direction and interchanging Ag and Sb atoms in the third and the fourth Ag-Sb- $Q$   $xy$  planes starting from the top. This leads to a mixing of Ag and Sb atoms in the Ag- $Q$  and Sb- $Q$  planes of AF-I. AF-III still has Ag- $Q$ -Ag- $\cdots$  and Sb- $Q$ -Sb- $\cdots$  chains (along the  $x$  and  $y$  directions). It turns out that AF-III with bct symmetry is the ground state structure obtained in MC simulation studies of the CLG model [13]. In order to disrupt the above chains and to see how they control the energetics, we constructed an interrupted chain model (AF-IIb) that has sequence of Sb- $Q$ -Ag- $Q$ -Sb- $\cdots$  chains in all three directions [Fig. 1(b)]. AF-IIb can also be visualized as alternating Ag-Sb and  $Q$  planes normal to the [111] direction. Finally, AF-II with alternating Ag,  $Q$ , and Sb planes normal to the [111] direction is obtained from AF-IIb by rotating the second and the fourth layers of AF-IIb by  $90^\circ$  around the  $z$  axis. AF-I and AF-II were used in the crystal structure refinements [10]. We will discuss how the presence of Ag in the Sb- $Q$ -Sb- $\cdots$  chains affects the electronic structure near  $E_F$  and the energetics.

We find that after cell shape and ion position relaxations, all the structures of  $\text{AgSb}Q_2$  (except AF-IIb) change their lattice parameters from their initial values obtained after only volume optimization. The cubic AF-I ( $Pm\bar{3}m$ ) becomes tetragonal with  $a = 6.1502 \text{ \AA}$  and  $c/a = 0.9853$  for  $Q = \text{Te}$  due to the interlayer contraction (expansion) along the  $x$  ( $y$  and  $z$ ) direction [see Fig. 1(a)]. Except for a small distortion, the results agree well with the available data in the literature, where it has been reported that  $\text{AgSbTe}_2$  crystallized in the fcc NaCl structure [9,10]. The primitive cells of AF-I, AF-II, AF-IIb, and AF-III are, respectively, simple tetragonal ( $P4/mmm$ , 4 atoms/cell), rhombohedral ( $R\bar{3}m$ , 4 atoms/cell), fcc ( $F\bar{3}dm$ , 16 atoms/cell), and bct ( $I4_1/amd$ , 8 atoms/cell) (see Ref. [11] for the calculated versus experimental lattice parameters). AF-I and AF-II are in excellent agreement with the XRD refinement results using the  $P4/mmm$  and

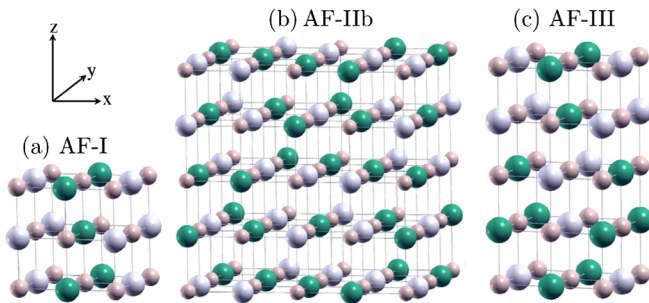


FIG. 1 (color online). Possible ordered structures of  $\text{AgSb}Q_2$  ( $Q = \text{Te, Se, S}$ ): (a) AF-I (space groups:  $Pm\bar{3}m, P4/mmm$ ), (b) AF-IIb ( $F\bar{3}dm$ ), and (c) AF-III ( $I4_1/amd$ ). Large balls are for Ag/Sb; small balls are for  $Q$ .

