The Origin of the Metal-insulator Transitions in Non-stoichiometric TlCu$_{3-x}$S$_2$ and $\alpha$-BaCu$_{2-x}$S$_2$

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The structure-property relations of ternary copper chalcogenides, TlCu$_{3-x}$S$_2$ and $\alpha$-BaCu$_{2-x}$S$_2$, are examined. The density of states, band dispersions, and Fermi surfaces of these compounds are investigated to verify the reason of the metal-insulator transitions by extended Hückel tight-binding band calculations. The origin of the metal-insulator transitions of non-stoichiometric TlCu$_{3-x}$S$_2$ and $\alpha$-BaCu$_{2-x}$S$_2$ is thought to be the electronic instability induced by their Fermi surface nesting.

Key Words: Metal-insulator transition, Fermi surface nesting

Introduction

Ternary copper chalcogenides exhibit a large variety of anomalies in physical properties. Both K$_2$Cu$_8$S$_8$ and ACu$_{4}$S$_8$ (A=K, Tl) exhibit resistivity anomalies and superlattice modulations, whereas Na$_2$Cu$_{4}$S$_8$ does not despite its one-dimensional (1D) metallic character. TlCu$_{7}$S$_8$, as a quasi-one dimensional sulfide, exhibits successive phase transitions at 60, 165, 190, 220, 245, and 395 K. Electron diffraction study on this compound also shows the evidence of superlattice modulations at 165 and 245 K. Similar results are collected in the isostructural phases KCu$_{3}$S$_4$ and $\alpha$-BaCu$_{3}$S$_4$. In addition, phase transitions can be found in other copper chalcogenide, $\alpha$-BaCu$_{4}$S$_4$ at 190 K. The origin of the superlattice modulations in copper chalcogenides is rather diverse. DiSalvo and Sato groups suggest that phase transitions of K$_2$Cu$_8$S$_8$, RbCu$_{3}$S$_4$, and Tl$_{2}$Cu$_{3}$S$_4$ are induced by their Fermi surface nesting. In addition, phase transitions can be found in $\alpha$-BaCu$_{4}$S$_4$ despite its quasi-one dimensional metallic character. The valence bands consist of mainly the Cu d-orbital block. Therefore, stoichiometric ternary copper sulfides are non-metals by definition that there is no partially filled band. However, similar to other ternary sulfides ACu$_{4}$S$_8$ (A=K, Tl, Rb), the non-stoichiometric TlCu$_{3}$S$_2$ and $\alpha$-BaCu$_{2}$S$_2$ become metallic and show phase transitions. This was recently shown by Ohnani et al. who prepared both stoichiometric and non-stoichiometric TlCu$_{3}$S$_2$ and $\alpha$-BaCu$_{2}$S$_2$ using solid state reaction, and found that these two compounds exhibit metal-insulator transitions at 120 K and 200 K, respectively. They suggested that the origin of the phase transition of TlCu$_{3}$S$_2$ would be an electron correlation effect which occasionally causes the Mott transition, while that of $\alpha$-BaCu$_{2}$S$_2$ is not yet clear. In the present work, we calculate the electronic structure of TlCu$_{3}$S$_2$ and $\alpha$-BaCu$_{2}$S$_2$ using the extended Hückel tight-binding (EHTB) method to investigate the origin of the phase transitions of the compounds. The atomic orbital parameters used in the calculation are given in Table 1.

Table 1. Atomic Orbital Parameters used in EHTB Calculations:

<table>
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<tr>
<th>atom</th>
<th>orbital</th>
<th>$H_a$(eV)</th>
<th>$\zeta$ (e)</th>
<th>$\zeta$ (e)</th>
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<tr>
<td>Cu</td>
<td>3d</td>
<td>-14.0</td>
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<td>2.30 (0.5744)</td>
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<tr>
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<td>-11.4</td>
<td>2.2000</td>
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</tr>
<tr>
<td>S</td>
<td>3p</td>
<td>-20.0</td>
<td>2.12 (1.00)</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>3p</td>
<td>-13.3</td>
<td>1.82 (1.00)</td>
<td></td>
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<tr>
<td>Tl</td>
<td>6s</td>
<td>-11.6</td>
<td>2.30 (1.00)</td>
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</tr>
<tr>
<td>Tl</td>
<td>6p</td>
<td>-5.80</td>
<td>1.60 (1.00)</td>
<td></td>
</tr>
</tbody>
</table>

