Electronic structure and photoelectron spectra of calaverite, AuTe$_2$

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Abstract. Photoelectron spectra of calaverite, AuTe$_2$, show a Au 5d band extending from -3 to -8 eV below the Fermi energy. Photoemission peaks from Au 4f core levels are sharp, indicating that all Au atoms have the same valency. The binding energies of Au 4f electrons in AuTe$_2$ and metallic Au are approximately the same. According to these observations all Au atoms in AuTe$_2$ are monovalent Au(I).

  Photoelectron spectra of Te 4d and 3d core levels show single sharp peaks, characteristic of a single valency for Te.

  These investigations clearly establish the absence of appreciable valency fluctuations or mixed valency Au(I)–Au(III) in AuTe$_2$.

1. Introduction

The mineral calaverite AuTe$_2$ is a compound with interesting and anomalous properties. Contrary to the case for normal crystals, the morphology of single crystals of AuTe$_2$ cannot be described by rational indices [1, 2]. The x-ray diffraction pattern shows satellites in addition to the main reflections associated with a three-dimensional periodic crystal lattice [3]. These features arise from the fact that AuTe$_2$ has an incommensurably modulated structure [4]. The full crystal structure including the atomic positions in the modulated structure was determined by Schutte and de Boer [5]. It was found that as a result of the modulation the coordination of the gold atoms changes continuously from a linear coordination by Te to a square-planar coordination; all intermediate coordinations also occur. The modulation also affects the coordination of the Te atoms: the Te zig-zag chains present in the average structure are broken and isolated Te–Te pairs occur.

Schutte and de Boer [5] suggested as the driving force for the modulation of AuTe$_2$ a valence fluctuation of the Au atoms. This was based on the following argument. In many transition-metal dichalcogenides the chalcogen atoms dimerize to form anion pairs ((S_2)$^{2-}$ pairs in FeS$_2$, (Te$_2$)$^{2-}$ in FeTe$_2$). The interatomic distance in the Te–Te pairs in AuTe$_2$ is approximately the same as it is in FeTe$_2$. This suggests an average (formal) valency of two for the gold atoms in AuTe$_2$. However, a (formal) valency of two for Au(Au(II), corresponding in an ionic model to Au^{2+} ions with configuration

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$5d^9$) is usually not stable. In compounds with an average valency of two for Au, such as $AuCl_2$ [6], $Cs_2Au_2Cl_6$ [7] and AuSe [8], the crystal structure shows the presence of two types of Au atoms, one with a linear coordination by anions, and one with a square-planar coordination. A linear coordination of Au is commonly observed for monovalent Au (examples are AuCl [9], AuBr [10]), a square-planar coordination for trivalent Au ($AuCl_3$ [11], $AuBr_3$ [12]). The preference of atoms with a d^{10} configuration for a linear coordination is also observed in Cu^+ compounds (Cu_2O); it is probably related to configuration interaction with d^9s states [13]. The preference of atoms with a d^8 configuration for a square-planar coordination is well known; it is due to crystal-field stabilization [14]. Therefore the two types of Au atoms in $AuTe_2$, which occur at the extremes of the modulation, i.e. for $t = 0$ and $t = \frac{1}{4}$, were assigned by Schutte and de Boer to Au(I) (linear coordination) and Au(III) (square-planar coordination). Thus the driving force of the modulation in $AuTe_2$ was suggested to be the valence disproportionation of 2Au(II) into Au(I) and Au(III).

In the crystal structure of $AgAuTe_4$ [3], which is related to that of $AuTe_2$, the Ag atoms have a linear coordination, and Au atoms have a square-planar coordination. This suggests valencies Ag(I) and Au(III) in $AgAuTe_4$.

A recent *ab initio* calculation of the electronic structure of $AuTe_2$ cast doubt on the interpretation of the modulation in terms of Au(I) and Au(III) atoms [15]. According to these calculations the Au 5d band is completely occupied and the electronic configurations of all Au atoms are (nearly) the same. The Au 5d states show appreciable hybridization with Te 5p states. We remark that a fully occupied Au 5d band corresponds to a formal valency I for Au. Such a formal valency of I is not in contradiction with an orbital occupation of approximately $5d^9$ as deduced from band structure calculations. In fact, only in a completely ionic description (without hybridization or covalency) does a formal valency I correspond to $Au^+(5d^{10})$ ions, and a formal valency III to $Au^{3+}(5d^8)$ ions. The conclusion is that the band structure calculations give no evidence for valence fluctuations in $AuTe_2$.

