

Photoelectron spectroscopy study of the electronic structure of the incommensurate intergrowth compounds  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  with  $n=1,2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 5949

(<http://iopscience.iop.org/0953-8984/7/29/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 21:47

Please note that [terms and conditions apply](#).

# Photoelectron spectroscopy study of the electronic structure of the incommensurate intergrowth compounds $(\text{SbS})_{1.15}(\text{TiS}_2)_n$ with $n = 1, 2$

Y Ren, C Haas and G A Wiegers

Chemical Physics, Materials Science Centre, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

Received 14 March 1995, in final form 2 May 1995

**Abstract.** The electronic structure of the inorganic misfit-layer compounds  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  ( $n = 1, 2$ ) has been investigated using x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) and x-ray absorption spectroscopy (XAS). These compounds are built of alternating modulated double-layers of SbS with the NaCl-type structure and sandwiches  $\text{TiS}_2$  (for  $n = 1$ ) or paired sandwiches  $\text{TiS}_2$  (for  $n = 2$ ) with 1T- $\text{TiS}_2$  structure. The XPS spectra of the Sb 3d core levels show a splitting of 1.1 eV, indicating two states for Sb, corresponding to the two types of Sb atoms present in the crystal structure. The XPS of 2s and 2p of sulphur atoms are a superposition of the spectra of S in SbS and in  $\text{TiS}_2$ . The valence band spectrum is mainly from the S 3p bands; a small peak just below the Fermi energy is attributed to electrons in the Ti 3d  $t_{2g}$  conduction band. The Ti 2p x-ray absorption spectrum shows structure, due to multiplet and crystal field interactions. The electronic structures of the misfit-layer compounds can be considered to be a superposition of the electronic structures of the two subsystems SbS and  $\text{TiS}_2$ , but with energy bands broadened due to the incommensurate modulation.

## 1. Introduction

There is a growing interest in structures and properties of crystals without three-dimensional periodicity, such as the incommensurate intergrowth compounds. So-called misfit-layer compounds, denoted by  $(\mathcal{M}\mathcal{X})_{1+\delta}(\mathcal{T}\mathcal{X}_2)_n$  ( $\mathcal{M} = \text{Sn, Pb, Sb, Bi}$  or rare earth elements;  $\mathcal{T} = \text{Ti, V, Cr, Nb}$  or  $\text{Ta}$ ;  $\mathcal{X} = \text{S}$  or  $\text{Se}$ ; and  $n = 1$  or  $2$ ), have intergrowth structures [1]. They are built up by an alternate stacking of double layers of  $\mathcal{M}\mathcal{X}$  with a distorted rock-salt structure and  $(\mathcal{T}\mathcal{X}_2)_n$  sandwiches with  $\mathcal{T}$  in trigonal prisms or trigonal antiprisms of  $\mathcal{X}$  depending on the transition metal  $\mathcal{T}$ . For all misfit compounds found so far, the two subsystems have a common reciprocal plane ( $b^*$ ,  $c^*$ ). The periodicities along the two collinear  $a$  axes are generally incommensurate, so that the complete structure is characterized by the two mutually modulated subsystems, and is accurately described using *superspace* symmetry [2].

The electronic structure and the physical properties of these compounds have been investigated using various methods [1, 3, 4]. For some misfit-layer compounds the electronic structure was considered as a superposition of energy bands of the two subsystems. However, a recent band structure calculation on  $(\text{SnS})_{1.20}\text{NbS}_2$  using a supercell approximation showed that there is a strong covalent interaction between the two subsystems SnS and  $\text{NbS}_2$  [5]. Hall measurements on the Sn- and Pb-containing compounds indicated a small transfer of electrons from SnS or PbS to the  $\mathcal{T}\text{S}_2$  sandwiches [1], which was confirmed by x-ray absorption and reflection electron-energy-loss spectroscopy performed

by Ohno [3]. Photoelectron spectra showed that charge transfer is absent or small in these compounds [4, 7, 8]. Rare-earth-containing misfit-layer compounds showed clearly a charge transfer from the rare-earth elements to the transition-metal sulphide layers, leading to a trivalent state for the rare-earth elements [6]. The Bi-containing compounds form a separate class. Hall measurements showed that there is no significant charge transfer from the BiS layer to the  $\text{TaS}_2$  layer in  $(\text{BiS})_{1.08}\text{TaS}_2$ , which points to the divalent state for Bi [9]. A valence of three for Bi was deduced from interatomic distances in  $(\text{BiSe})_{1.09}\text{TaSe}_2$  [10]. X-ray photoemission spectroscopy showed the valency for Bi in  $(\text{BiS})_{1.09}\text{NbS}_2$  to be close to three [8]. On the other hand, it was concluded by Ohno [11] from various spectroscopic measurements that charge transfer does occur in the Bi-containing compounds, and it was proposed that the transferred electrons, which lie primarily between the  $\mathcal{M}\mathcal{X}$  plane and the  $\mathcal{X}$  plane of the  $\mathcal{T}\mathcal{X}_2$  sandwiches, participate in weak bonds between the two subsystems.