*Parameters are collected from the following data: (a) Clementi, E.; Roetti, C. Atomic Data Nuclear Data Tables 1974, 14, 177. (b) McLeen, A. D.; McLeen, R. S. Atomic Data Nuclear Data Tables 1981, 26, 197. (c) Richardson, J. W.; Blackman, M. J.; Runochak, J. E. J. Chem. Phys. 1973, 58, 3010.*

The structure-property relations of ternary copper chalcogenides, TlCu$_{3-x}$S$_2$ and $\alpha$-BaCu$_{2-x}$S$_2$, are examined. The density of states, band dispersions, and Fermi surfaces of these compounds are investigated to verify the reason of the metal-insulator transitions by extended Hückel tight-binding band calculations. The origin of the metal-insulator transitions of non-stoichiometric TlCu$_{3-x}$S$_2$ and $\alpha$-BaCu$_{2-x}$S$_2$ is thought to be the electronic instability induced by their Fermi surface nesting.

Key Words: Metal-insulator transition, Fermi surface nesting
the edge-sharing tetrahedra. [hereafter the copper atoms of CuS₄ columns are referred as Cu(1) atoms and those of the tetrahedral chains are the Cu(2) atoms]. So it is convenient to represent TlCuS₂ as Tl₃(CuS₄)(Cu₂), in a unit cell. The (CuS₄)Cu₂ unit is repeating infinitely along the a-axis and hence, the compound shows layered structure. Each layer is separated by thallium atoms, as shown in Figure 1. The number of Cu(2) atoms in TlCuS₂ per unit cell are smaller than those in K₂CuS₄ by 1 and the rest of the structure is similar. In a non-stoichiometric TlCuₓS₂, vacancy in Cu(2) atom site increases as increasing the x value. The interatomic distances indicate that the bonding in the compound has partial ionic and partial covalent character. The Tl-S distances, for instance, are near the sum of the ionic radii of S²⁻ and monovalent Tl⁺ [i.e., d(Tl-S) = 3.33 Å, (r₃ + r₃)ionic = 3.33 Å] whereas the Cu-S distances are a little beyond the covalent radii sum of Cu and S [i.e., d(Cu-S) = 2.32 Å, (r₄ + r₄)covalent = 2.19 Å].

BaCu₂S₄S₂ exhibits two different phases α- and β-form. In the α-phase, a CuS₄ unit forms a distorted octagon which is similar to the chair shape. Each CuS₄ unit is edge-shared with the next unit along both a- and b-directions. Two CuS₄tetrahedra are also edge-shared along the diagonal directions as shown in Figure 2. CuS₄octagon is connected continuously along the c-direction by forming trigonal prisms of anions thereby constructing the infinite tube by sharing their basal faces. Ba atoms sit at the center of the tube, as shown in Figure 2. Two tetrahedral holes which are occupied by Cu atoms are made at the center of adjacent four tubes by sharing two edges in neighboring tubes. The Cu atoms construct zigzag chains of CuS₄ tetrahedra, which are formed by sharing two adjacent edges of each tetrahedron. All Cu and S in CuS₄ units are occupied in constructing the CuS₄tube and the CuS₄ tetrahedra. Differently from TICuS₂, therefore, there is no differentiation of Cu(1) and Cu(2) in α-BaCu₂S₄S₂. Similarly to TICuₓS₂, there are ionic and covalent characters in α-BaCu₂S₄S₂. The Tl-S distances ranging from 3.09 Å to 3.29 Å which are shorter than the ionic radii sum of Tl and S indicate that those bonds are ionic, whereas the Cu-S distances ranging from 2.37 Å to 2.55 Å are larger well beyond the covalent radii sum of Cu and S which means that the weak covalent character exists.