the  $R\bar{3}m$  space groups, respectively [10]. Energetically, AF-IIb has the lowest energy for  $\text{AgSbTe}_2$ ; however, the energy difference between AF-II and AF-IIb is small,  $\Delta E \sim 4 \text{ meV/f.u.}$  (f.u. = formula unit). AF-I turns out to be the highest energy structure,  $\sim 196 \text{ meV/f.u.}$  higher than AF-IIb and  $\sim 121 \text{ meV/f.u.}$  higher than AF-III [11]. As will be made clear later, the physical reason why AF-II and AF-IIb have lower energies is the presence of Ag in the Sb-Te-Sb- $\cdots$  chains. The Ag in the chains strongly perturbs hybridized Sb and Te  $p$  bands. This leads to a rearrangement in the DOS by shifting states near  $E_F$  ( $\sim -0.5 \text{ eV}$  to  $0 \text{ eV}$ ) to lower energy. Also it leads to an enhanced pseudogap feature near  $E_F$  (for  $Q = \text{Te}$ ) and a gap ( $Q = \text{Se}$  and  $\text{S}$ ; see below). In the case of  $\text{AgSbSe}_2$  and  $\text{AgSbS}_2$ , we find the lowest energy structure to be the rhombohedral AF-II; again the energy difference between AF-II and AF-IIb is small,  $\Delta E = 1.3, 1.6 \text{ meV/f.u.}$  for  $Q = \text{Se}$  and  $\text{S}$ , respectively. For comparison we find that the chalcopyrite structure gives for  $\text{AgSbTe}_2$  considerably ( $\sim 0.5 \text{ eV/f.u.}$ ) higher energy than those discussed here.

Summarizing the structural aspects, our theoretical calculations support the  $R\bar{3}m$  picture among the three space groups used in the XRD refinement of  $\text{AgSbTe}_2$ . However, it will be interesting to reanalyze the data using the  $F\bar{3}dm$  space group to see if this gives a superior fit. Although AF-III found in MC simulations of the CLG model [13] is not the one with the lowest energy, it turns out that it has the lowest electrostatic energy. Our *ab initio* studies clearly indicate that covalency effects play a role in the energetics of different ordered structures. We also carried out extensive investigation of other structures (up to 64 atoms/supercell) which are the derivatives of AF-II and AF-IIb, but we did not find any that has lower energy than AF-II ( $Q = \text{Se, S}$ ) or AF-IIb ( $Q = \text{Te}$ ). Exploring different ordered structures is essential here, because in real samples we might have either a particular ordered structure or a mixture of several ordered structures depending on the synthesis conditions. In fact, one may not even have the one with the lowest energy. Besides, x-ray and

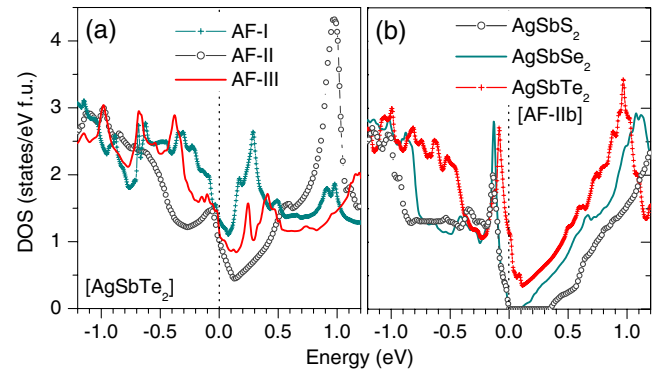


FIG. 2 (color online). Total DOS of  $\text{AgSb}Q_2$ : (a)  $Q = \text{Te}$  (AF-I, AF-II, and AF-III), and (b)  $Q = \text{Te, Se, and S}$  (AF-IIb). The Fermi energy ( $E_F$ ) is at  $0 \text{ eV}$ ; f.u. =  $\text{AgSb}Q_2$ .

neutron diffractions may not be able to differentiate between similar ordered structures because of the very similar form factors of Ag and Sb.

We now discuss the bonding, semiconducting, or semi-metallic nature of the compounds and the role Ag plays in determining this. We find that the DOS of AgSbTe<sub>2</sub> in AF-I and AF-III have pseudogaplike features with large DOS above  $E_F$  at  $\sim 0.2$ – $0.5$  eV [Fig. 2(a)].  $E_F$  lies near the rapidly decreasing part of the DOS near the pseudogap region. A careful analysis of the projected DOS [11] and band character shows that there is a strong hybridization between  $p$  states of Sb and those of Te coming from the Sb-Te planes (in AF-I). These hybridized states predominantly contribute to the region near  $E_F$  in addition to the  $p$  states of Te coming from the Ag-Te planes. In going from AF-I to AF-III, the DOS near  $E_F$  coming from Sb and Te  $p$  states are significantly suppressed. A natural question arises: can we manipulate these states to further lower the DOS in the pseudogap region by changing the ordering of Ag and Sb in these systems or even open up a real gap? In Figs. 2(a) and 2(b), we show the total DOS of AgSbTe<sub>2</sub> in AF-II and AF-IIb. In both cases, although there is no real gap in the DOS, the peaks just above  $E_F$  (found in AF-I and AF-III) disappear, there is a suppression of DOS below  $E_F$ , and the pseudogap feature is enhanced. The projected DOS analysis shows that the states coming from the Sb and Te atoms have been suppressed drastically in the region near  $E_F$ . Thus interruption of the Sb-Te-Sb- $\cdots$  chains by Ag helps in developing a true pseudogap structure.

