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An x-ray photoemission spectroscopy study of interlayer charge transfer in some misfit layer compounds

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Abstract. The misfit layer compounds with a general formula $(MX)_{1+\delta}TX_2$ (with $M = \text{Sn, Pb, Bi}$ or rare earth metal; $X = \text{S, Se}$; $T = \text{Ti, V, Cr, Nb, Ta}$ and $0.05 < \delta < 0.25$) have a stacking of MX double layers with a NaCl-type structure alternated by TX_2 sandwiches. The unit cell axes in the plane of the layers of both subsystems are equal in the b direction but are incommensurate in the a direction. To understand the stability of this remarkable and ordered stacking of the two different layers, charge transfer from the MX subsystem to the TX_2 subsystem has been suggested. In this study misfit layer compounds with Sn, Pb and Bi as the M element have been investigated with x-ray photoelectron spectroscopy. The information obtained from the core levels shows that for the Sn and Pb containing compounds the Pb and Sn atoms are divalent, and no significant charge transfer takes place between the layers. The spectra of the Bi misfit layer compound indicate a valency close to three for Bi. The stability of the misfit layer compounds is attributed to the presence of covalent interlayer bonds.

1. Introduction

The misfit layer compounds with general formula $(MX)_{1+\delta}TX_2$ (with $M = \text{Sn, Pb, Bi}$ or rare earth metal; $X = \text{S, Se}$; $T = \text{Ti, V, Cr, Nb, Ta}$ and $0.05 < \delta < 0.25$) have attracted attention in recent years. In the early seventies several authors [1, 2] studied the crystallographic properties of ternary systems MTX_3 . A layer-type structure with a large unit cell was found. A few years ago Wiegers *et al* [3] showed that these compounds have a misfit-layer-type structure, with alternating layers of MX and TX_2 (figure 1). The unit cell axes of the subsystems MX and TX are equal in the b direction and are incommensurate in the a direction. For an accurate description of the crystal structure the concepts of superspace group symmetry have been applied to these compounds [4]. Many of these misfit layer compounds have been synthesized and their crystallographic properties have been determined [5].

For a better understanding of the stability of this remarkable alternated stacking and the lattice mismatch of the two subsystems, the electronic structure is a subject of interest. Recently, several studies appeared with results obtained by different spectroscopic techniques, like resonant photoemission spectroscopy (RPES) [6], angle-resolved photoemission spectroscopy (ARUPS) [7], x-ray absorption spectroscopy (XAS) [8, 9] and reflection electron energy loss spectroscopy (REELS) [10]. X-ray photoemission spectroscopy (XPS) data were reported in some of these papers but an accurate study of the core levels in the misfit layer compounds has not appeared so far.

A careful study of the core levels in these misfit layer compounds is nevertheless worthwhile. The stability of the alternated stacking of these compounds has been ascribed

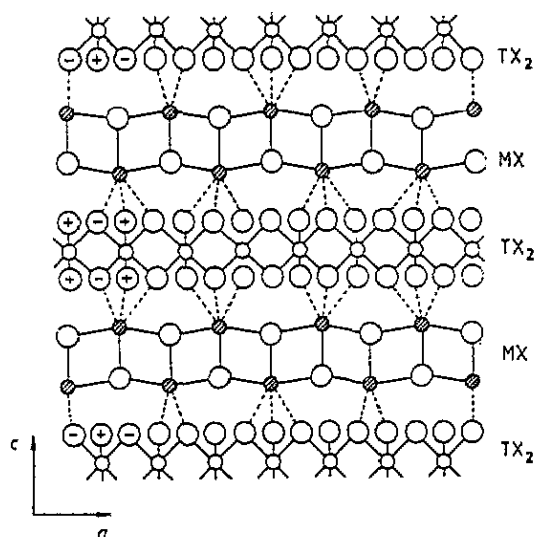


Figure 1. Projection of the crystal structure of a misfit layer compound on the ac plane. Intralayer bonds are indicated by solid lines, interlayer bonds by dashed lines. The x -atoms of the TX_2 layers are shifted by $+\frac{1}{2}b$ or $-\frac{1}{2}b$ indicated by $+$ and $-$. The coordination of M atoms (small shaded circles) by sulphur atoms changes from one M atom to another, as a result of the incommensurability of MX and TX_2 layers.