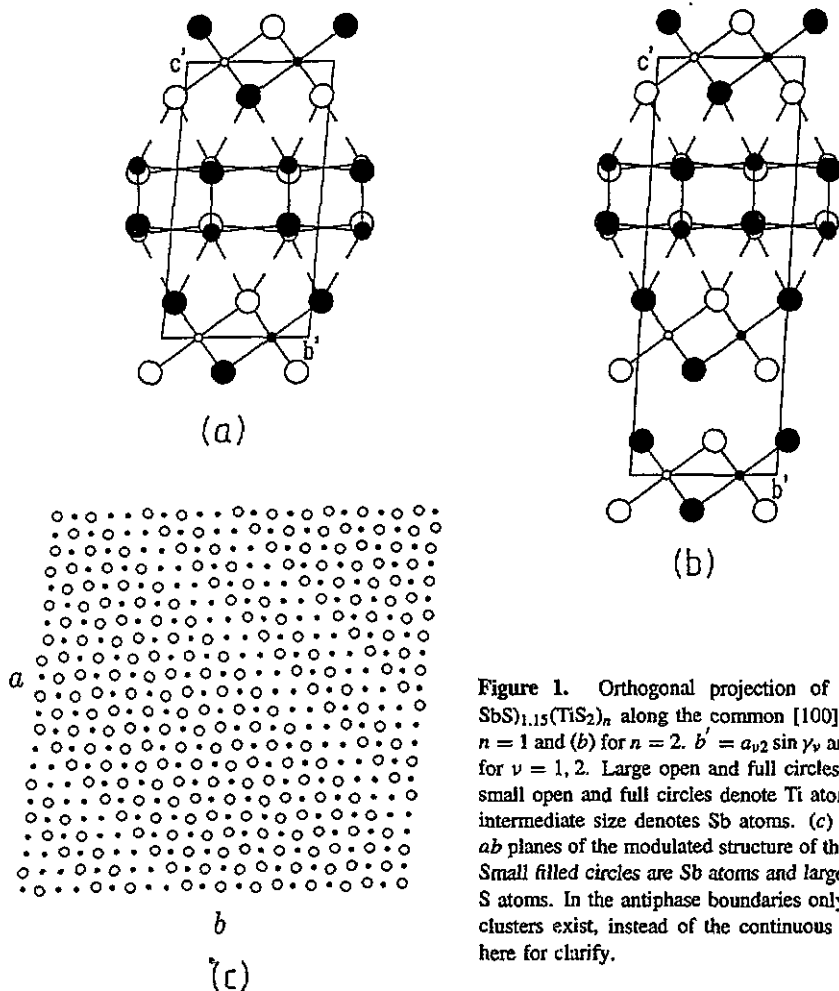


Figure 1. Orthogonal projection of the structure of  $\text{SbS}_{1.15}(\text{TiS}_2)_n$  along the common [100] direction (a) for  $n = 1$  and (b) for  $n = 2$ .  $b' = a_{\nu 2} \sin \gamma_{\nu}$  and  $c' = a_{\nu 3} \sin \beta_{\nu}$  for  $\nu = 1, 2$ . Large open and full circles denote S atoms, small open and full circles denote Ti atoms and circles of intermediate size denotes Sb atoms. (c) One layer of the  $ab$  planes of the modulated structure of the  $\text{SbS}$  subsystem. Small filled circles are Sb atoms and large open circles are S atoms. In the antiphase boundaries only Sb-Sb and S-S clusters exist, instead of the continuous chains as shown here for clarity.

Recently, we have reported the crystal structures of the Sb-containing compounds  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  with  $n = 1$  and 2. These compounds form a new type of misfit-layer compounds. The structure can be described in terms of  $(3 + 2)$ -dimensional superspace [12, 13]. In the compound  $(\text{SbS})_{1.15}\text{TiS}_2$  the two subsystems  $\text{SbS}$  and  $\text{TiS}_2$  are

**Table 1.** Subsystem unit cell dimensions of  $(\text{SbS})_{1.15}\text{TiS}_2$  and  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$ .

Compound	Subcell	$\nu$	$a_{\nu 1}$ (Å)	$a_{\nu 2}$ (Å)	$a_{\nu 3}$ (Å)	$\alpha_{\nu}$ (deg)	$\beta_{\nu}$ (deg)	$\gamma_{\nu}$ (deg)
$(\text{SbS})_{1.15}\text{TiS}_2$	$\text{TiS}_2$	1	3.403(1)	5.911(1)	11.385(1)	84.39(1)	82.817(8)	90.01(1)
	SbS	2	5.908(2)	5.936(2)	11.311(1)	83.973(8)	85.87(1)	84.06(1)
$(\text{SbS})_{1.15}(\text{TiS}_2)_2$	$\text{TiS}_2$	1	3.405(4)	5.898(4)	17.030(2)	86.39(2)	84.94(2)	89.96(2)
	SbS	2	5.902(4)	5.924(4)	17.019(2)	85.93(2)	85.38(2)	84.23(2)