There are several generic features of the total DOS. The pseudogap structure (in AF-IIb) changes to a gapped one in going from Te to Se and S [Fig. 2(b)]. There are 2 sharp peaks in the total DOS, one below  $E_F$  by  $\sim 0.1$  eV with a width of  $\sim 0.15$  eV, and the other at about 1.0 eV above  $E_F$ , of much broader width. The latter is formed predominantly by Sb  $p$  states (hybridized with Ag  $s$  and  $Q$   $p$  states), while the former is predominantly by  $Q$   $p$  states (hybridized with Ag  $d$  and Sb  $p$  states). Similar features are also seen in AF-II, but the lower energy peak is suppressed and there is a transfer of spectral weight to the higher one. AF-I and AF-III give AgSbSe<sub>2</sub> and AgSbS<sub>2</sub> pseudogaps. Spin-orbit interaction does not have significant effects on the total DOS near  $E_F$ .

In Fig. 3(a) we show the band structure of AgSbTe<sub>2</sub> (in AF-IIb) along the high symmetry lines of the fcc Brillouin zone. We find that in both AF-II and AF-IIb, the top of the valence band is predominantly  $p$  states of the chalcogenide (hybridized with the Sb  $p$  and Ag  $d$  states). Ag plays a very interesting role. In addition to helping suppress Sb  $p$  and Te  $p$  hybridization (as compared to AF-I and AF-III), its  $s$  state, which strongly hybridizes with Sb  $p$  states near the  $L$  point, has a large dispersion. For simplicity, we will refer to this as the “Ag  $s$  band,” which is the broadly dispersed conduction band coming across  $E_F$ , centered at the  $L$  point and not split by spin-orbit interaction. If this band were not

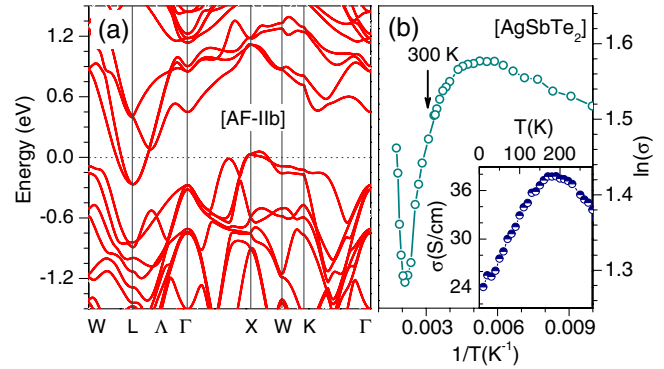


FIG. 3 (color online). (a) Band structure (in AF-IIb) and (b) the logarithm of electrical conductivity ( $\sigma$ , in  $\text{S cm}^{-1}$ ) of AgSbTe<sub>2</sub> versus  $T^{-1}$ ;  $\sigma$  at low  $T$  is also given (inset).

present, then the system would be a semiconductor. However, it comes down and goes below the top of the valence band and the system becomes a semimetal (negative-gap semiconductor or pseudogap system). In going from Te to Se and S, the relative separation of the Ag  $s$  band and the valence band increases, and the latter two systems are semiconductors. If we replace Ag with another monovalent cation with higher  $s$  state energy (such as Na and K), then we should get a good narrow band-gap semiconductor for the Te compound. One can also replace Ag with Cu to manipulate the narrow peak below  $E_F$  through its  $d$  level. However, Cu  $4s$  lies below Ag  $5s$ , which will lead to increased DOS above  $E_F$  and reduce the pseudogap feature.