by several authors [8–11] to charge transfer from one layer to the other. Since XPS is a technique which is sensitive to the chemical environment of the atoms, it is a useful tool in the study of possible charge transfer between the two subsystems. In this paper we present a study of the core levels in several misfit layer compounds with SnS , PbS and BiS as the MX subsystem and TiS_2 , NbS_2 and TaS_2 as the TX_2 subsystem. The core levels of the different atoms in these misfit layer compounds are compared with those of atoms in similar chemical surroundings.

2. Experimental details

The misfit layer compounds and the TS_2 layer compounds were synthesized by adding the correct amounts of the elements in an evacuated quartz ampoule and heating the quartz ampoule for two weeks at $900^\circ C$ in a furnace. Single crystals were grown by vapour transport in a temperature gradient with Cl_2 as transport agent, which was obtained by the decomposition of $Pb(NH_4)_2Cl_6$ at high temperatures. Only for $2H-NbS_2$ was the growth of single crystals unsuccessful. The SnS , Sn_2S_3 , SnS_2 , PbS and Bi_2S_3 samples were synthesized by heating the metals Sn , Pb and Bi with the correct molar amount of S in an evacuated quartz ampoule for one week. After cooling, small crystals were selected from the SnS , SnS_2 and PbS batches. For the NbS_2 , Sn_2S_3 and Bi_2S_3 samples the powders were compressed into pellets and sintered at $900^\circ C$ in evacuated quartz tubes in a furnace.

The XPS measurements were carried out in a small spot ESCA machine of VG. The spot size could be varied from $150\ \mu m$ to $1000\ \mu m$. Depending on sample size, a spot size of $600\ \mu m$ was generally used. The resolution chosen was $0.2\ eV$ for most core levels. The radiation source was an Al anode using the $K\alpha$ -line with a photon energy of $1486.6\ eV$. The sample surfaces of the misfit layer compounds, TiS_2 , TaS_2 , SnS and SnS_2 were cleaned

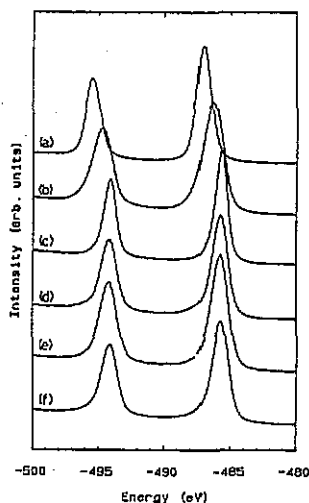


Figure 2. The Sn 3d core level spectra of the compounds (a) SnS_2 , (b) Sn_2S_3 , (c) SnS , (d) $(\text{SnS})_{1.20}\text{TiS}_2$ (e) $(\text{SnS})_{1.17}\text{NbS}_2$ and (f) $(\text{SnS})_{1.16}\text{TaS}_2$.

by stripping with Scotch tape in the preparation chamber at a base pressure of 10^{-9} Torr. The samples PbS , NbS_2 , Sn_2S_3 and Bi_2S_3 were scraped with a diamond scraper in order to clean the surfaces. The samples with fresh surfaces were transported to the main chamber (base pressure 10^{-10} Torr) within half a minute. The fresh surfaces showed hardly any contamination by oxygen and carbon. The samples did not show any charging effects, and all given energies are relative to the Fermi level.