**Electrical properties.** Electrical resistivity ρ as a function of temperature on cooling of TlCuₓS₂ (x = 0, 0.05, 0.07, 0.09) is shown in Figure 3a. As expected from the electronic structure, the stoichiometric TICuS₂ (i.e., x = 0) shows insulating behavior within the whole temperature range. However, the samples with Cu(2) vacancy (i.e., x = 0.05, 0.07, and 0.09) exhibit metallic character above 120 K, which means that resistivity of these samples increases with temperature. In the long run, TICu₀S₂ (x = 0.05, 0.07, and 0.09) samples show a metal-insulator transition at 120 K. Although the metal-insulator transition is not shown, the resistivity of the stoichiometric sample also increases abruptly below this temperature. Interestingly, the resistivity is reduced as x increases up to 0.07, and futher Cu(2) removal results in the increase of the resistivity again. The resistivity data for α-BaCu₂S₄S₂ are shown in Figure 3b. In this compound, the samples having Cu(2) vacancy show a metal-insulator transition at 200 K. Differently from TICuₓS₂, the resistivity of α-BaCu₂S₄S₂ is continuously getting smaller as x (i.e., hole density) increases.

**Electronic structure.** The DOS and the projected density of states (PDOS) for the Cu and S atoms in TlCuₓS₂ and α-BaCu₂S₄S₂ are shown in Figures 4a and 4b, respectively. The vertical dashed lines represent the Fermi energies of stoichiometric TICuS₂ and α-BaCu₂S₄S₂. At the Fermi energy, the DOS values for the stoichiometric samples are both zero, which means that stoichiometric TICuS₂ and α-BaCu₂S₄S₂ are non-metallic as expected. The resistivity of TICuₓS₂ and α-BaCu₂S₄S₂ at room temperature are about 0.016 W cm⁻¹ and 3.98 W cm⁻¹, respectively. These values are
consistent with the band gaps depicted in the DOS figures. Cu vacancies in both samples create the partially filled bands, thereby changing those compounds be metallic. Cu vacancy is nothing more than the electron deficiency in a unit cell. Since the orbitals of the Cu atoms do not contribute much to the top portion of the bands as shown in the PDOS figures, the electronic structures of non-stoichiometric TlCu_{3-x}S_{2} and α-BaCu_{2-x}S_{2} can be analyzed by simply lowering the Fermi energy according to the x values (i.e., 0.05 × 11 and 0.07 × 11 electrons per formula unit for x = 0.05 and 0.07 in TlCu_{3-x}S_{2}, respectively. Same electron counting is applied for α-BaCu_{2-x}S_{2}).

Electrical resistivity of non-stoichiometric TlCu_{3-x}S_{2} (x = 0.05, 0.07, 0.09) is reduced up to x = 0.07 but it goes up again according to further removal of Cu (i.e., x > 0.07), while that of α-BaCu_{2-x}S_{2} is reduced continuously as x increases. In other words, electrical conductivity of TlCu_{3-x}S_{2} increases up to x = 0.07 then decreases afterwards, while that of α-BaCu_{2-x}S_{2} increases continuously within the experimental range of x. Generally electrical conductivity is strongly related to the DOS value around the Fermi energy. As shown in Figure 4a, the DOS of TlCu_{3-x}S_{2} increases with increasing x values until the Fermi energy goes down to –9.5 eV and then it decreases as the Fermi energy goes down further. Although not shown, the Fermi energy of TlCu_{3-x}S_{2} at x = 0.7 is about –9.5 eV. The DOS profile of TlCu_{3-x}S_{2} well explains why the conductivity maximum exists in the compound. On the contrary, DOS of α-BaCu_{2-x}S_{2} compounds increases steadily as x increases (see Fig. 4b). This result is consistent with the experimental resistivity.
measurement data.

