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# Valence band photoemission study of the copper chalcogenide compounds, Cu<sub>2</sub>S, Cu<sub>2</sub>Se and Cu<sub>2</sub>Te

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#### Abstract

The electronic structures of the copper chalcogenide compounds,  $Cu_2S$ ,  $Cu_2S$  and  $Cu_2Te$  have been investigated by taking photoemission data with synchrotron photon sources. The band calculations are done using the full-potential linear-muffin-tin-orbital method. Since the crystal structures are not clarified well, several simplified structure models are used. The calculated densities of states are compared with the observed spectra. The analysis shows that a sharp peak at -3.5 eV is due to the Cu 3d states, and that the tails at the high and low energy sides of the Cu 3d peak are due to the chalcogen p states. © 2003 Elsevier Ltd. All rights reserved.

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#### 1. Introduction

The copper chalcogenide compounds, Cu<sub>2</sub>S, Cu<sub>2</sub>Se and Cu<sub>2</sub>Te are known to have complicated crystal structures, in spite of their simple chemical formula. Above 743 K, Cu<sub>2</sub>S (mineral chalcocite) has a cubic (anti-)fluorite structure [1]. Between 743 and 376.6 K, Cu<sub>2</sub>S changes to a hexagonal structure called high chalcocite [2]. At room temperature, Cu<sub>2</sub>S takes a superstructure called low chalcocite, space group  $P2_1/c$   $(a = 3a_h, b = 4\sqrt{3}a_h, c = 2c_h$  and Z = 48)[3,4]. A slightly non-stoichiometric compound  $Cu_{1.96}S$ (mineral djurleite) has another superstructure, space group  $P2_1/n \ (a = 4c_h, b = 4a_h, c = 2\sqrt{3}a_h \text{ and } Z \simeq 64)$  [4]. Here we take the ortho-hexagonal cell as the base. Cu1.8S (mineral digenite) also has the cubic fluorite structure. The lattice constant of  $Cu_{1.8}S$  (a = 5.575 Å) is a little smaller than that of the cubic  $Cu_2S (a = 5.735 \text{ Å}) [1,5]$ . Below 353 K,  $Cu_{1.8}S$ changes to have a fluorite-based incommensurate structure.

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The crystal is reported to have an ordered arrangement of copper vacancies [5-7].

Above 413 K, Cu<sub>2</sub>Se (mineral berzelianite) has the cubic fluorite structure ( $\alpha$ -Cu<sub>2</sub>Se). At room temperature, it has a fluorite-based superstructure ( $\beta$ -Cu<sub>2</sub>Se). The structure has been studied by a number of researchers using powder X-ray and electron diffractions. Until now, different crystal structures (tetragonal [8], pseudo-orthorhombic [9], monoclinic [10,11]), have been proposed. According to a recent X-ray study [12], superlattice reflections appear at  $\mathbf{a}^* = [1/8, 1/8, 1/8]_c$ ,  $\mathbf{b}^* = [3/4, -7/12, 1/12]_c$ and  $\mathbf{c}^* = [0, 2/3, -2/3]_c$ . The deduced unit cell is triclinic,  $\mathbf{a} = [2, 3, 3]_c$ ,  $\mathbf{b} = 1/2[2, -1, -1]_c$  and  $\mathbf{c} = 1/2[1, 1, -2]_c$ . Due to the lack of single crystal samples, detailed crystal structure is not yet clarified. The  $\alpha - \beta$  transition temperature is concentration dependent. As the Cu atoms are removed from the specimen, the transition temperature decreases [13,14].  $Cu_{1.8}$ Se remains cubic at room temperature.

The phase sequence of Cu<sub>2</sub>Te is most complicated. It undergoes successive phase transitions ( $\alpha$ -548 K- $\beta$ -593 K- $\gamma$ -638 K- $\delta$ -848 K- $\epsilon$ ) [15–17]. The highest temperature  $\epsilon$ -Cu<sub>2</sub>Te has the cubic fluorite structure. The phases

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 $(\delta, \gamma, \beta \text{ and } \alpha)$  are based on the same *ortho*-hexagonal subcell  $(a = a_h, b = \sqrt{3}a_h \text{ and } c = c_h)$ .  $\delta$ -Cu<sub>2</sub>Te is the normal (prototypic) phase, and  $\gamma$  and  $\beta$  are incommensurate phases. Electron diffraction studies done on y-Cu2Te disclosed satellite reflections at (0,0,delta), where delta = $0.14 \simeq 1/7$  [16,17]. The room temperature  $\alpha$ -Cu<sub>2</sub>Te is composed of several commensurate structures,  $a = a_h$ , b = $\sqrt{3a_h}$  and  $c = 2, 4, 5, 7c_h$ , where  $5c_h$  is dominant.