In this paper we report investigations of the photoelectron spectra of $AuTe_2$ and $AgAuTe_4$. We study the valence band and core-electron spectra in order to obtain experimental information about the valencies of Au and Te in $AuTe_2$.

2. Experimental details

2.1. Experimental procedures

$AuTe_2$ was synthesized from the elements using the Bridgman method. An evacuated quartz tube with Au and Te was lowered in 20 h in a two-zone oven from a temperature of 470 to 600 °C. The product was cooled slowly over a period of 50 h to room temperature. The crystal structure was checked using x-ray diffraction. $AgAuTe_4$ was synthetized by heating the elements in an evacuated quartz tube for one week at 750 °C. After repowdering, the material was annealed in an evacuated quartz tube for one week at 400 °C. X-ray powder diffraction showed that the main product was $AgAuTe_4$, but that small amounts of Ag and Au were present.

Photoelectron spectra were measured using monochromatized Al Kα (1486.6 eV) radiation. The spectral resolution was about 0.5 eV. The spectra obtained were corrected for background and satellites of the x-ray source. The samples were mounted on a copper plate. The reported binding energies are with respect to the Fermi energy of the sample.
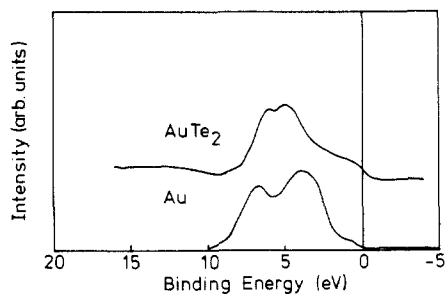
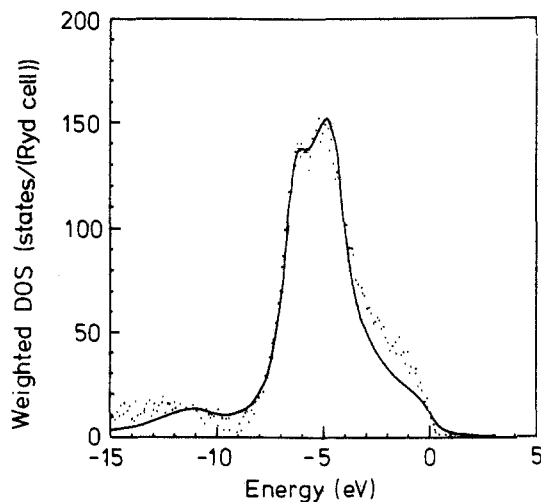**Figure 1.** Experimental valence band spectra of AuTe₂ and Au.

Figure 2. The weighted density of states obtained from band structure calculations [15] compared with the experimental valence band spectrum (dots).

Because the tellurides investigated are good metallic conductors, no charging of the sample takes place during the experiments.

The surface of AuTe₂ was cleaned by scraping in ultrahigh vacuum with a diamond file. Sputtering with argon ions proved not to be a suitable technique of surface treatment, because of preferential disappearance of Te from the sample. The AgAuTe₄ sample was too small for scraping; the surface was treated by argon-ion sputtering and subsequent annealing for 12 h at 100 °C in ultrahigh vacuum.

2.2. Valence band spectra

The x-ray photoelectron spectrum of the valence band of AuTe₂, measured with synchrotron radiation $h\nu = 50$ eV, is compared in figure 1 with the spectrum of Au metal. Excitation with $h\nu = 50$ eV is chosen because at this energy the Au 6s cross section is large, so an accurate determination of the Fermi energy of Au metal is possible. The spectrum of figure 1 clearly shows a region of high intensity due to emission of electrons from the Au 5d band. The 5d band in AuTe₂ is narrower than it is in Au metal. The maxima of the Au 5d band in AuTe₂ are at binding energies of 5.0 eV and 6.0 eV. The splitting of 1.0 eV is smaller than the expected spin–orbit splitting of 1.5 eV of atomic Au 5d levels [16]. This reduction of the splitting is generally observed in gold intermetallic compounds [17].

