Electronic Structure Of (AgSb)$_x$Pb$_{n-2x}$Te$_n$

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ABSTRACT

Complex quaternary chalcogenides (AgSb)$_x$Pb$_{n-2x}$Te$_n$ (0<x<n/2) are thought to be narrow band-gap semiconductors which are very good candidates for room and high temperature thermoelectric applications. These systems form in the rock-salt structure similar to the well known two component system PbTe (x=0). In these systems Ag and Sb occupy Pb sites randomly although there is some evidence of short-range order. To gain insights into the electronic structure of these compounds, we have performed electronic structure calculations in AgSbTe$_2$ (x=n/2). These calculations were carried out within ab initio density functional theory (DFT) using full potential linearized augmented plane wave (LAPW) method. The generalized gradient approximation (GGA) was used to treat the exchange and correlation potential. Spin-orbit interaction (SOI) was incorporated using a second variational procedure. Since it is difficult to treat disorder in ab initio calculations, we have used several ordered structures for AgSbTe$_2$. All these structures show semimetallic behavior with a pseudogap near the Fermi energy. Te and Sb p orbitals, which are close in energy, hybridize rather strongly indicating a covalent interaction between Te and Sb atoms.

INTRODUCTION

Quaternary (AgSb)$_x$Pb$_{n-2x}$Te$_n$ systems are potentialy very good thermoelectrics at room and high temperature, particularly for low concentrations of Ag and Sb. These systems form in the NaCl structure similar to their binary PbTe (x=0) and ternary AgSbTe$_2$ (n=2x) components. Ag and Sb atoms occupy the Pb sites and they are disordered. The nature of chemical bonding in these crystals is mixed ionic-covalent. With decreasing ionicity the NaCl structure becomes unstable and a cubic to rhombohedral phase transition occurs at room temperature with ordering of Ag and Bi in AgBiS$_2$ and AgBiSe$_2$. For AgSbSe$_2$ and AgSbTe$_2$ (n=2x) the disordered cubic structures persist even at room temperature [1]. In AgSbTe$_2$, experimental measurements by Noda et. al. give room temperature values of thermopower S, electrical conductivity $\sigma$, and thermal conductivity $\kappa$: 266 $\mu$V/K, 1470 S/cm, and 1.07 W/mK. These give a value of ~0.29 for the thermoelectric figure of merit $ZT$ ($ZT=S^2\sigma T/\kappa$) [2].

Extensive electronic structure studies have been carried out in PbTe [3], whereas, as far as we know, there are no electronic structure calculations in the ternary (n=2x) and quaternary
compounds. To understand the nature of bonding between the Te and Sb atoms in these systems, we first perform electronic structure calculations in AgSbTe2.

METHOD OF CALCULATION

Electronic structure calculations were performed using the self-consistent full-potential linearized augmented plane wave method [4] (LAPW) within density functional theory [5] (DFT), using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof [6] for the exchange and correlation potential. The values of the atomic radii were taken to be: 2.2 a.u. for K, 2.4 a.u. for Se and 2.7 a.u. for Bi, where a.u. is the atomic unit (0.529 Å). Convergence of the self-consistent iterations was performed for 18 k points inside the reduced Brillouin zone to within 0.0001 Ry with a cutoff of -6.0 Ry between the valence and the core states. Scalar relativistic corrections were added for both systems and spin-orbit interaction was incorporated using a second variational procedure [7].

RESULTS

The unit cell lattice parameter of AgSbTe2 is a=6.06 Å. In the simple ionic model this system is charge balanced Ag+Sb+3Te-2. For the cations, the fluctuating charge from the average +2 charge (Pb+2) is -1 for Ag and +1 for Sb. We use the magnetic analogy (Ag=↑ and Sb=↓) for designing the ordered structures. These structures are antiferromagnetic (AF) type I, II, IIIA and IIIB. In addition to these antiferromagnetic orders, we choose two additional structures which we name type 1_AgSbTe2 and type 2_AgSbTe2 (consist of alternating layers of Ag and Sb along the 111 direction). The face centered cubic (fcc) lattices formed by Ag and Sb of the ordered structures are given in Figure 1 (for the sake of clarity we do not include the Te fcc lattice).
Figure 1. The fcc lattices of ordered structures: (A) type I, (B) type II, (C) type IIIA, and type IIIIB AF order; (E) type 1\_AgSbTe$_2$, and (F) type 2\_AgSbTe$_2$.