3. Results

3.1. Sn core levels

The Sn 3d core levels for the samples SnS_2 (a), Sn_2S_3 (b), SnS (c), $(\text{SnS})_{1.20}\text{TiS}_2$ (d), $(\text{SnS})_{1.17}\text{NbS}_2$ (e) and $(\text{SnS})_{1.16}\text{TaS}_2$ (f) are shown in figure 2. Other Sn core levels in the energy range of 0 eV to 1000 eV which have been measured are also listed in table I. From the core level spectra in figure 2 it is clear that the Sn 3d electrons have the same binding energy in the misfit layer compounds with SnS as a subsystem as in the pure SnS compound. A comparison of data for SnS and SnS_2 shows that the core level binding energies are sensitive to the valency of the Sn atoms. For example the binding energy of Sn 3d electrons increases by 1.3 eV if the valency changes from two (in SnS) to four (in SnS_2).

The binding energy of the Sn 3d electrons in the Sn_2S_3 has an intermediate value. However, the linewidth of the Sn 3d levels in Sn_2S_3 is much larger than the linewidths for

Table 1. Binding energies (eV) and widths (full width at half maximum in (eV) in brackets) of the measured core electrons of Sn. The values of Sn metal are obtained from [12].

	Sn 4d	Sn 4p	Sn 3d _{5/2}	Sn 3d _{3/2}	Sn 3p _{3/2}	Sn 3p _{1/2}
Sn	24.4	83.6	484.9	493.2	714.6	756.5
SnS	24.9 (2.2)	89 (10)	485.7 (1.1)	494.1 (1.1)	715.2 (3.6)	757.2 (3.6)
Sn ₂ S ₃	25.9 (2.3)	89 (10)	486.3 (1.8)	494.7 (1.8)	715.9 (4.7)	757.8 (4.5)
SnS ₂	26.7 (1.9)	89 (10)	487.0 (1.3)	495.4 (1.3)	716.4 (3.7)	758.4 (3.6)
(SnS) _{1.20} TiS ₂	25 (3)	89 (10)	485.9 (1.4)	494.3 (1.4)	715.3 (4.3)	757.3 (4.3)
(SnS) _{1.17} NbS ₂	25 (3)	89 (10)	485.8 (1.5)	494.2 (1.5)	715.4 (4.2)	757.4 (4.4)
(SnS) _{1.16} TaS ₂	25 (3)	89 (10)	485.7 (1.5)	494.2 (1.5)	715.2 (4.4)	757.3 (4.4)

SnS and SnS₂. The average valency of three for the Sn atom in Sn₂S₃ is therefore likely to be due to Sn atoms with valencies of two and four, which are common valencies for Sn. The possibility of a mixed valence state is also indicated by the fact that the Sn atoms in Sn₂S₃ occupy two different crystallographic sites [13]. For the core levels of the Sn atoms in the misfit layer compounds there is no shift larger than 0.2 eV (which is the resolution limit of the apparatus) compared to the pure SnS compound.

The widths of the Sn 3d core levels are 0.3 to 0.4 eV larger in the misfit layer compound than in the SnS sample. For the Sn 3p levels in the misfit layer compounds the width is 0.6 to 0.8 eV larger than in the SnS sample. This additional broadening of the core levels can be understood by the observation that the Sn atoms of the MX subsystem in the misfit layer compounds have a wide variety of chemical surroundings i.e. neighbour atoms in the layers of the TX₂ subsystem, as a consequence of the incommensurate crystal structure. Therefore the (Madelung) potential at the Sn atoms varies from one site to another.