stacked alternately, forming a stage-1 phase, whereas the stage-2 phase  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  has paired sandwiches  $\text{TiS}_2$  with a stacking sequence  $\dots [\text{TiS}_2][\text{SbS}][\text{TiS}_2][\text{TiS}_2][\text{SbS}][\text{TiS}_2] \dots$ . The projections of the structures along the common [100] directions are depicted in figure 1(a) and (b) for  $n = 1, 2$ , respectively; the subsystem unit cell dimensions for the two compounds are listed in table 1. The Ti atoms are coordinated octahedrally by S atoms as in 1T- $\text{TiS}_2$ . Besides the mutual modulation of the two subsystems, an additional modulation is present with a wave vector  $\mathbf{q} = 0.818(\mathbf{a}_{\text{SbS}}^* + \mathbf{b}_{\text{SbS}}^*)$  along the [110] diagonal of the SbS reciprocal lattice. The structure determination revealed zigzag clusters, with Sb-Sb and S-S contacts along the  $[1\bar{1}0]$  direction of the SbS lattice. The interface modulated ordering of Sb/S of the SbS subsystem is illustrated in figure 1(c), where the zigzag chains of closed circles are mainly Sb (occupancy larger than 0.60) while the zigzag chains of open circles are mainly S atoms. From the x-ray structure refinements [12, 13], one finds that about 22% of Sb atoms have Sb-Sb contacts. Electrical transport properties measured on single crystals of  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  for  $n = 1, 2$  showed charge transfer from the SbS to the  $\text{TiS}_2$  layers [14]. In this paper we present an experimental investigation on the electronic structure of these new type misfit-layer compounds, using x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) and soft x-ray absorption spectroscopy (XAS). The results are compared with the spectra of Ti, 1T- $\text{TiS}_2$  and  $\text{Sb}_2\text{S}_3$ .

## 2. Experimental

The preparation of the misfit-layer compounds  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  with  $n = 1, 2$  has been described previously [12, 13]. The XPS data were measured using a small-spot VG ESCA machine. The background pressure is in the low  $10^{-10}$  Torr range. The radiation source was an Al anode using a monochromatized Al  $K\alpha$  line ( $\hbar\omega = 1486.6$  eV). Different spot sizes were used for different resolutions. The energy resolution is 0.72 eV for the Sb 3d peaks, 0.99 eV for the S 2s and S 2p peaks and 1.16 eV for the Ti 3p peaks. The UPS measurements were performed using the He I resonance line at  $\hbar\omega = 21.2$  eV. The XAS spectra were collected at the 5U.1 beam line station of the Synchrotron Radiation Source, Daresbury Laboratory, UK. The spectra were recorded using the total electron yield (TEY) mode by measuring the drain current. The mean-probing depth of XAS in the TEY mode is estimated to be about 40 Å. The intensity of the XAS spectra was scaled by dividing by the photoyield of a clean Al mesh. The photon energy resolution at the Ti 2p absorption edge ( $\sim 460$  eV) was approximately 0.2 eV. The energy scale was calibrated by using the known peak position of the Ti 2p spectrum of  $\text{TiO}_2$ .

For the misfit-layer compounds and  $\text{TiS}_2$  all measurements were performed on single crystals. Each specimen was glued with silver epoxy to an aluminium frame. The sample surfaces were cleaned by stripping several layers with scotch tape, putting them in the chamber and stripping again in the preparation chamber with a base pressure of  $10^{-9}$  Torr for XPS and UPS. An as-grown bulk sample  $\text{Sb}_2\text{S}_3$  was scraped with a diamond file in

order to clean the surface. The samples with fresh surfaces were immediately transported to the measurement chamber. For the XAS measurements, the sample surfaces were cleaned by stripping (for the single crystals) or by scraping (for bulk materials) in the measurement chamber just before measurement. In order to focus the beam line for x-ray absorption spectroscopy, a luminescent spray was painted on one side (opposite to the incident x-ray beam) of a movable diamond file which was used to scrape bulk samples. This painted file enabled us to focus the beam spot exactly on any part of the samples as desired. The fresh surfaces showed hardly any contamination by oxygen and carbon. For comparison, during data analysis each spectrum is normalized to the maximum intensity in the scanning region.

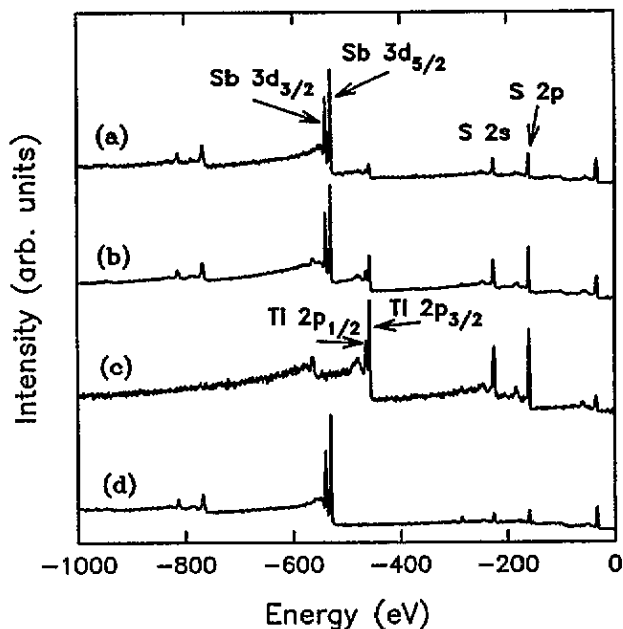


Figure 2. Core-level XPS spectra of the compounds (a)  $(\text{SbS})_{1.15}\text{TiS}_2$ , (b)  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$ , (c)  $\text{TiS}_2$  and (d)  $\text{Sb}_2\text{S}_3$ .