The density of states (DOS) analysis of type I AF structure shows semimetallic character with a pseudogap near the Fermi energy (Figure 2 (A)). The Ag d orbitals are located below the Fermi energy and they are fully occupied (Figure 2 (B)). The Ag s orbitals are mostly located above the Fermi energy with small contributions to the states below Fermi energy due to a small Ag s-Te p hybridization (Figure 2 (C)). This suggests that Ag atoms are in a +1 oxidation state. The Te and Sb s states are very well stabilized in energy between -12eV and -8eV. These states do not mix with the p states of Te and Sb atoms. The Te and Sb p states, which lie in the range -5eV and 0eV hybridize with each other, indicating a strong covalent interaction between Te and Sb atoms. The overlap of the p states of Te and Sb gives a semimetal band structure.

Figure 2. Density of states of type I AF structure.
Figure 3. Total DOS of: (A) type II, (B) type IIIA, and (C) type IIIB AF structure; (D) type 1_AgSbTe₂, and (E) type 2_AgSbTe₂.

The DOS results for all other ordered structures show similar semimetallic behavior with low DOS near the Fermi energy. This is a result of the hybridization between the p states of Te and Sb atoms. In Figure 3 we show only the total DOS of these different structures. The rapid increase in the DOS near the Fermi energy (both above and below) suggests that these systems will show large thermopower when the chemical potential moves away from the minimum with doping.

In order to compare the total energy $E_{\text{tot}}$ of the ordered structures we have performed volume optimization and force minimization up to 1mRy/a.u. The total energies per formula unit f.u. (f.u.=AgSbTe₂) are given in Table 1. The lowest energy $E_0$ correspond to type II AF order (see Figure 1). The total energies/f.u. relative to $E_0$ are in the range 0-0.5eV. A pure ionic model
Table 1. Total energy of the ordered structures.

<table>
<thead>
<tr>
<th>Type</th>
<th>atoms/cell</th>
<th>$E_{\text{tot}}$/f.u. (Ry)</th>
<th>$E_{\text{tot}}-E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I AF</td>
<td>8</td>
<td>-50789.51585</td>
<td>0.49</td>
</tr>
<tr>
<td>II AF</td>
<td>64</td>
<td>$E_0= -50789.55191$</td>
<td>0</td>
</tr>
<tr>
<td>IIIA AF</td>
<td>16</td>
<td>-50789.51815</td>
<td>0.46</td>
</tr>
<tr>
<td>IIIB AF</td>
<td>16</td>
<td>-50789.5259</td>
<td>0.35</td>
</tr>
<tr>
<td>1$_{\text{AgSbTe}_2}$</td>
<td>32</td>
<td>-50789.52858</td>
<td>0.32</td>
</tr>
<tr>
<td>2$_{\text{AgSbTe}_2}$</td>
<td>12</td>
<td>-50789.53113</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Simulation gives the lowest energy structure to be IIIB AF [8]. In all these structures the local nearest neighbor environment of every Sb is the same whereas Te atoms have different environments.

CONCLUSION

Ab initio electronic structure calculations for all ordered structures of AgSbTe$_2$ show semimetallic behavior with a pseudogap in the DOS near the Fermi Energy. It is of interest to find out how Ag and Sb disorder will affect the electronic structure of AgSbTe$_2$, particularly in the neighborhood of the pseudogap. Disorder may create localized states near the Fermi energy.

Experimental measurements in AgSbTe$_2$ give rather intriguing results. Electrical conductivity and Hall coefficient measurements in single crystal AgSbTe$_2$ by Gochev et al. [9] in the temperature range 300-600K show a temperature dependence not typical for semiconductors. There is a minimum in the conductivity at T~500K. Fitting the data to an exponential in the range 500-600K gives an energy gap $E_g$ ~0.2eV. Energy gaps ranging between 0.27-0.35eV have been obtained in earlier studies. Later measurements by Elsayed et al. [10] in the range 600-700K gives $E_g$~0.218eV for the solid state. Whether we can understand these unusual electrical properties of AgSbTe$_2$ within a pseudogap picture needs to be investigated further.

ACKNOWLEDGMENTS

Financial support from the Office of Naval Research (Contract No. N00014-02-1-0867) is greatfully acknowledged.

REFERENCES