3.2. Pb core levels

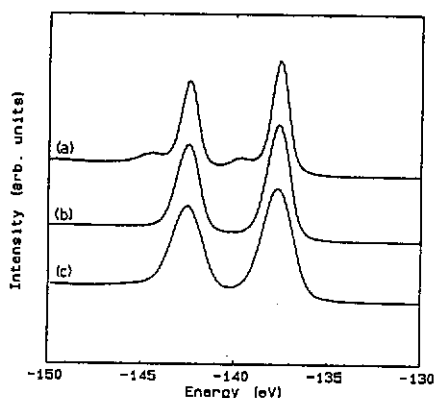
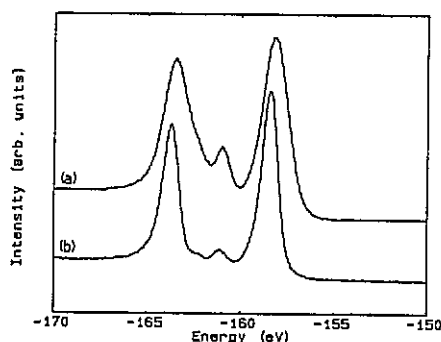
For the misfit layer compounds (PbS)_{1.14}NbS₂ and (PbS)_{1.13}TaS₂ the Pb 4f core levels are compared with the Pb 4f core levels in PbS in figure 3. The Pb core levels are listed in table 2. The Pb 4f core level spectrum of (PbS)_{1.14}NbS₂ shows no difference in binding energy with respect to the Pb 4f binding energy in PbS. But the widths of all the core levels are increased by 0.4 eV–1 eV, indicating that in these compounds also the (Madelung) potential varies at the Pb sites in (PbS)_{1.14}NbS₂. The (PbS)_{1.13}TaS₂ sample used in the experiment was rather small, and as a consequence a small spot size had to be selected, resulting in a resolution of about 0.5 eV. The width of the Pb core levels for this misfit layer compound is larger than in PbS and also larger than in (PbS)_{1.14}NbS₂. The broadening of the levels in (PbS)_{1.13}TaS₂ can be attributed to the poor resolution. For the Pb 5p core level, the natural linewidth is much larger than the resolution of the apparatus and no shift in binding energy is observed. The satellite structure of the Pb level in PbS is caused by some oxygen contamination.

3.3. Bi core levels

In table 3 the core levels of Bi in Bi metal, Bi₂S₃ and (BiS)_{1.09}NbS₂ are compared. The Bi 4f spectra in figure 4 are slightly disturbed by the presence of S 2p lines at binding energies of 161 eV and 162 eV. The binding energies of the Bi core electrons in the misfit layer compound are 0.2 eV smaller than in the compound Bi₂S₃ and 1.5 eV larger than in Bi metal. The shifts of the core levels for Sn²⁺ and Pb²⁺ in SnS and PbS with respect to the same core levels in Sn metal and Pb metal are approximately 0.8 eV. The shifts at the Sn sites between the Sn²⁺ ions in SnS and the Sn⁴⁺ ions in SnS₂ are 1.3 eV. This

Table 2. Binding energies (eV) and widths (full width at half maximum (eV) in brackets) of the measured core electrons of Pb. The values of Pb metal are obtained from [12].

	Pb 5d _{5/2}	Pb 5d _{3/2}	Pb 5p _{3/2}	Pb 5p _{1/2}	
Pb	18.1	20.7	83.3	106.4	
PbS	19.1 (1.0)	21.6 (1.0)	84 (8)	108 (8)	
(PbS) _{1.14} NbS ₂	19.1 (1.5)	21.7 (1.6)	84 (8)	107 (8)	
(PbS) _{1.13} TaS ₂	19.1 (1.9)	22.8 (1.9)	85 (8)	108 (8)	
	Pb 4f _{7/2}	Pb 4f _{5/2}	Pb 4d _{5/2}	Pb 4d _{3/2}	Pb 4p _{3/2}
Pb	136.9	141.7	412.2	434.3	643.5
PbS	137.8 (1.0)	142.7 (1.1)	413.0 (3.8)	435.0 (4.0)	644.4 (6)
(PbS) _{1.14} NbS ₂	137.9 (1.0)	142.8 (1.5)	413.0 (4.6)	435.1 (5.3)	644.5 (6)
(PbS) _{1.13} TaS ₂	138.0 (1.8)	142.8 (1.8)	413.1 (4.7)	435.1 (5.3)	644.4 (6)