Band dispersions calculated for TlCu$_{3-x}$S$_2$ and α-BaCu$_{2-x}$S$_2$ are shown in Figures 5a and 5b, respectively. Γ, X, Y, Z represent the wave vector points (0, 0, 0), (a*/2, 0, 0), (0, b*/2, 0), (0, 0, c*/2) in the first Brillouin zone of the reciprocal lattice, respectively. Bands are similarly dispersive along the a-, b-, and c-directions in TlCu$_{3-x}$S$_2$ while they are strongly dispersive only along the b-direction in α-BaCu$_{2-x}$S$_2$. Structural features suggest that TlCu$_{3-x}$S$_2$ may be 2-dimensional since it is a layered compound. Band dispersion of this compound, however, tells us that this compound is 3-dimensional by forming strong interactions between thallium and sulfur atoms in layers of both sides as pointed out in the structure analysis (See Figure 1). α-BaCu$_{2-x}$S$_2$ seems to be 3-dimensional from the view point of structural aspects (See Figure 2). However, its band dispersion curve suggests that the orbital interactions along the chain direction (i.e., crystallographic b-direction) are stronger than the other two directions. The Fermi surface of a partially filled band is defined as the boundary surface of wave vectors that separate the wave vector region of filled band levels from that of the wave vector region of unfilled band levels. Since there are several bands cut by the Fermi energy, many Fermi surfaces can be drawn according to the x values for both TlCu$_{3-x}$S$_2$ and α-BaCu$_{2-x}$S$_2$. Among them, the representative Fermi surfaces calculated for TlCu$_{3-x}$S$_2$ and α-BaCu$_{2-x}$S$_2$ are shown in Figures 6a and 6b when x = 0.07 and x = 0.12, respectively. One piece of a Fermi surface may be superimposable, by translating it with wave vector q, onto another piece of the Fermi surface. In such a case, the two pieces are said to be nested by the wave vector q. A metallic system with a nesting vector q gives rise to a CDW of wave vector q, which can be detected by diffuse X-ray scattering as diffuse reflections in between the main Bragg reflections. Essentially two Fermi surfaces given in the Figures 6a and 6b are one-dimensional in nature. Generally, a compound that possesses one-dimensional property shows well nested Fermi surfaces and finally exhibits higher susceptibility to a metal-insulator transition. In both compounds, the Fermi surface nesting phenomena exist with the nesting vectors q=0.943b' in TlCu$_{3-x}$S$_2$ and q=0.80b' in α-BaCu$_{2-x}$S$_2$ as illustrated by arrow in Figure 6. Although not shown, the Fermi surface nesting phenomena occur at different x values and different bands with different q. The electronic instability induced by these Fermi surface nestings may cause the charge density waves (CDWs) and hence the non-stoichiometric TlCu$_{3-x}$S$_2$ and α-BaCu$_{2-x}$S$_2$ exhibit the metal-insulator transitions at 120 K and 200 K, respectively. To verify the origin of the phase transition in TlCu$_{3-x}$S$_2$ and α-BaCu$_{2-x}$S$_2$ more clearly, the crystal data below the transition temperature are needed.

**Conclusions**

The origin of the metal-insulator transitions exhibited in...
The ternary copper chalcogenides are still going into controversy. According to the EHTB calculations of the non-stoichiometric TlCu$_{3-x}$S$_2$ and α-BaCu$_{2-x}$S$_2$, the Fermi surfaces of both compounds possess one-dimensional property and are partially nested. In the long run, the electronic instability caused by the Fermi surface nesting may be the origin of the metal-insulator transitions of these compounds. The electrical resistivity data obtained from the experimental procedure are well explained with calculated DOS results. The DOS value increases with increasing x up to x = 0.07, then decreases beyond x = 0.07 in TlCu$_{3-x}$S$_2$. The electrical resistivity of this compound show same pattern. In α-BaCu$_{2-x}$S$_2$, however, the DOS value increases continuously according to x value, which is consistent with resistivity experiments.

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References