These copper chalcogenide compounds have a common feature at their high temperature phases, chalcogen atoms form regular lattices such as fcc or hcp, while copper atoms are in disorder occupying the interstices of the chalcogen lattice, randomly. The compounds show wide deviation from stoichiometry, as expressed by the formula  $Cu_{2-\delta}X$ . They have characteristic feature of p-type semiconductor and attract wide interest as electrode materials for solar cells. Due to the lack of the crystallographic data, however, their physical property is not well understood. The present study is aimed to investigate the electronic structure of the compounds, using photoemission experiments on the one hand, and the linear-muffin-tin-orbital (LMTO) band structure calculation on the other hand. To the authors knowledge, X-ray photoemission (XPS) studies have been reported for Cu<sub>2</sub>S and Cu<sub>2</sub>Se [18,19], tight-binding and linear augmented-plane-wave calculations have been reported only for fluorite Cu<sub>2</sub>Se [20] and Cu<sub>2</sub>Te [21].

## 2. Experimental and calculational methods

The samples were synthesized from the elements (99.999%) by direct reaction. Stoichiometric mixtures of the elements were melted in evacuated silica tubes at about 1373 K and solidified by slow cooling. The structures of the crystals were checked by taking single crystal X-ray photographs and powder X-ray diffraction patterns. The photoemission data were taken using the synchrotron radiation at BL8B2 of the UVSOR, the Institute of Molecular Science. Specimens suitable for photoemission studies were prepared by cutting polycrystalline samples, and mounted on sample holders using conducting epoxy cement. Clean surfaces were made by Ar sputtering. The experiments were done at room temperature in the vacua of approximately  $1 \times 10^{-8}$  Pa. The angle integrated photoemission data were taken with incident photon energies from 16 to 48 eV. The energy resolution of the measurements ( $\Delta E$ ) was 0.25 eV at 40 eV. The absolute values of binding energies were determined from the Fermi edge of Au metal. Details of the experimental apparatus are reported elsewhere [22].

The band calculations were done using the full-potential linear-muffin-tin-orbital (FP-LMTO) method [23], where the local density approximation (LDA) was used. The space was divided into muffin-tin spheres and the interstitial region. Within the muffin-tin spheres, the charge density and potential were expanded using spherical harmonics, and in the interstitial region they were expanded in plane waves. Details of the calculation are reported elsewhere [23,24]. In order to compare with the experimental spectra, calculated density of states (DOS) values were convoluted with a Gaussian having a line width of 0.3 eV.

## 3. Results and discussion

## 3.1. Valence band spectra

Fig. 1(a1)-(a3) shows the energy distribution curves (EDCs) measured on Cu<sub>2</sub>S, Cu<sub>2</sub>Se and Cu<sub>2</sub>Te. The sharp peak around -3.5 eV is ascribed to Cu 3d states. This peak was already identified in previous XPS studies of Cu2S and Cu<sub>2</sub>Se [18,19]. The Cu 3d peak has tails both on the higher energy (around -2 eV) and the low energy (below -5 eV) sides. The intensity of the tails around the Cu 3d peak increases as photon energy decreases. This fact suggests that the tails contain contributions from chalcogen p states. The change of the peak profile is ascribed to the rise of the photoionization cross-sections of the chalcogen p states relative to that of the Cu 3d states [25], see Table 1. The chalcogen p peak on the low energy side of the Cu 3d peak (denoted by  $\alpha$  in Fig. 1) is lowest in Cu<sub>2</sub>S and highest in Cu<sub>2</sub>Te. The tail on the high-energy side of the Cu 3d peak also suggests that the chalcogen p-level is lowest in Cu<sub>2</sub>S and highest in Cu2Te. The photoemission data show that the chalcogen p states are below the Cu 3d states in these compounds, however, the top of the valence bands has some chalcogen p character.

## 3.2. Calculated DOS and comparison with the observed spectra

## 3.2.1. Cu<sub>2</sub>S

The structure of Cu<sub>2</sub>S above 376.6 K (high chalcocite) is shown in Fig. 2(a) (cf. Table 2(a)). Sulfur atoms form a regular hcp lattice, while copper atoms split into three parts (2b, 4f and 6g positions). As described above, two structure types are reported for the room temperature phase, low chalcocite (Cu<sub>2</sub>S) and djurleite (Cu<sub>1.96</sub>S). It was found, however, that in synthesized crystals low chalcocite and djurleite coexist and there is no compositional difference between them, and that the latter type is more stable [26]. We found in X-ray photographs that the crystal used is of the djurleite type. These structures are not suitable for the present band calculation, because low chalcocite and djurleite contain too many atoms (144 and 188 atoms in the unit cells), and high chalcocite has a disorder structure where Cu atoms occupy the sites only partially.