**Figure 3.** The Pb 4f core level spectra of the compounds (a) PbS, (b) (PbS)_{1.14}NbS₂ and (c) (PbS)_{1.13}TaS₂.**Figure 4.** The Bi 4f core level spectra of the compounds (a) (BiS)_{1.09}NbS₂ and (b) Bi₂S₃.

comparison shows that the assumption that Bi has a valency of two in the misfit layer compound (BiS)_{1.09}NbS₂ is not justified. The spectra indicate a valency for Bi close to three (a linear interpolation between the Bi and Bi₂S₃ values leads to a value of 2.7 for the valency of Bi, but the accuracy is not high).

Table 3. Binding energies (eV) and widths (full width at half maximum (eV) in brackets) of the measured core electrons of Bi.

	Bi 5d _{5/2}	Bi 5d _{3/2}	Bi 5p _{3/2}	Bi 5p _{1/2}
Bi	23.3 (0.9)	27.1 (0.9)	93.5 (4)	118.8 (4)
Bi ₂ S ₃	25.7 (1.2)	28.8 (1.2)	95 (6)	124 (6)
(BiS) _{1.09} NbS ₂	25.4 (1.5)	28.6 (1.4)	95 (6)	120 (6)
	Bi 4f _{7/2}	Bi 4f _{5/2}	Bi 4d _{5/2}	Bi 4f _{3/2}
Bi	157.0 (1.1)	162.3 (1.0)	440.3 (3.9)	463.8 (3.9)
Bi ₂ S ₃	158.7 (1.1)	164.0 (1.1)	441.8 (4.3)	465.4 (4.8)
(BiS) _{1.09} NbS ₂	158.5 (1.5)	163.8 (1.5)	441.5 (4.5)	465.3 (5.9)

For Bi metal and Bi_2S_3 the Bi 4f lines are sharp with a full width at half maximum (FWHM) of 1.1 eV. In the compound $(\text{BiS})_{1.09}\text{NbS}_2$ the 4f core electrons have a FWHM of 1.5 eV. The larger width and the small energy shift is ascribed to inequivalent Bi sites in the lattice, and the corresponding variation of the (Madelung) potential at the Bi sites [14].

3.4. Ti core levels

It is generally observed that charge transfer from intercalated species to the transition metal d band in the early transition metal dichalcogenides does not lead to large changes of the core level binding energy. Due to the high density of states near the Fermi level, these compounds can adopt a considerable number of electrons without a large change of the electronic structure (rigid bands), and without a large shift of the Fermi level.

The Ti 2p core level spectra of TiS_2 and $(\text{SnS})_{1.20}\text{TiS}_2$ are presented in figure 5, and the Ti 3p, the Ti 3s and the Ti 2p core levels are compared in table 4. As expected, the binding energy in the misfit layer compound does not shift with respect to the value for the pure TiS_2 compound. The linewidths are slightly larger than for TiS_2 . Apparently the MX layers affect the (Madelung) potential at the Ti sites, although the Ti atoms are very well shielded by the six nearest-neighbour sulphur atoms.

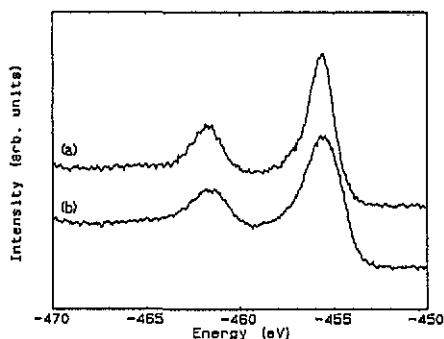


Figure 5. The Ti 2p core level spectra of the compounds (a) TiS_2 and (b) $(\text{SnS})_{1.20}\text{TiS}_2$.