### 3. Results and discussion

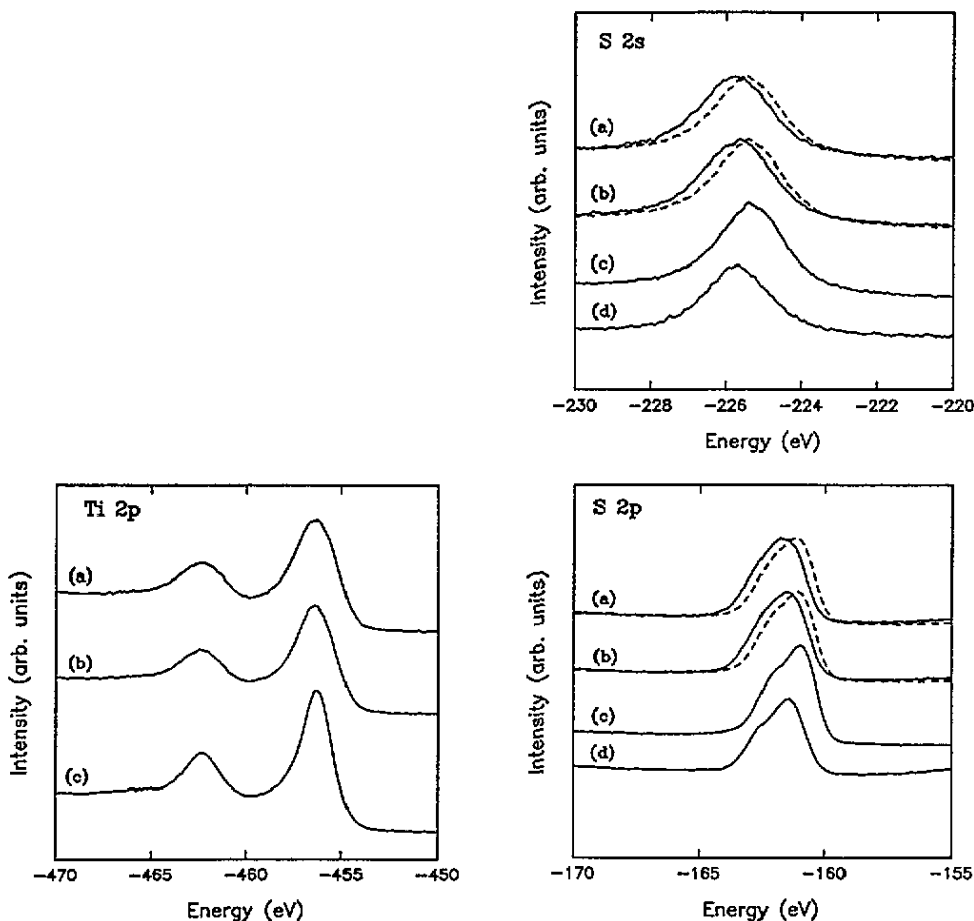
Figure 2 shows a wide scan of the core-electron XPS spectra of  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  with  $n = 1, 2$ ,  $\text{TiS}_2$  and  $\text{Sb}_2\text{S}_3$ . The relative intensities in the spectra give no evidence for preferential cleavage, but indicate the bulk composition. Binding energies of core-level electrons with respect to the Fermi energy of the sample as obtained from XPS measurements are given in table 2.

The Ti 2p core-level XPS spectra for the misfit-layer compounds and for  $\text{TiS}_2$  are shown in figure 3. There is no energy shift between the spectra of different compounds, which means the average environment for Ti in the misfit compounds is almost the same as in  $1\text{T-TiS}_2$ . However, the peaks become broader (see the change of FWHM in table 2) from  $\text{TiS}_2$  to the stage-2 compound to the stage-1 compound. The broadening is stronger than in the compounds  $(\text{SnS})_{1.20}\text{TiS}_2$  [8]. This shows that the incommensurate mutual modulation of  $\text{TiS}_2$  by  $\text{SbS}$  strongly influences the Ti atoms in the misfit-layer compounds. Note that the ratio of the area of the Ti 2p<sub>3/2</sub> peak and that of the Ti 2p<sub>1/2</sub> is about 3:1, instead of 2:1 as expected for spin-orbit splitting only.

**Table 2.** Core-level electron binding energies in eV. The FWHM of each peak is given in parentheses.

Core electron	$(\text{SbS})_{1.15}\text{TiS}_2$	$(\text{SbS})_{1.15}(\text{TiS}_2)_2$	$\text{TiS}_2$	$\text{Sb}_2\text{S}_3$	$\text{Sb}_2\text{S}_3^{(a)}$	$\text{Sb}_2\text{S}_5^{(a)}$	$\text{Sb}^{(a)}$
Sb 3d <sub>3/2</sub>	538.86(1.26)	538.93(1.50)	—	538.72(1.44)	539.0	538.7	—
Sb 3d <sub>5/2</sub>	537.77(1.08)	537.75(1.67)	—	—	—	—	537.8
	529.53(1.32)	529.57(1.57)	—	529.36(1.48)	529.7	529.4	—
	528.43(1.18)	528.42(1.83)	—	—	—	—	528.5
Ti 2p <sub>1/2</sub>	462.27(2.70)	462.33(2.54)	462.25(1.94)	—	—	—	—
Ti 2p <sub>3/2</sub>	456.29(2.55)	456.32(2.34)	456.24(1.89)	—	—	—	—
S 2s	225.73(2.18)	225.64(2.21)	225.28(2.00)	225.68(2.03)	—	—	—
S 2p <sub>1/2</sub>	162.66(1.42)	162.56(1.47)	162.16(1.27)	162.57(1.33)	—	—	—
S 2p <sub>3/2</sub>	161.43(1.52)	161.33(1.56)	160.92(1.36)	161.36(1.37)	—	—	—

(a) Taken from [15].

