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$(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$

The x-ray emission spectra and electronic structure of the misfit layer compounds $(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$

Yu M Yarmoshenko†, V A Trofimova†, S N Shamin†, I V Solovyev†, E Z Kurmaev†, A R H F Ettema‡ and C Haas‡

† Institute of Metal Physics, Russian Academy of Sciences, Ural Division, 620219 Ekatarinburg GSP-170, Russia
‡ Laboratory of Chemical Physics, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract. The x-ray emission lines S $K\beta$ ($3p \rightarrow 1s$) and S $L_{2,3}$ ($3s \rightarrow 2p$) have been measured for the misfit layer compounds $(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$ and the corresponding binary sulphides Bi_2S_3, NbS_2, PbS and TaS_2. The x-ray emission data are compared with x-ray photoelectron spectra and band structure calculations of isolated model layers. The experimental data show very clearly the character of the different valence band states, and partial density of states schemes are easily deduced from these data. A comparison with band structure calculations shows a good agreement with the measured spectra.

1. Introduction

The misfit layer compounds have a general chemical formula of $(MX)_{1+\delta}TX_2$ (with M = Sn, Sb, Pb, Bi; T = Ti, V, Cr, Nb, Ta; X = S, Se and $0.05 < \delta < 0.25$). It has been shown that these compounds have an alternated stacking of the MX and TX_2 layers, whereby the b-axes of the subsystems match perfectly and the a-axes are incommensurate with respect to each other [1]. The MX part consists of two-atom thick layers with a distorted rocksalt structure. The M atoms are surrounded by five X atoms in the same layer, and by two to three X atoms from the TX_2 layer at a significantly larger distance. The TX_2 layers are hardly distorted from the pure TX_2 layered structure. In the TX_2 layers the transition metal atom T is surrounded by six X atoms at equal distances in a trigonal prismatic geometry. A projection along the incommensurate direction of a misfit layer compound is shown in figure 1. For an accurate description of the crystal structure of these compounds super space group symmetry has been applied [2].

The electronic structure of these compounds is a subject of particular interest. It was assumed that the alternation of the stacking of the layers is stabilized by charge transfer from one subsystem to the other [3]. However, photoemision data showed very clearly that charge transfer is marginal (or absent) in the compounds with M as a main group element [4]. Several spectroscopic studies appeared on this topic using techniques such as angle-resolved ultraviolet photoelectron spectroscopy [5], resonant photoelectron spectroscopy [6], x-ray absorption spectroscopy [3, 7, 8], electron energy loss spectroscopy [9] and x-ray photoelectron spectroscopy (XPS) [4]. In this paper we present x-ray emission spectroscopy (XES) spectra and density of states from linear muffin-tin orbital (LMTO) band structure calculations of the misfit layer compounds $(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$ and the binary sulphides NbS_2, TaS_2, Bi_2S_3 and PbS
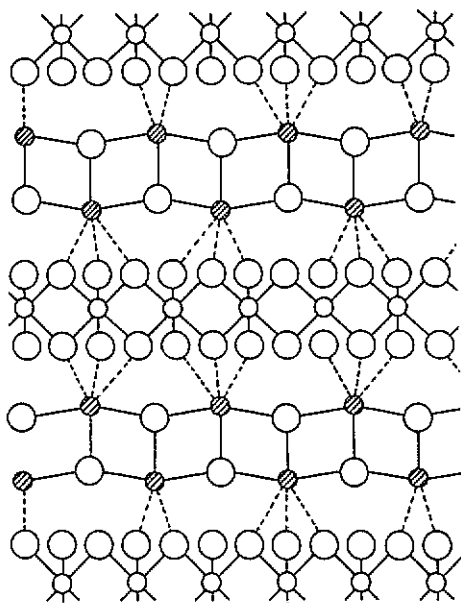
Figure 1. A projection of the crystal structure of a misfit layer compound $(MX)_{1+\delta}TX_2$ along the incommensurate direction. The small open circles are the T atoms, the hatched circles the M atoms and the large open circles represent the X atoms.

2. Experimental details

The S $K\beta_1$ (1s–3p transition) and the S $L_{2,3}$ (2p–3s transition) x-ray emission and the valence band XPS spectra of the misfit layer compounds $(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$ and the corresponding binary sulphides have been measured.

The S $K\beta_1$ XES spectra are measured with a Johann-type x-ray type spectrometer with a position-sensitive detector [10] using fluorescence excitation (by Pd L x-ray radiation). A bent quartz crystal $(10\bar{1}1)$ $(R = 1.4$ m) is used as a crystal analyser. The instrumental resolution is about 0.25 eV. The S $L_{2,3}$ x-ray emission data are obtained with a small-spot x-ray spectrometer, which uses electron excitation $(V = 8$ kV, $I = 300$ nA), and has a diffraction grating $(R = 2$ m and $N = 600$ lines mm$^{-1})$ as a monochromator. The XPS spectra are measured using a small-spot electron spectroscopy for chemical analysis (ESCA) facility of Vacuum Generators (VG) with an Al Kα source $(h\nu = 1486$ eV) and an instrumental resolution of 0.2 eV.