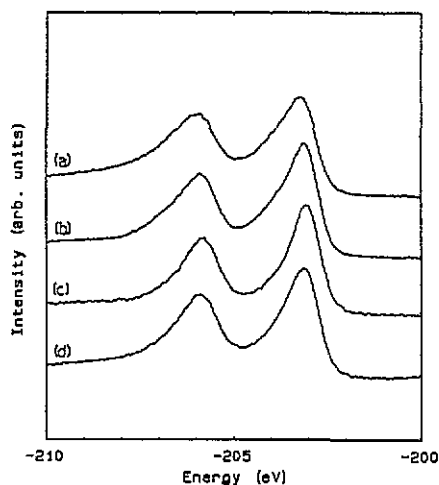


Figure 6. The Nb 3d core level spectra of the compounds (a) NbS_2 , (b) $(\text{SnS})_{1.17}\text{NbS}_2$, (c) $(\text{PbS})_{1.14}\text{NbS}_2$ and (d) $(\text{BiS})_{1.09}\text{NbS}_2$.

Table 4. Binding energies (eV) and widths (full width at half maximum (eV) in brackets) of the measured core electrons of Ti. The values for Ti metal are obtained from [12].

	Ti 3p	Ti 3s	Ti 2p _{3/2}	Ti 2p _{1/2}	Ti 2s
Ti	37.2	66.3	453.8	461.2	560.9
TiS_2	35.5 (3.0)	60.3 (5.0)	456.4 (2.0)	462.4 (2.1)	562.9 (5.3)
$(\text{SnS})_{1.20}\text{TiS}_2$	35.5 (3.1)	60.1 (5.1)	456.4 (2.2)	462.4 (2.2)	562.9 (5.5)

3.5. Nb core levels

In figure 6 the Nb 3d core levels are compared for NbS₂, (SnS)_{1.17}NbS₂, (PbS)_{1.20}NbS₂, and (BiS)_{1.09}NbS₂. The binding energies and the widths of the Nb 4p, Nb 3d and Nb 3p emission lines of the same compounds are compared in table 5. From the figure and the binding energies listed in the table there is no sign of shifts of the core levels. The shifts are all small with respect to the resolution and the natural linewidths.

Table 5. Binding energies (eV) and widths (full width at half maximum (eV) in brackets) of the measured core electrons of Nb. The values from Nb metal are obtained from [12].

	Nb 4p _{3/2}	Nb 4p _{1/2}	Nb 4s	Nb 3d _{5/2}	Nb 3d _{3/2}	Nb 3p _{3/2}	Nb 3p _{1/2}	Nb 3s
Nb	30.8	32.6	56.4	202.3	205.0	360.6	376.1	466.6
NbS ₂	32.1 (2.4)	34.4 (3.3)	57 (7)	203.5 (1.6)	206.3 (2.0)	361.9 (3.1)	377.3 (2.8)	468 (5)
(SnS) _{1.17} NbS ₂	32.0 (2.0)	33.9 (2.3)	57 (3)	203.6 (1.3)	206.4 (1.8)	362.0 (2.6)	377.4 (2.6)	468 (6)
(PbS) _{1.14} NbS ₂	32.1 (2.0)	34.1 (2.4)	57 (4)	203.7 (1.6)	206.5 (1.9)	362.1 (2.9)	377.6 (3.0)	468 (6)
(BiS) _{1.09} NbS ₂	32.1 (1.6)	33.9 (2.3)	57 (3)	203.4 (1.0)	206.3 (1.2)	361.8 (2.9)	377.2 (3.0)	468 (6)

3.6. Ta core levels

The comparison of the Ta core lines is not very accurate. The Ta 4f lines in (SnS)_{1.6}TaS₂ overlap with the emission of Sn 4d states, the Ta 5p_{1/2} peak contains a contribution of a plasmon satellite of the Ta 4f peak. The Ta 4d_{5/2} states have nearly the same energy as the S 2s states and the Ta 4p states have a large natural linewidth. The spectra of the Ta 4d states of the investigated compounds are shown in figure 7 and the values of the binding energies and widths of the measured Ta emission lines are tabulated in table 6. Only the Ta 5p_{3/2} and the Ta 4d_{3/2} allow a fair comparison. For these emission lines there is no significant shift in energy. The linewidths for these two emission lines tend to be a little larger in the misfit layer compounds.