**Figure 3.** The Ti 2p core-level XPS spectra of the compounds (a)  $(\text{SbS})_{1.15}\text{TiS}_2$ , (b)  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  and (c)  $\text{TiS}_2$ .**Figure 4.** The S 2s (top) and S 2p (bottom) core-level XPS spectra of the compounds (a)  $(\text{SbS})_{1.15}\text{TiS}_2$ , (b)  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$ , (c)  $\text{TiS}_2$  and (d)  $\text{Sb}_2\text{S}_3$ .

Since the S atoms are located in two different subsystems in the misfit layer compounds,

one expects additional peaks for the S core-level XPS spectra. However, XPS measurements on  $(\text{PbS})_{1.18}\text{TiS}_2$  did not show any evidence for this, which implies that the S atoms in the PbS subsystem are similar to the S atoms in the  $\text{TiS}_2$  sandwiches [3]. The S 2s and 2p XPS spectra for the Sb-containing misfit-layer compounds are plotted in figure 4; no additional structure is found. The peaks are rather broad, but the width might be due to the superposition of corresponding peaks of the two subsystems. Assuming that the S atoms in the misfit-layer compounds have the same chemical environment as in  $1\text{T-TiS}_2$  and  $\text{Sb}_2\text{S}_3$ , and that the ratio of the different states is determined by the composition of misfit compounds, a spectrum can be calculated by adding the spectra of  $\text{TiS}_2$  and  $\text{Sb}_2\text{S}_3$  (the dotted curves in figure 4). The spectra calculated in this way show a distinct shift with respect to the observed spectra of the misfit-layer compounds. Also, a direct comparison with the spectra of  $\text{TiS}_2$  and  $\text{Sb}_2\text{S}_3$  shows clear differences: the peaks for the misfit-layer compounds shift to higher binding energy with respect to  $\text{TiS}_2$ , but are located at nearly the same position as in  $\text{Sb}_2\text{S}_3$ . The energy shift of S 2s and 2p peaks may be ascribed to an increase of the Fermi energy ( $E_F$ ) of the misfit-layer compounds as a result of a transfer of electrons to the Ti 3d  $t_{2g}$  conduction band. However, the Ti core-level XPS spectra are not shifted compared to  $\text{TiS}_2$  (see figure 3). This may be due to the following factors: (a) assuming the rigid band model is valid, increase of  $E_F$  by charge transfer should result in an increase of all core-level binding energies; but (b) since the transferred electrons fill the Ti 3d band, the Ti atoms will be less positive, which leads to a decrease of the binding energy of Ti core-level electrons. Although the S atoms around van de Waals gaps of the paired  $\text{TiS}_2$  layers are not bonded with the Sb atoms of SbS, the S 2s and 2p spectra of  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  are very similar to the spectra of  $(\text{SbS})_{1.15}\text{TiS}_2$ .

In these misfit-layer compounds, two different types of Sb atoms in SbS can be distinguished: one type of Sb is surrounded by five S atoms in the SbS subsystem; but for the other type two Sb-S bonds along the  $a_{\text{SbS}}$  and  $b_{\text{SbS}}$  axes are replaced by two short Sb-Sb contacts (see figure 1 (c)). This will make the electronic state of the Sb atoms within the Sb-Sb clusters different from that of the other Sb atoms. The Sb 3d core-level XPS spectra (figure 5) clearly show additional structure at the low binding energy side of the main Sb  $3d_{3/2}$  and  $3d_{5/2}$  peaks. An analysis reveals two sets of peaks from the two Sb states with a splitting energy of 1.1 eV (see table 2). From the ratio of the area of the two sets of peaks, one finds about 22% of the Sb atoms with lower binding energy for  $(\text{SbS})_{1.15}\text{TiS}_2$  and 24% for  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  (the same within the experimental accuracy). The crystal structure determination of the misfit-layer compounds has shown that about 22% of the Sb atoms form Sb-Sb bonds. This indicates that the state of lower binding energy should be assigned to the Sb atoms in the Sb-Sb clusters. The other Sb atoms have nearly the same binding energy as found in  $\text{Sb}_2\text{S}_3$ , indicating a valency of three. According to data of Sb in  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_5$  and metal Sb measured by Morgan and co-workers [15] (see table 2), the Sb 3d core-level electron binding energy difference between trivalent Sb in  $\text{Sb}_2\text{S}_3$  and the metallic Sb is about 1.2 eV. Recently, the core-level binding energies of metallic Sb was measured using XPS. The binding energy of the Sb  $3d_{5/2}$  core electron is 528.4 eV with a FWHM of 1.6 eV [16]. Comparison with our data indicates that the Sb atoms in the Sb-Sb clusters have a valency similar to Sb atoms in metal.

Since no antimony monosulphide could be prepared, the Sb-containing misfit layer compounds provide the first example of an SbS phase, though existing only as an interface between  $\text{TiS}_2$  sandwiches. Charge transfer as well as the interface modulation could stabilize this SbS phase. How much transferred charge is enough for the stabilization, and why is the SbS part modulated in this way? This is not yet fully understood. Another question is whether the interface modulation of the SbS subsystem is a unique one, or is dependent

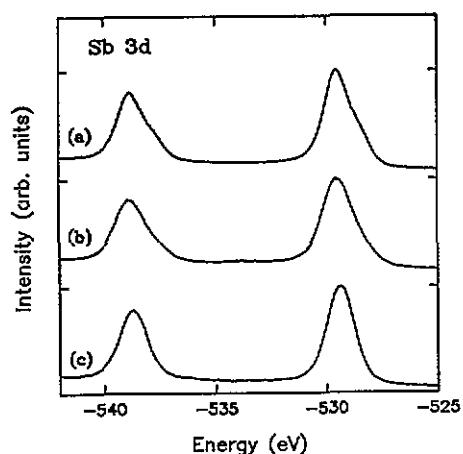


Figure 5. The Sb 3d core-level XPS spectra of the compounds (a)  $(\text{SbS})_{1.15}\text{TiS}_2$ , (b)  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  and (c)  $\text{Sb}_2\text{S}_3$ .