As a tentative model, we take the structure shown in Fig. 2(b) (see also Table 2(b)). It is a hexagonal version of the cubic fluorite. In the hexagonal polytype, Cu atoms



Fig. 1. Photoemission data taken at 16–42 eV (UVSOR). (a) Cu<sub>2</sub>S, (b) Cu<sub>2</sub>Se, and (c) Cu<sub>2</sub>Te. The largest peak is ascribed to Cu 3d states. The spectra are normalized using the height of this peak. The peaks denoted by  $\alpha$  are due to chalcogen p states.

occupy the tetrahedral and octahedral sites alternately and S atoms have 7-fold Cu coordination. It is in contrast to the fluorite polytype where Cu atoms occupy only the tetrahedral sites. The Cu coordinates are relaxed, in Fig. 3, the total energy is plotted as a function of Cu coordinates. We see that for Cu(1) the minimum is near the tetrahedral point, while for Cu(2) it is fairly deviated from the octahedral point, showing that the Cu atom favor trigonal S coordination.

The calculated DOS is shown in Fig. 4(a). The lowest band located at -13.5 eV is derived from S 3s states. The main valence bands split into two parts, and there is a gap between them. In the lower part, the bands from -7 to

Table 1

Energy dependence of the photoionization cross-sections (in Mb) taken from Ref. [25]

Atom/Orbital	26.8 eV	40.8 eV	132.3 eV
Cu 3d	8.190	9.934	5.139
S 3s	0.2482	0.4493	0.1637
Se 4s	0.050	0.2065	0.1022
Te 5s	0.1163	0.2123	0.078
S 3p	0.9827	0.6028	0.3610
Se 4p	3.089	0.5578	0.1005
Te 5p	2.028	0.5043	0.069

-4.5 eV are the S 3p-Cu 3d bonding states, mainly composed of S 3p states. In the upper part, the bands from -3.2 to -1.6 eV are the Cu 3d non-bonding states, the bands from -1.6 to 0 eV are the Cu 3d-S 3p antibonding states, mainly composed of the Cu 3d states. The conduction bands above 0 eV are composed mainly of Cu 4s and S 3p



Fig. 2. Schematic drawing of the two hexagonal structures for  $Cu_2S$ (a) the disorder structure (high chalcocite) and (b) the hypothetical ordered structure. The large circles mean sulfur ions, small circles mean copper ions and thin lines show the unit cells. In (a), there are three types of Cu atoms, 2-fold sulfur coordinated (open circle), 3fold sulfur coordinated (gray circle) and 4-fold sulfur coordinated (filled circle). In (b), only 4- and 3-fold sulfur coordinations are assumed.

Table 2			
Crystal	data	of	Cu <sub>2</sub> S

(a)	Crystal	data c	of $Cu_2S$	(high	chalcocite)	taken	from	Ref.	[2]
Spa	ice grou	p. latt	ice para	ımeter	rs (in Å)				

Space group	а	С		
$P6_3/mmc$	3.89	6.88		
Atomic coordin	nates			
Atom	x	У	z	Occupation ratio
S	1/3	2/3	0.250	1.00
Cu(1)	0.000	0.000	1/4	0.62
Cu(2)	1/3	2/3	0.578	0.815
Cu(3)	0.000	1/2	0.000	0.565

(b)	Crystal	data of	<sup>c</sup> the	hypothetical	hexagonal	$Cu_2S$
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Space group P6 <sub>3</sub>	а 3.89	с 6.88		
Atomic coordin Atom	nates x	у	z	
S Cu(1) Cu(2)	1/3 0.0000 1/3	2/3 0.000 2/3	1/4 0.375 0.545	



Fig. 3. Calculated total energy in the hypothetical hexagonal Cu<sub>2</sub>S, plotted as a function of Cu coordinates. In (a), Cu(1) is fixed at the tetrahedral point (0,0,3/8), and Cu(2) is moved along the *c*-axis. In (b), Cu(2) is fixed at (1/3,2/3,1/8) and Cu(1) is moved along the *c*-axis. Note in (a) that the energy minimum is located near the trigonal point (1/3,2/3,0) and far from the octahedral point (1/3,2/3,1/4), and that the curvature is relatively flat. Note also in (b) that the energy minimum is located near the tetrahedral point (0,0,3/8), and that the curvature is relatively sharp.