Table 6. Binding energies (eV) and widths (full width at half maximum (eV) in brackets) of the measured core electrons of Ta. The values for Ta metal are obtained from [12].

	Ta 4f _{7/2}	Ta 4f _{5/2}	Ta 5p _{3/2}	Ta 5p _{1/2}	Ta 4d _{5/2}	Ta 4d _{3/2}	Ta 4p _{3/2}	Ta 4p _{1/2}
Ta	21.6	23.5	32.7	42.2	226.4	237.9	400.9	463.4
TaS ₂ (1T)	23.6 (1.2)	25.5 (1.7)	34.7 (2)	46.6 (6)	226.9 (5.2)	239.6 (4.0)	402 (8)	464 (9)
(SnS) _{1.16} TaS ₂	23.1 (1.0)	25.1 (2.3)	34.2 (2)	44.0 (8)	226.6 (3.0)	239.3 (4.6)	401 (5)	465 (6)
(PbS) _{1.13} TaS ₂	23.1 (1.9)	25.2 (1.9)	34.7 (3)	43.6 (10)	226.5 (4.2)	239.2 (4.2)	401 (4)	465 (5)

4. Discussion

The core levels of the metal atoms in these misfit layer compounds are compared with those in the non-intergrowth compounds. Not all the core levels provide accurate information to draw conclusions about a possible charge transfer between the two subsystems in these misfit layer compounds. The transition metal core levels of the TX₂ subsystem are not expected to change very much in energy when a (small) transfer of electrons takes place.

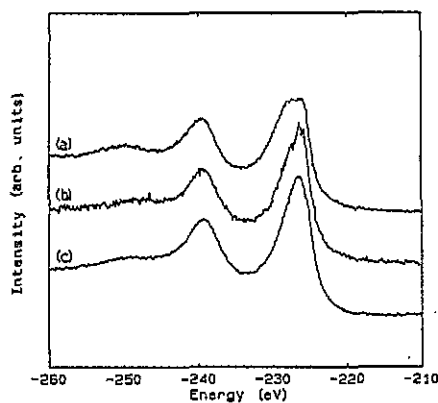


Figure 7. The Ta 4d core level spectra of the compounds (a) $\text{TaS}_2(1\text{T})$, (b) $(\text{SnS})_{1.16}\text{TaS}_2$ and (c) $(\text{PbS})_{1.13}\text{TaS}_2$.

The information about the core level spectra is sometimes limited due to small samples, a poor resolution and to overlap with (satellites from) other core levels.

A comparison of the core level energies of the metal atoms in the SnS and PbS subsystems is very valuable. The surfaces of the pure SnS and PbS compounds are expected to be n-type semiconducting in ultra-high vacuum (UHV). This is due to the fact that in UHV sulphur atoms evaporate from the top surface layer, yielding a small excess of metal atoms in this layer which provide charge carriers in the semiconductor conduction band. The Sn and Pb core levels of the SnS and PbS containing misfit layer compounds are thus compared with n-type SnS and PbS. A charge transfer from these monosulphide layers to the TS_2 subsystem would inevitably lead to a p-type semiconductor MS subsystem if a rigid band model is assumed. This would correspond to a change in binding energy equal to the band gap of SnS ($E_g = 1.04$ eV) or PbS ($E_g = 0.3$ eV). Such a change from n-type to p-type has not been observed in the spectra of figures 1 and 2.