The XES and XPS measurements were carried out on single-crystal platelets of $(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$, which were grown with the vapour transport method in a temperature gradient [1]. The samples of Bi_2S_3, NbS_2 and PbS were made from the elements, and these reaction products were pressed into pellets.

3. Band structure calculations

Band structure calculations of separated NbS_2 and TaS_2 sandwich layers, and BiS and PbS double layers, were performed on the basis of the spin-polarized relativistic LMTO method [11], which allows us to treat all relativistic effects (including spin–orbit interaction) and those of spin polarization in the framework of the local spin density approximation. It is necessary to point out that relativistic effects were found to be very important for heavy elements such as Ta, Pb and Bi. The von Barth–Hedin exchange correlation potential [12] has been used in the parametrization as was proposed by Janak [13]. In the unit cell

the layers of the systems (NbS_2, TaS_2, BiS and PbS) were alternated with several layers of empty spheres. The number of the spheres was chosen from the condition of suppressing the interaction between the layers; as a consequence the layers can be considered as independent two-dimensional systems. The band structure calculations for the MX layers (BiS and PbS) were for tetragonal layers with equal M–X distances in the plane of the layers and perpendicular to the layers. The radii of the muffin-tin spheres used in the band structure calculations are given in table 1.

Table 1. Radii of the muffin-tin spheres used in the band structure calculations.

PbS	$R(Pb) = 1.997$ Å	$R(S) = 1.546$ Å
BiS	$R(Bi) = 2.051$ Å	$R(S) = 1.546$ Å
NbS_2	$R(Nb) = 1.546$ Å	$R(S) = 1.546$ Å
TaS_2	$R(Ta) = 1.546$ Å	$R(S) = 1.546$ Å

4. Results and discussion

The S $L_{2,3}$ (3s $\rightarrow$ 2p) XES spectra of the misfit layer compounds $(BiS)_{1.08}NbS_2$ and $(PbS_{1.14})TaS_2$, and the corresponding binary sulphides, are presented in figure 2. The spectra, which represent the contribution of S 3s orbitals, exhibit a rather broad maximum at a photon energy of $h\nu = 148$ eV, and a weak broad maximum at a photon energy of $h\nu = 158$–160 eV.

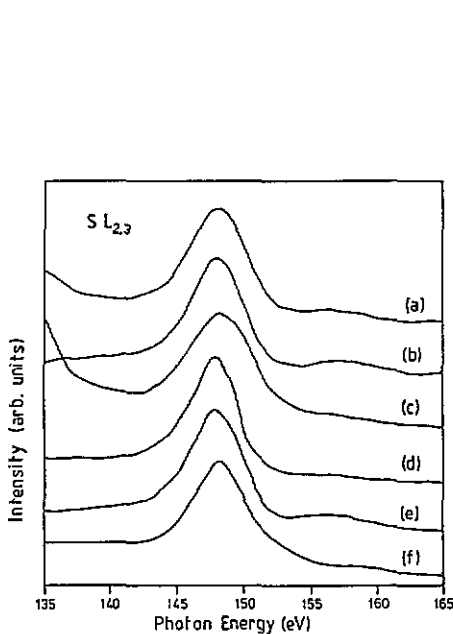**Figure 2.** The S $L_{2,3}$ x-ray emission line (3s $\rightarrow$ 2p transition) for the compounds $(BiS)_{1.08}NbS_2$ (a), NbS_2 (b), Bi_2S_3 (c), $(PbS)_{1.14}TaS_2$ (d), TaS_2 (e) and PbS (f).