The spectrum of AuTe₂ shows a low intensity at the Fermi energy. This indicates that the Au 5d band, which has a high density of states, is completely occupied.

In figure 2 the observed photoelectron spectrum is compared with the weighted total density of states, obtained from band structure calculations [15]. The calculated atomic partial densities of states were multiplied with atomic cross sections for Au and Te in order to obtain a good estimate for the photoelectron spectrum. The correspondence with the observed spectrum is very good.

Table 1. Binding energy (BE) and width (FWHM) of Au 4f peaks.

		BE (eV)	FWHM (eV)
Au	$4f_{5/2}$	87.6	1.4
	$4f_{7/2}$	84.0	1.4
$AuTe_2$	$4f_{5/2}$	87.6	1.4
	$4f_{7/2}$	84.0	1.4
$AgAuTe_4$	$4f_{5/2}$	86.9	1.4
	$4f_{7/2}$	83.2	1.3

We conclude that the valence band spectra and the band structure calculations both indicate the presence of a fully occupied Au 5d band, i.e. a formal valency of one for all Au atoms in $AuTe_2$.

It is not possible to obtain a good spectrum of the valence band of $AgAuTe_4$, because of the paucity of material available and the overlap with the valence band of the copper plate on which the powder sample was spread.

2.3. Au 4f spectra

Figure 3 shows the photoemission spectra of Au 4f levels in Au, $AuTe_2$ and $AgAuTe_4$. The peak positions and widths (FWHM = full width at half maximum) of the peaks are given in table 1.

The spectra clearly show the spin–orbit splitting of 3.6 eV, approximately the same in all three cases. Also, the width is the same within the experimental errors. The peak positions are the same for Au and $AuTe_2$; the peaks in $AgAuTe_4$ are shifted by about 0.8 eV.

The Au 4f photoelectron spectra of many solid inorganic compounds and metal–organic complexes have been reported in the literature [18–20]. It is found that different Au valencies lead to different 4f peak positions, the shift between the Au $4f_{7/2}$ peaks for Au(I) and Au(III) being about 2 eV (with a larger binding energy for Au(III)). Thus the presence of Au atoms with formal valences of I and III can be easily established with x-ray photoelectron spectra.

The Au 4f spectra of $AuTe_2$ show no splitting that can be ascribed to a possible valence disproportionation into Au(I) and Au(III). Also, no broadening is observed, while broadening would be expected for a continuous distribution of valences between I and III. From the Au 4f spectra we conclude that all Au atoms in $AuTe_2$ have the same valency.

The 4f core electron binding energies in $AuTe_2$ are equal to those of Au metal. Therefore the formal valency of Au in $AuTe_2$ is the same as it is in Au metal (a fully occupied Au 5d band, corresponding to a formal valency of one). The Au 4f binding energy in $AuTe_2$ is close to the binding energy values reported for Au(I) in inorganic and organometallic compounds [18–20].

The Au 4f peaks of $AgAuTe_4$ are shifted with respect to the peaks in Au and $AuTe_2$. Comparison with differences in binding energies between Au(I) and Au(III) atoms [18–20] indicates that formal valency is certainly not higher than I for Au atoms in $AgAuTe_4$.
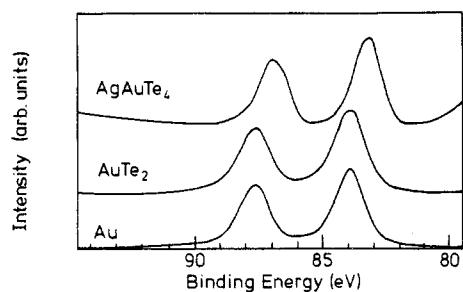
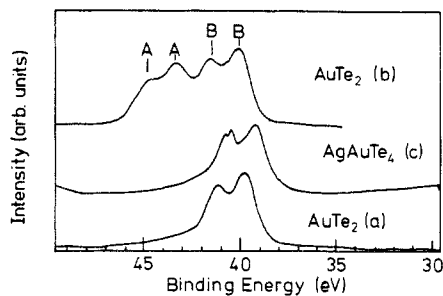**Figure 3.** Au 4f spectra of AuTe₂, AgAuTe₄ and Au.