In the AF-IIb telluride, one has light electron pockets centered around the  $L$  points and heavy hole pockets centered around the  $X$  points [Fig. 3(a)]. This compound appears to be a classic semimetal. Both electrons and holes will contribute to transport properties. Since the valence band maximum is quite flat, the holes are expected to be heavy compared to the electrons. In addition, there is a multipeak valence band structure with anisotropic band maxima. These will result in a large positive thermopower [15] as seen in experiments [12]. In the Se and S compounds, the band gap is indirect and the conduction band minimum is Sb-Se or Sb-S derived and lies along the  $\Lambda$  line; these gaps are respectively  $\sim 0.1$  eV and 0.3 eV. AF-II gives for AgSbTe<sub>2</sub> similar band structure with electron pockets at the  $L$  points and hole pockets near the  $T$  points (of the rhombohedral Brillouin zone) and a multipeak valence band structure. However, there are also some differences due to the different Ag/Sb/ $Q$  connectivities in these two structures.

It is well-known that most DFT calculations tend to underestimate the band gaps of semiconductors [16], and we cannot exclude the possibility that AgSbTe<sub>2</sub> is a semiconductor with a small band gap. To resolve this “band-gap problem” associated with our present DFT calculations, we carried out electrical conductivity measurements

in the temperature range  $T = 10\text{--}573$  K on carefully made  $\text{AgSbTe}_2$  samples. As seen in Fig. 3(b),  $\sigma$  increases with increasing  $T$  and reaches its maximum (of  $\sim 38 \text{ S cm}^{-1}$ ) at  $\sim 170$  K; it then decreases and reaches its minimum (of  $\sim 19 \text{ S cm}^{-1}$ ) at  $\sim 473$  K and then increases again with increasing  $T$ . Estimation of the activation energies gives a band gap of  $\sim 0.1$  eV in the intrinsic (high  $T$ ) range and an impurity binding energy of  $\sim 1\text{--}2$  meV in the extrinsic (low  $T$ ) range. This suggests that  $\text{AgSbTe}_2$  is a narrow band-gap semiconductor. To further confirm the gap picture, heat capacity [17] and magnetic susceptibility [11] measurements were carried out on the same sample. The latter shows a weak  $T$ -dependent diamagnetism, and the former gives a very small  $\gamma$  factor, indicating that there are no or very few electronic states near  $E_F$ . The discrepancy between the experimental data and the calculated band structure can be ascribed to the deficiency of our DFT calculations in obtaining a true gap. In this case, because of the diffuse nature of Te  $p$  orbitals, and also that of Ag  $s$ , our calculations give a negative band gap (of  $\sim -0.3$  eV). The Se(S) compounds suffer less in this regard and give gaps that are, however, smaller than their true ones. Improvements beyond present DFT calculations [16] can give a better picture of the gap structure.

Because of the near degeneracy of AF-II and AF-IIb, one can expect mixed phases and disorder effects to be important. To examine the latter, we carried out calculations for (Ag, Sb) antisite defects and found an enhancement in the DOS near  $E_F$  (see Ref. [11]), which should increase the low  $T$  heat capacity. In view of the fact that the measured low  $T$   $\gamma$  value is extremely small [17], we believe that disorder effects are not very significant in the samples under investigation, although energetically it is possible to have the antisite defect (the energy difference is  $\sim 20$  meV/defect in a 64-atom supercell).

In summary, we have carried out a detailed investigation of the structural orderings of Ag and Sb atoms in ternary chalcogenides and how they impact the electronic properties. Total energy calculations are consistent with the observed atomic structures [10] and indicate that as one goes from Te to Se to S, the (indirect) band gap goes from negative to positive values. The Ag/Sb ordering has a huge impact on the electronic structure of  $\text{AgSbQ}_2$  in the neighborhood of  $E_F$ . It gives pseudogap structure in some ordered structures (AF-I and AF-III) and either pseudogap ( $Q = \text{Te}$ ) or gap ( $Q = \text{Se, S}$ ) structure in others (AF-II and AF-IIb). The anomalous electronic properties of  $\text{AgSbTe}_2$  can, however, be understood in terms of a small intrinsic band gap and shallow impurity states. Finally, we expect

$\text{NaSbTe}_2$  and  $\text{KSbTe}_2$  to be promising narrow band-gap semiconductors for good  $p$ -type thermoelectrics.

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