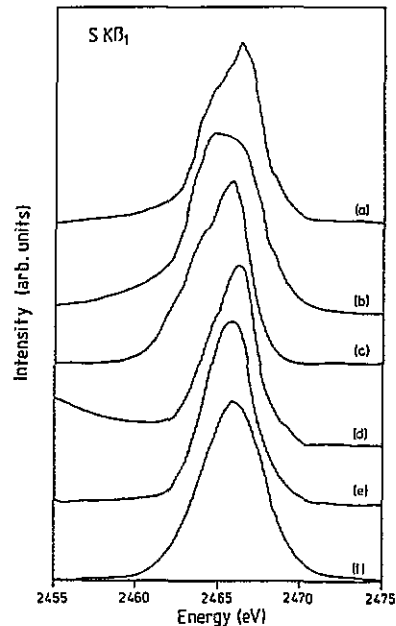**Figure 3.** The S $K\beta_1$ x-ray emission line (3p $\rightarrow$ 1s transition) for the compounds $(BiS)_{1.08}NbS_2$ (a), NbS_2 (b), Bi_2S_3 (c), $(PbS)_{1.14}TaS_2$ (d), TaS_2 (e) and PbS (f).
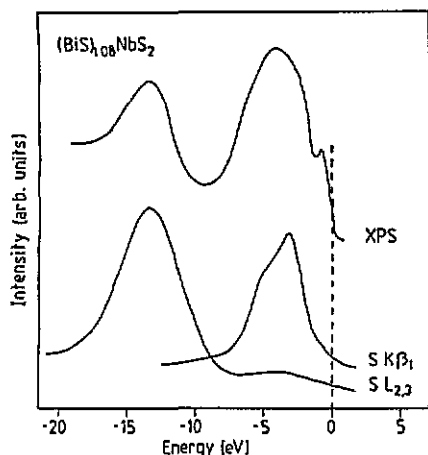
Figure 4. A comparison of the x-ray emission spectra and the valence band x-ray photoelectron spectrum of $(BiS)_{1.08}NbS_2$. The energy is given with respect to the Fermi level.

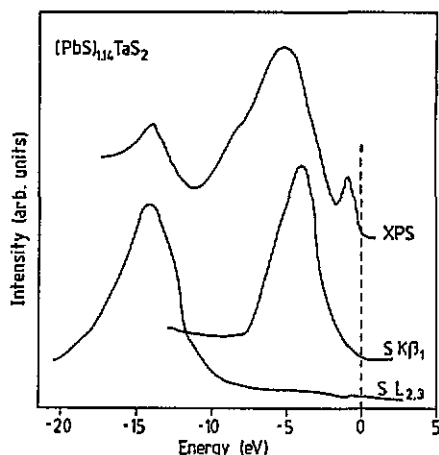**Figure 5.** A comparison of the x-ray emission spectra and the valence band x-ray photoelectron spectrum of $(PbS)_{1.14}TaS_2$. The energy is given with respect to the Fermi level.

The S $K\beta_1$ x-ray emission spectra of these compounds are shown in figure 3. According to the dipole selection rules these spectra reflect the S 3p density of states. The S $K\beta_1$ emission edge coincides with the Nb $L\gamma_1$ edge in NbS_2 and $(BiS)_{1.08}NbS_2$ and is therefore more complicated. The maxima of the x-ray emission spectra of the misfit layer compounds in figure 3 are shifted by 0.5 eV towards higher energy, and the widths seem to be slightly less than for the binary sulphides. This narrowing of the emission lines for the misfit layer compounds can be explained by a stronger localization of the valence band states of the MS layers in the misfit layer compounds than in the three-dimensional MS bulk compounds.