Figure 4. Te 4d spectra of AuTe₂ ((a) freshly scraped; (b) two days after scraping) and AgAuTe₄ (c).

Table 2. Binding energies (eV) of Te 3d and Te 4d peaks.

			$4d_{3/2}$	$4d_{5/2}$	$3d_{3/2}$	$3s_{5/2}$
Te [23]			42.0	40.5	583.5	573.1
TeO₂ [23]			44.9	43.4	586.5	576.1
AuTe₂	Freshly scraped		41.3	39.9	582.2	571.9
	After	A	44.6	43.2	585.6	575.2
	two days	B	41.4	40.1	582.3	571.9
AgAuTe₄			40.5	39.2	581.9	571.6

We also measured Ag 3d spectra of AgAuTe₄. The observed binding energies 372.1 and 367.5 eV are close to the values 374.3 and 368.3 eV for metallic Ag [21] and the values 368.1 ($3d_{5/2}$) for Ag₂Te [22]. Thus Ag atoms in AgAuTe₄ have a formal valency I.

2.4. Te 4d and Te 3d spectra

The photoelectron spectra of Te 4d electrons are shown in figure 4, the peak positions are given in Table 2. The spectrum of AgAuTe₄ was obtained after argon–ion sputtering and subsequent annealing. The spectrum of a freshly scraped AuTe₂ sample shows two peaks; the splitting corresponds to the expected spin–orbit splitting of the Te 4d core levels. However, when making measurements on the same sample after two days, four Te 4d peaks are observed (the Au 4f spectrum remains unchanged). This indicates the presence of two types of Te atom after two days. We remark that a difference between a freshly prepared surface and the surface after two days was also observed in the optical properties [24].

The effect of aging is also observed in the Te $M_{4,5}N_{45}N_{45}$ Auger spectrum (figure 5). However, these spectra are too complicated for further analysis in terms of two types of Te atoms.

The Te 3d spectra of AuTe₂ and AgAuTe₄ are reported in figure 6; the peak positions and widths are given in table 2. The spectrum of AgAuTe₄ shows two peaks, with a splitting of 10.3 eV, which is the characteristic spin–orbit splitting of Te 3d levels. The
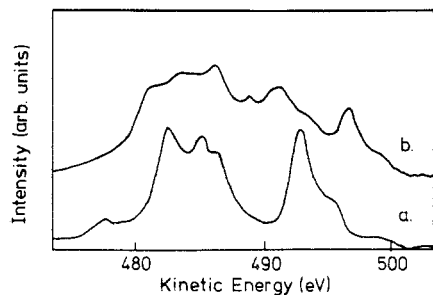
Figure 5. Te($M_{4,5}N_{45}N_{45}$) Auger spectra of $AuTe_2$ excited with Mg $K\alpha$ radiation ((a) freshly scraped; (b) two days after scraping).
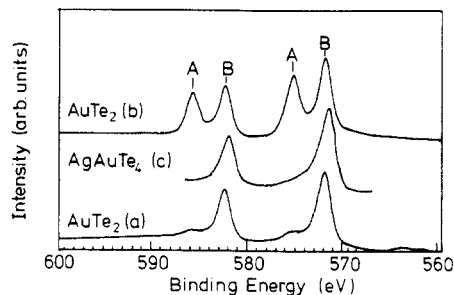
Figure 6. Te 3d spectra of $AuTe_2$ ((a) freshly scraped; (b) two days after scraping) and $AgAuTe_4$ (c).

spectrum of freshly scraped $AuTe_2$ is very similar; however, the spectrum taken two days after scraping shows two new peaks shifted by 3.3 eV to higher binding energies (very weak peaks at these positions are observed in spectra (a) and (c)). This is similar to the observations for the Te 4d spectra, where a shift of 3.3 eV was also found.

The Te 3d and Te 4d binding energies of the new peaks appearing two days after scraping (peaks A in figures 4 and 6) coincide closely with the values reported for TeO_2 [23] and for an oxidized Te surface [25] (see table 2). Therefore we attribute the change of the spectrum that has taken place two days after scraping to the formation of TeO_2 at the surface.