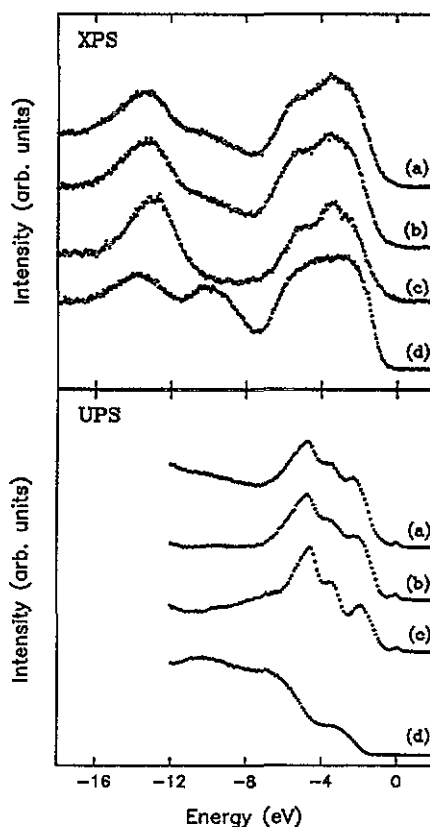


Figure 6. Valence band XPS (top) and UPS (bottom) spectra of the compounds (a)  $(\text{SbS})_{1.15}\text{TiS}_2$ , (b)  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$ , (c)  $\text{TiS}_2$  and (d)  $\text{Sb}_2\text{S}_3$ .

on sample preparation conditions. In order to answer this question, we synthesized the same Sb-containing compounds, but quenched the samples from high temperature to room temperature, instead of slowly cooling the samples. XPS measurements performed on a crystal of  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  obtained in this way *did not* show the extra splitting of the Sb core-level spectra, indicating that only one state of Sb (the trivalent state) is present in this crystal, instead of two states for Sb found in the samples obtained by slow cooling. The absence of the Sb 3d splitting suggests that the quenched crystal may have another structure. It is worth noting that the misfit layer compound 'BiTaS<sub>3</sub>' prepared by different research groups has different interface modulations, and thus different structures [9, 17]. In the quenched crystal the Sb-Sb as well as S-S contacts are probably more randomly arranged. Unfortunately, the complete structure of the quenched crystal is still not yet clear.

The valence band of these misfit-layer compounds has been studied using XPS and UPS (figure 6). The overall structure is well represented by a superposition of bands of  $\text{TiS}_2$  and  $\text{Sb}_2\text{S}_3$ . In the UPS spectra of the misfit-layer compounds and  $\text{TiS}_2$ , a small peak just below the Fermi level originates from a partial occupation of the Ti 3d  $t_{2g}$  conduction band. The Ti 3d electrons are not visible in the XPS spectra, because the photoionization cross section of Ti 3d electrons at 1486.6 eV is small. The triplet in the energy region 1–7 eV below the Fermi level consists of the bonding state of Sb-S bonds of the SbS subsystem and the



Ti-S bonding state of  $\text{TiS}_2$ , and has mainly S 3p character. The shoulder at about 8–12 eV is attributed to the Sb 5s core-level electrons and, as is expected, its intensity is stronger for  $(\text{SbS})_{1.15}\text{TiS}_2$  than for  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$ . The S 3s peak of the misfit-layer compounds is located at about 13.5 eV, with a small shift of about 0.2 eV to the higher binding-energy side with respect to the S 3s peak of the  $\text{TiS}_2$  compound. Since the peak area in the UPS spectra is proportional to the cross section and the number of electrons in the energy band, the occupancy for the Ti 3d energy band was estimated by comparing the area of the Ti 3d peak to that of the S 3p triplet. The cross section of the Ti 3d and S 3p electrons for the He I resonance energy ( $\hbar\omega = 21.2 \text{ eV}$ ) are known. The number of electrons in S 3p bands is six per atom. We assume that the number of Ti and S atoms involved in UPS is proportional to the composition of the compounds. The occupancy of the Ti 3d conduction band was *estimated* to be about 0.06 electrons per Ti for  $\text{TiS}_2$  as well as the misfit-layer compounds. This is much smaller than values obtained from Hall effect measurements [14], which show the population of the Ti 3d band to be  $0.57e/\text{Ti}$  for  $(\text{SbS})_{1.15}\text{TiS}_2$  and  $0.34 e/\text{Ti}$  for  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$ . We have no explanation for the discrepancy.