Fig. 4. (a) Calculated partial DOS for the hypothetical hexagonal  $Cu_2S$ . (b) Total DOS of the hypothetical hexagonal  $Cu_2S$  weighted by the photoionization cross-sections at 26.8 eV (cf. Table 1). The thick lines show the photoemission data taken at 24 and 42 eV, where the effect of the secondary photoelectrons is subtracted.

states, mixed somewhat with Cu 3d, 4p and S 3s states. The valence and conduction bands overlap near  $\Gamma(0, 0, 0)$ , and there is no band gap. The energy gap of Cu<sub>2</sub>S is estimated from the photoabsorption data as 1.2 eV [27]. The discrepancy may be attributed to drawback of the LDA, which tends to underestimate the energy gap. For comparison, the total DOS weighted for the photoionization crosssections is shown in Fig. 4(b), along with the observed spectra. The calculated DOS seems to reproduce the spectra, such as the two-peak nature of the main valence bands, qualitatively. However, the absolute position of the Cu 3d peak is not reproduced. If we shift, considering the discrepancy of the gap energy, the energy scale of the calculated DOS about 1.2 eV downward, the disagreement in the position of the Cu 3d peak will be much improved. The ionic valences are estimated from the calculated charge transfer as,  $Cu_{tet}(0.11)$ ,  $Cu_{tri}(0.12)$  and S (-0.22).

## 3.2.2. Cu<sub>2</sub>Se

The room temperature  $\beta$ -Cu<sub>2</sub>Se has a Frenkel type defect fluorite structure [12], see Fig. 5. Tetrahedral copper vacancies form a  $\sqrt{3} \times \sqrt{3}$  network in the (111)<sub>c</sub> plane. The vacant copper layers stack at every four metal layer. Since detailed crystal structure is not known yet, here we

a=[-1,-1,:

(b)  $\beta$ -Cu2Se Fig. 5. Schematic drawing of the two structures in Cu<sub>2</sub>Se. (a)  $\alpha$  (fluorite) Cu<sub>2</sub>Se, and (b)  $\beta$ -Cu<sub>2</sub>Se taken from Ref. [12]. For clarity, only the vacant metal layers are displayed in (b), where filled circles show Cu atoms and open circles show vacant Cu sites. The vacant Cu sites form a  $\sqrt{3} \times \sqrt{3}$  network in the (111)<sub>c</sub> plane. The vacant

copper layers stack at every four metal layer.

b=[2,-1,-1]/2

(a) α-Cu2Se (fluorite)

// [1, 1,

take the high temperature cubic fluorite structure shown in Fig. 5(a) (space group  $F_{m3m}$ , a = 5.760 Å). It should be noted that Cu<sub>1.8</sub>Se retains the cubic fluorite structure and that its photoelectron spectra are similar to those of Cu<sub>2</sub>Se.

The calculated partial DOS and the weighted total DOS are shown in Fig. 6(a) and (b). The band around -14.5 eV is derived from Se 4s states. In a ligand-field view [28], the tetrahedral field splits the Cu 3d orbitals into two terms, e and t<sub>2</sub>, the former has a lower energy, while the latter forms hybridized orbitals with Se 4p states. In the real band structure, both the e and t2 state are mixed and form hybridized bands with the Se 3p states. The lower part of the main valence bands are composed mainly of Se 4p states, the bands around -6 and -5 eV are the Se 4p–Cu 4s and 3d bonding states. The upper valence bands, from -3.5 to 0 eV are the Cu 3d non-bonding states, and the Cu 3d  $(t_2)$ -Se 4p antibonding states. The highest valence band is located along the  $\Gamma$ -L(1/2, 1/2, 1/2) line, and the top is at  $\Gamma$ . The lowest conduction band is also located along the  $\Gamma$ -L line. This band is very flat and sensitive to parameters used in the band calculation. The valence and conduction bands touch at  $\Gamma$ , and there is no band gap. The wave function at the valence band top is composed of Se 4p and Cu 3d mixed states, and that of the conduction band bottom is composed of the Cu 4s states mixed somewhat with the Cu 3d and Se 4p states. Since the wave functions Cu 4s and Se 4p have a relatively large overlap, the interaction between these two orbitals is rather strong. Thus, the hybridized Se 4p-Cu 4s states appear at the bottom of the main valence band around -6 eV and also at the bottom of the conduction bands. The overall feature of the calculated bands is in agreement with that reported for the fluorite  $Cu_2Te$  [21], but not with