The peaks of spectrum B (figures 4 and 6) and the spectrum of a freshly scraped sample are assigned to Te atoms in $AuTe_2$. These peaks have a normal width (about 1 eV), indicating that all Te atoms in $AuTe_2$ have the same valency. The same is true for the Te atoms in $AgAuTe_4$. A comparison with Te 3d and Te 4d peak positions in different compounds indicates a small negative valency of Te in $AuTe_2$ [23, 26].

3. Discussion

Crystal structure determination showed that in the modulated structure of $AuTe_2$ there is a continuous variation of the coordination of the Au atoms. The coordination of Au changes from a linear to a square-planar coordination. There are also changes of Te–Te interatomic distances associated with the modulation.

The photoelectron spectra presented in the previous sections show no evidence of mixed valency or valence fluctuations in $AuTe_2$. In the spectra no indications of different types of Au or Te atom could be detected, nor indications of a continuous distribution of types of atoms that would result in excessive broadening of spectral lines. Moreover, the spectra show a broad Au 5d band lying several electron volts below the Fermi energy. From the position of the core levels, tentative values for the valencies of the atoms can be obtained. The data suggest that in $AuTe_2$ all Au have a formal valency Au(I). In an ionic picture this corresponds to the charge distributions $Au^+(5d^{10})$ and $Te^{-1/2}(5p^{4.5})$.

These observations for $AuTe_2$ are in good agreement with band structure calculations by Krutzen and Inglesfield [15]. These are fully relativistic *ab initio* calculations using the spherical wave approximation. The calculations were carried out for the average structure (without modulation), and for the modulated structure (approximated by a

commensurable supercell). The calculated band structure shows a Au 5d contribution extending from -6.5 eV to -4.0 eV below the Fermi energy E_F, with a small extended tail up to 1.5 eV above E_F. The main contribution near E_F comes from Te 5p states. The differences in occupation numbers between the average and the modulated structure were found to be quite small. Moreover, the charge differences between the two types of Au atom in the modulated structure are very small (only 0.08 electrons). The differences between the binding energies of the two types of Au atom are also small (less than 0.03 eV for Au; less than 0.05 eV for Te).

The conclusion from the spectra and from the calculations is that the large variation in coordination and interatomic distances along the modulation direction hardly influences the charge distribution and the valences of the atoms in $AuTe_2$.

The band structure calculations show that the modulation of the structure induces large changes of the energy bands near the Fermi energies. These bands have predominantly Te 5d character. Therefore the modulation is presumably driven by Te–Te bonding interactions, associated with the formation of Te–Te pairs, and not by a valence disproportionation into Au(I) and Au(III).

$AuTe_2$ is a metallic conductor. The band structure calculations show that the Fermi level lies in the Te 5p band; the density of Au 5d states at E_F is small. Therefore the electrical conductivity is due to holes mainly located at the Te atoms.

It may be interesting to compare $AuTe_2$ with $BaBiO_3$. This compound has received attention because partial substitution of Ba by K leads to superconductivity with values of T_c up to 13 K [27]. The chemical formula $BaBiO_3$ suggests a formal valency of four for Bi. However, a valency of four is usually not stable for Bi. The fact that undoped $BaBiO_3$ is a semiconductor was ascribed initially to a static charge-density wave, corresponding to a valence disproportionation into Bi(III) and Bi(V) [27]. However, recent band structure calculations [28] and x-ray absorption spectra [29] showed no evidence for this valence disproportionation of Bi. The best interpretation is one in terms of a charge-density wave on the oxygen lattice. There is strong hybridization between O(2p) and Bi(6s) orbitals. The electrical conductivity is attributed to electron holes mainly on the oxygen atoms.

This discussion is also related to the high-T_c superconductors $YBa_2Cu_3O_{7-\delta}$ and related compounds. Initially it was assumed that doping leads to a mixed valency of the Cu atoms, with the valences Cu(II) and Cu(III) [29]. Later spectroscopic investigations showed that the electron holes, responsible for the conductivity, are located predominantly on the oxygen atoms [30].

Acknowledgments

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