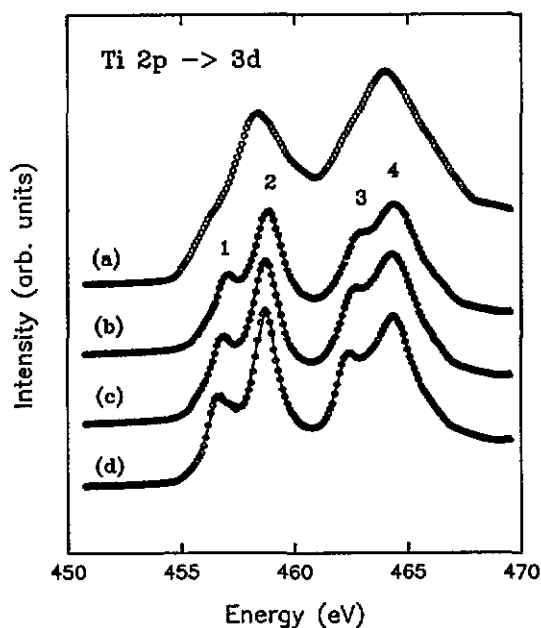


Figure 7. Ti 2p XAS spectra of (a) Ti, (b)  $(\text{SbS})_{1.15}\text{TiS}_2$ , (c)  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  and (d)  $\text{TiS}_2$ .

Since the development of soft x-ray absorption spectroscopy using synchrotron radiation sources, the  $L_{2,3}$  x-ray absorption edges of the transition metals have been extensively studied, both experimentally and theoretically. The transition metal 2p XAS spectra are dominated by the  $2p \rightarrow 3d$  transitions. The created 2p core hole has strong Coulomb and exchange interactions with the 3d electrons. These interactions cause a redistribution of intensities of the  $L_2$  and  $L_3$  peaks; there is a shift of the spectral weight away from the thresholds, and a reduction of the peak splitting [19]. The 2p XAS spectra of transition metal compounds are characteristic for the ground-state configuration and the crystal-field strength and symmetry [20,21]. These effects are well illustrated by the Ti 2p absorption spectra of metallic Ti,  $\text{TiS}_2$  and the two misfit-layer compounds (figure 7). The spectrum of metallic Ti has two main peaks due to the spin-orbit coupling of the 2p core holes.

The spin-orbit splitting (defined as the energy difference of the  $L_3$  and  $L_2$  peak maxima) is found to be  $\Delta_{SO} = 5.6$  eV, close to the electron-energy-loss spectroscopy (EELS) result  $\Delta_{SO} = 5.7$  eV [18], but smaller than the value of  $\Delta_{SO} = 6.2$  eV obtained from the XPS spectrum [22]. The Ti 2p XAS spectrum shape of Ti metal is quite different from that obtained using EELS [18]. The ratio of the  $L_3$  to  $L_2$  near-edge structure intensities strongly deviates from the statistical value 2:1, which is expected if the effect of spin-orbit interaction of the 3d electrons and 2p-3d Coulomb and exchange interactions can be neglected. In the spectra of the  $\text{TiS}_2$ -based compounds, the spin-orbit doublet is further split into two groups of peaks, mainly as a result from crystal-field splitting. The absorption edge starts at a photon energy of about 456.0 eV, close to the Ti  $2p_{3/2}$  peak position of the XPS data. The Ti atoms in  $\text{TiS}_2$  are located in trigonal-antiprisms of S atoms with distorted octahedral symmetry. Thus the spectra can be explained in the following way: the first and second peak from the left are related to the  $t_{2g}$  and the  $e_g$  symmetries of the  $L_3$  edge, respectively, and the third and fourth peak are related to  $t_{2g}$  and  $e_g$  states of the  $L_2$  edge. The splitting between the first and second peak is closely related to the crystal field strength, although it is not equal to it [20]. Fitting the spectra using Lorentz peak shape, the position and the full width at half maximum (FWHM) of each peak in the Ti 2p XAS spectra were obtained, which together with the splitting for the  $L_3$  edge ( $\Delta_{21}$ ) and for the  $L_2$  edge ( $\Delta_{43}$ ) are listed in table 3. It can be seen that from  $\text{TiS}_2$  to  $(\text{SbS})_{1.15}(\text{TiS}_2)_2$  to  $(\text{SbS})_{1.15}\text{TiS}_2$  the first peak systematically shifts to higher energy; the splitting of the  $L_3$  edge ( $\Delta_{21}$ ) becomes smaller, while the peaks become broader. A comparison with a theoretical calculation of the  $L_{2,3}$  x-ray absorption edges of  $\text{Ti}^{4+}$  in octahedral symmetry using an atomic description of the  $2p^6 3d^0$  to  $2p^5 3d^1$  excitation with the inclusion of the crystal field [20] shows that the crystal-field strength for  $\text{TiS}_2$  is  $10Dq \approx 1.2$  eV. The reduced splitting in the misfit-layer compounds  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  could be due to a smaller crystal field splitting in these compounds. However, an increased occupation of the Ti 3d  $t_{2g}$  band in the misfit-layer compounds  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$ , due to charge transfer as indicated by the Hall measurements [14], would lead to a shift to higher energy of the first 3d  $t_{2g}$ -type peak, and this would also lead to a smaller splitting between 3d  $e_g$  and 3d  $t_{2g}$ -type peaks, as observed.

Table 3. Energy positions of the peaks ( $E_n$  for  $n = 1, \dots, 4$ ) with the FWHM given in parentheses and the splitting for the  $L_3$  edge ( $\Delta E_{21} = E_2 - E_1$ ) and for the  $L_2$  edge ( $\Delta E_{43} = E_4 - E_3$ ). In each case the region is Ti 2p.