Fig. 6. (a) Calculated partial DOS for fluorite Cu<sub>2</sub>Se. (b) Total DOS weighted by the photoionization cross-sections at 26.8 eV. The thick lines show photoemission spectra.

the previous tight-binding calculation [20], where the top of the valence band is at  $\Gamma$  but the bottom of the conduction band is at X = (1,0,0) suggesting the p states. The calculated charge transfer suggests almost null valences, Cu (+0.04) and Se (-0.08). The calculated positions of Cu 3d and Se 4s peaks are in accord with the experiments, except for the splitting in the main valence bands. From optical studies, it is reported that Cu<sub>2</sub>Se has a band gap of 1.23 eV [29], while electrical measurements always show metallic conduction [30], and the reason is ascribed to Cu deficiencies.

## 3.2.3. Cu<sub>2</sub>Te

A series of hexagonal-based superstructures,  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are reported for Cu<sub>2</sub>Te [16,17]. In prototypic  $\delta$ -Cu<sub>2</sub>Te, tellurium atoms form trihedral prisms stacked along the *c*-axis. Every second stack of the prisms is filled by a pair of Cu ions, see Fig. 7. This structure model was proposed by Nowotny [31]. Since the room temperature structure is not yet clarified, in this band calculation we take the Nowotny model. Copper atoms form a hexagonal network, where a Cu atom has three Cu neighbors at 2.46 Å, while it has Se neighbors at 2.68 Å. The Cu–Cu distance is shorter than that in Cu metal (2.56 Å). The crystallographic parameters are listed in Table 3.



Fig. 7. Schematic drawing of the structure of  $Cu_2Te$  (Nowotny phase [31]).

The calculated partial DOS and the weighted DOS are shown in Fig. 8(a) and (b). The lowest two bands from -14to -13 eV are derived from Te 5s states. Contrary to the cases of Cu<sub>2</sub>S and Cu<sub>2</sub>Se, there is no splitting in the main valence bands, from -7.5 to 0 eV. This is due to the proximity of the Te 5p and Cu 3d levels. It seems to be consistent with the single peak nature of the observed valence band spectra. The bands from -7.5 to -5 eV are the Te 5p-Cu 3d bonding states, mainly composed of Te 5p states. The bands from -2.5 to 0 eV are the non-bonding Cu 3d states. The bands from -2.5 to 0 eV are the Cu 3d-Te 5p antibonding states, mainly composed of Cu 3d states. Owing to the short Cu-Cu distance, strong hybridization occurs between the Cu orbitals, which results in relatively

Table 3					
Crystal data	of Cu <sub>2</sub> Te	taken	from	Ref.	[31]

(a) Space group, lattice parameters (in Å)					
Space group	а	с			
P6/mmm	4.237	7.274			
(b) Atomic coordir	nates				
Atom	x	у	z		
Ag	1/3	2/3	0.160		
Те	0.000	0.000	0.306		



Fig. 8. (a) Calculated partial DOS for  $Cu_2Te$ . (b) Total DOS of  $Cu_2Te$  weighted by the photoionization cross-sections at 26.8 eV. The thick lines show photoemission spectra.

large dispersion of the Cu d-bands. The valence-band top and the conduction-band bottom show similar character of the Cu 3d, 4s and Te 5p mixed states. The bands overlap severely near the  $\Gamma$  point. The present model calculation shows that Cu<sub>2</sub>Te is a semimetal. From optical studies, Cu<sub>2</sub>Te is reported to be a semiconductor with a band gap 1.04 eV [29], while electrical measurements showed metallic conduction [15]. The calculated electron densities show a charge transfer from Te to Cu atom. The estimated valences of Cu and Te are -0.20 and +0.40, respectively. The result suggests strong covalent bonding in Cu<sub>2</sub>Te. It is in contrast to the case of Cu<sub>2</sub>S, where the charge transfer occurs from Cu to S atoms. The position of the calculated Cu 3d peak is in agreement with the observation.

#### 3.3. Concluding remarks

In this paper, we have investigated the photoemission spectra of three copper chalcogenide compounds  $Cu_2S$ ,  $Cu_2Se$  and  $Cu_2Te$ . In the analysis of the data, LMTO band calculations are performed. Owing to the lack of structural data, we had to use simplified structure models. The calculated results indicate that  $Cu_2S$  and  $Cu_2Te$  are semimetals, while  $Cu_2Se$  is a zerogap semiconductor. The calculated band gaps are underestimated, but the tendency

of the chemical bondings is reproduced, that is, ionic in  $Cu_2S$  and more covalent in  $Cu_2Te$ . The qualitative features of the Cu 3d peak and the top valence states are also reproduced by the calculation.

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