The comparisons of the XES and the XPS valence band spectra for $(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$ are shown in figures 4 and 5, respectively. The position of the Fermi level was obtained from values of the electron binding energies of the elements [14]. It was found that the position of the S 3s states obtained in this way accurately corresponds to the binding energy obtained from XPS spectra (figures 4 and 5). For both compounds it can be seen that the states at 13 eV have predominantly S 3s character. The low intensity of the S $L_{2,3}$ x-ray emission in the binding energy range between 1 and 7 eV shows that the contribution of S 3s states to the upper valence band is small. The highest density of S 3p states is located at binding energies between 1 and 7 eV. The peak just below the Fermi level in the XPS spectrum is not revealed by the XES spectra in either compound. For $(PbS)_{1.14}TaS_2$, the states just below the Fermi level are expected to be dominated by the Ta 5d states, as has been shown with RPES [6]. For $(BiS)_{1.08}NbS_2$ the narrow band in the XPS spectrum just below the Fermi level corresponds to Nb 4d states. The width of the S $K\beta_1$ XES peak is smaller than the width of the corresponding peak in the XPS spectrum. At binding energies between 7 and 10 eV, in figure 5, the intensity of the S $K\beta_1$ XES spectrum is less than the intensity in the XPS spectrum. This is caused by the Pb 6s states, which do not contribute to the XES spectrum, but do contribute to this peak in the XPS spectrum. In the spectra of $(BiS)_{1.08}NbS_2$ the Bi 6s states seem to contribute in the peak at 13 eV in the XPS spectrum. This causes a relatively high intensity at this binding energy with respect to the corresponding peak in the XPS spectrum of $(PbS)_{1.14}TaS_2$. The XES spectra show for both compounds well separated S 3s and S 3p contributions, indicating that hybridization
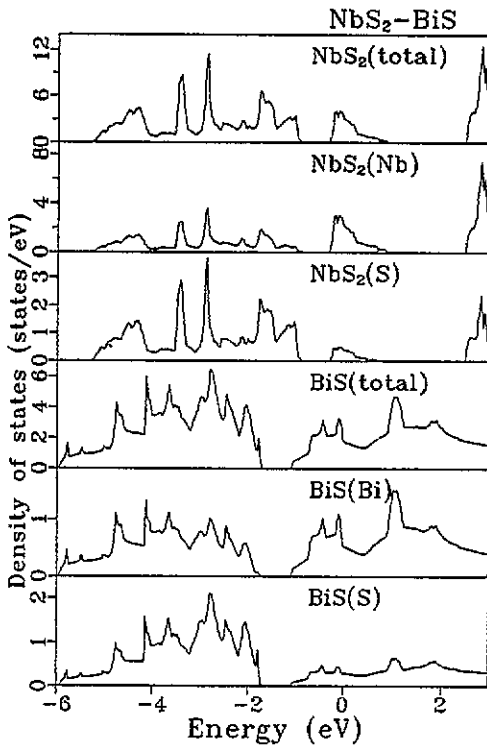
Figure 6. Total and partial densities of states for isolated layers of NbS₂ and two-atom-thick slabs of BiS in a distorted rocksalt structure.
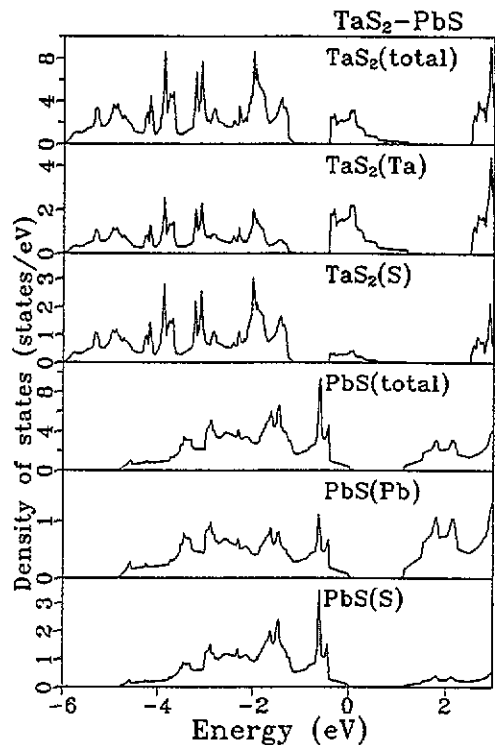
Figure 7. Total and partial densities of states for isolated layers of TaS₂ and two-atom-thick slabs of PbS.

effects are small.

The calculated densities of states for the two misfit layer compounds are presented in figures 6 and 7. From both figures it can be seen that hybridization effects are large within the layers, which is partially caused by the size of the muffin-tin spheres. The states with binding energies between 1 and 6 eV are dominated by S states. From the XES spectra it was shown that these states have largely S 3p character. The narrow band at the Fermi level in the NbS₂ and TaS₂ layers is dominated by states of the transition-metal atom. Other band structure calculations have shown that this band has a large contribution from the Ta $5d_{z^2}$ or Nb $4d_{z^2}$ states. The energy gap between the d_{z^2} band and the band of other d states of 1.6 eV for NbS₂ and 1.3 eV for TaS₂ in this calculation is comparable with other calculations where gaps of 1.8 eV for 2H-NbS₂ [15] and 1.2 eV for 2H-TaS₂ [16] have been obtained.

According to these calculations, the BiS double layers are metallic with electrical conduction by one electron per Bi in the Bi 6s/6p band. The BiS part has been calculated using a crystal structure similar to that of PbS; this means that a two-atom-thick slab with a rocksalt structure has been used. This is probably not an accurate description, because in (BiSe)₁.₁₀NbSe₂ and (BiSe)₁.₀₉TaSe₂ the BiSe layer has a complicated highly distorted structure with Bi–Bi pairs [17, 18]. The calculation for PbS shows a larger band gap than the experimental value of 0.3 eV. This is caused by the strong reduction of the dispersion perpendicular to the PbS slabs.

5. Conclusions

In this paper we have presented valence band XES and XPS spectra of the misfit layer compounds $(BiS)_{1.08}NbS_2$ and $(PbS)_{1.14}TaS_2$ and the corresponding binary sulphides NbS_2, TaS_2, Bi_2S_3 and PbS. The spectra were compared with band structure calculations of isolated layers of the binary sulphides. Generally we obtain a good agreement of the calculated partial density of states with the observed spectroscopic data. We conclude that the XES spectra proved to be very powerful for obtaining experimentally the partial density of states of the valence band. With the use of the dipole selection rules in XES the contribution of the S 3s states and the S 3p states to the valence band have been discriminated from the Nb 4d, Bi 6s and Bi 6p states in $(BiS)_{1.08}NbS_2$, and from the Ta 5d and the Pb 6s states in $(PbS)_{1.14}TaS_2$.

Acknowledgments

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