The properties of the Bi containing misfit layer compound $(\text{BiS})_{1.08}\text{NbS}_2$ are not easy to interpret. The crystal structure is more complicated than the structure of the corresponding Sn and Pb containing misfit layer compounds [14]. The BiS layers have a modulated structure with anti-phase domain boundaries; as a result a third of the Bi atoms form Bi-Bi pairs, with covalent Bi-Bi bonds. This behaviour is characteristic for Bi, it has been observed also in the misfit layer compounds $(\text{BiSe})_{1.09}\text{TaSe}_2$ and $(\text{BiSe})_{1.10}\text{NbSe}_2$ [15, 16]. Scanning tunnelling microscopy (STM) images of $(\text{BiS})_{1.09}\text{NbS}_2$ show a very smooth hexagonal pattern in the case where NbS_2 is uppermost in the sample, and images with very rough patterns of atoms with a square orientation if a BiS layer is at the surface [17]. The electrical transport properties of $(\text{BiS})_{1.09}\text{NbS}_2$ are very similar to the properties of the SnS and PbS containing misfit layer compounds, indicating the absence of transfer of electrons to the transition metal d band of the TX_2 layers. The photoelectron spectra show approximately the same binding energy for Bi in $(\text{BiS})_{1.09}\text{NbS}_2$ as in Bi_2S_3 , which suggests a valency close to three for Bi. The variety in chemical surroundings and the covalent Bi-Bi bonds for part of the Bi atoms in the BiS layer of $(\text{BiS})_{1.09}\text{NbS}_2$ will lead to a large width of the core lines of Bi.

The covalent bonding and the valency of the metal atoms in the misfit layer compounds have been analysed with the bond-valence method [16]. It is found that in $(\text{PbS})_{1.08}\text{TiS}_2$ the valency of the Pb atoms is two, and that there is no charge transfer from the PbS layers to the TiS_2 layer. Within the PbS layers there are strong covalent Pb-S bonds. In addition there are weaker covalent interlayer bonds between Pb atoms and S atoms of the TiS_2 layer.

The total bond strength of these interlayer bonds is 0.3 eV per Pb atom in $(\text{PbS})_{1.08}\text{TiS}_2$. We expect that this picture of covalent interlayer bonds and valencies is valid for all Pb and Sn containing misfit layer compounds $(\text{MX})_{1+\delta}\text{TX}_2$.

The bond–valence method leads to a valency of three for all Bi atoms in the misfit layer compound $(\text{BiSe})_{1.09}\text{TaSe}_2$ [16]. In this compound there are strong covalent Bi–Se bonds in the BiSe layer, and 1/3 of the Bi atoms takes part in a Bi–Bi covalent bond of bond order 1. There are covalent bonds between Bi atoms and Se atoms of the TaSe_2 layers. These interlayer bonds are somewhat stronger than they are in the Pb containing compound; the total bond order of these interlayer bonds is 0.4. There is no charge transfer from the BiSe to the TaSe_2 layers. The similarity of the crystal structures suggest a similar situation for other Bi containing misfit layer compounds.

An interesting phenomenon is the broadening of the core levels which is a direct result of the incommensurate character of the misfit layer structure. The coordination of metal atoms by other atoms in the same layer is the same for all metal atoms, but the coordination by atoms in the other type of layer changes due to the incommensurate structure (figure 1). As a consequence the (Madelung) potential will vary over the atomic sites. The (Madelung) potential therefore causes a broadening of all the core levels in the misfit layer compounds with respect to the pure non-intergrowth compounds.

In conclusion we find from the core level spectra that the valencies of Pb and Sn atoms in the misfit layer compounds is two, whereas the valency of Bi is three. This agrees with the results obtained with the valence–bond method. From the spectra of the Pb and Sn containing compounds we also find that charge transfer between the layers is absent or small. In the Bi compound charge transfer is probably also absent, and the Bi electrons are used for Bi–Bi bonds and for stronger interlayer and intra-layer Bi–Se bonds. We conclude that charge transfer is not an important factor for the stability and the alternated stacking of these misfit layer compounds containing Pb, Sn and Bi. We attribute the stability of the misfit layer compounds to the presence of weak covalent interlayer bonds.

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