Compound	$E_1$ (eV)	$E_2$ (eV)	$\Delta E_{21}$ (eV)	$E_3$ (eV)	$E_4$ (eV)	$\Delta E_{43}$ (eV)
$\text{TiS}_2$	456.69(0.67)	458.74(0.75)	2.05	462.35(0.68)	464.32(1.38)	1.97
$(\text{SbS})_{1.15}(\text{TiS}_2)_2$	456.78(0.66)	458.73(0.85)	1.95	462.48(0.76)	464.34(1.49)	1.86
$(\text{SbS})_{1.15}\text{TiS}_2$	456.95(0.69)	458.85(0.88)	1.90	462.67(0.83)	464.47(1.49)	1.80

#### 4. Conclusions

We have studied the electronic structure of new-type misfit-layer compounds  $(\text{SbS})_{1.15}(\text{TiS}_2)_n$  with  $n = 1, 2$  by means of XPS, UPS and XAS. The crystal structure consists of two subsystems of SbS and  $\text{TiS}_2$  which are mutually incommensurately modulated. The SbS subsystem itself shows an ordering of Sb/S atoms on the rock-salt-like structure, involving metallic Sb-Sb contacts which zigzag along a diagonal of the lattice in the  $ab$  plane. The splitting

in the Sb core-level XPS spectra clearly reveals two different electronic states for Sb: one is trivalent and the other is similar to Sb atoms in metallic Sb. 22% of the Sb atoms are found in this latter state, in perfect agreement with the crystal structure determination. These compounds are the first example of mixed-valent misfit-layer compounds. The valence bands of the misfit-layer compounds can be regarded as a superposition of the energy bands of the two types of layers. The conduction band consists of the partially filled Ti  $3d_{2g}$  band of  $TiS_2$ . However, no clear evidence for charge transfer has been found. The incommensurately mutual modulation leads to the broadened spectrum peaks.

### Acknowledgments

We are very grateful to Mr H J Terpstra for assistance with all experiments. We would like to thank Mr A Heeres for kind help with the XPS and UPS experiments and Dr M Roper for assistance with the XAS experiment in SRS, Daresbury, UK. This work is part of the research program of the Stichting voor Scheikundig Onderzoek Nederland (SON), which is financially supported by the Netherlands Organization for Pure Research (NWO).

### References

- [1] Wiegers G A and Meerschaut A 1992 *Incommensurate Sandwiched Layered Compounds (Material Science Forum 100 & 101)* ed A Meerschaut (New York: Trans. Tech.) pp 101–72
- [2] van Smaalen S 1992 *Incommensurate Sandwiched Layered Compounds (Material Science Forum 100 & 101)* ed A Meerschaut (New York: Trans. Tech.) pp 173–222
- [3] Ohno Y 1991 *Phys. Rev. B* **44** 1281
- [4] Ettema A R H F, Wiegers G A, Haas C and Turner T S 1992 *Surf. Sci.* **269–70** 1161
- [5] Fang C F, Ettema A R H F, de Groot R A, Haas C and Wiegers G A 1995 *Phys. Rev. B* at press
- [6] Ettema A R H F, van Smaalen S, Haas C and Turner T S 1994 *Phys. Rev. B* **49** 10585
- [7] Ettema A R H F, Wiegers G A, Haas C and Turner T S 1992 *Phys. Scr.* **41** 265
- [8] Ettema A R H F and Haas C 1993 *J. Phys.: Condens. Matter* **5** 3817
- [9] Wulff J, Meetsma A, Haange R J, de Boer J L and Wiegers G A 1990 *Synth. Met.* **39** 1
- [10] Petricek V, Cisarova I, de Boer J L, Zhou W Y, Meetsma A, Wiegers G A and van Smaalen S 1993 *Acta Crystallogr. B* **49** 258
- [11] Ohno Y 1994 *Preprint*
- [12] Ren Y, Meetsma A, Petricek V, van Smaalen S and Wiegers G A 1995 *Acta Crystallogr. B* at press
- [13] Ren Y, Meetsma A, van Smaalen S and Wiegers G A 1995 *Acta Crystallogr. B* submitted
- [14] Ren Y, Rütcher C H, Haas C and Wiegers G A 1995 in preparation
- [15] Morgan W E, Stec W J and van Wazer J R 1973 *Inorg. Chem.* **12** 953
- [16] Bastl Z, Spirovová I and Horák J 1994 *Preprint*
- [17] Gotoh Y, Onoda M, Akimoto J, Goto M and Oosawa Y 1992 *Japan. J. Appl. Phys.* **31** 3946
- [18] Fink J, Müller-Heinzerling Th, Scheerer B, Speier W, Hillebrecht F U, Fuggle J C, Zaanen J and Sawatzky G A 1985 *Phys. Rev. B* **32** 4899
- [19] Zaanen J, Sawatzky G A, Fink J, Speier W and Fuggle J C 1985 *Phys. Rev. B* **32** 4905
- [20] de Groot F M F, Fuggle J C, Thole B T and Sawatzky G A 1990 *Phys. Rev. B* **41** 928
- [21] Abbate M, de Groot F M F, Fuggle J C, Fujimori A, Tokura Y, Fujishima Y, Strebel O, Domke M, Kaindl G, van Elp J, Thole B T, Sawatzky G A and Tsuda N 1991 *Phys. Rev. B* **44** 5419
- [22] Fuggle J C and Martensson N 1980 *J. Electron Spectrosc. Relat. Phenom.* **21** 275