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## Electron energy structure of the semiconductors $\text{TlAsS}_2$ , $\text{Tl}_3\text{AsS}_3$ , $\text{Tl}_3\text{AsS}_4$ , $\text{Tl}_3\text{PS}_4$ and $\text{Tl}_3\text{TaS}_4$

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**Abstract.** The x-ray emission K and  $L_{2,3}$  bands of sulphur and phosphorus as well as their x-ray K absorption spectra are obtained for the semiconductors  $\text{TlAsS}_2$ ,  $\text{Tl}_3\text{AsS}_3$ ,  $\text{Tl}_3\text{AsS}_4$ ,  $\text{Tl}_3\text{PS}_4$  and  $\text{Tl}_3\text{TaS}_4$ . The upper part of the valence band in the compounds investigated is formed of the S p states mainly, but the S s states are localized near the bottom of the valence band and hardly take part in the bonding. Comparison of the x-ray spectra of S and P in the isoelectronic and isostructural compounds  $\text{Tl}_3\text{AsS}_4$  and  $\text{Tl}_3\text{PS}_4$  has made it possible to determine the energy position of the p states of arsenic in  $\text{Tl}_3\text{AsS}_4$ . The energy distributions of the valence electron states of sulphur and its neighbours in all the compounds investigated are analysed and the covalent-ionic mechanism of chemical bonding is proposed.

### 1. Introduction

The semiconductors  $\text{TlAsS}_2$ ,  $\text{Tl}_3\text{AsS}_3$ ,  $\text{Tl}_3\text{AsS}_4$  and  $\text{Tl}_3\text{AsSe}_3$  (denoted hereinafter as TAS compounds), and also  $\text{Tl}_3\text{PS}_4$  and  $\text{Tl}_3\text{TaS}_4$  are candidates for use in quantum electronics [1].

However, it should be noted that the electron energy structure and the particularities of the chemical bonds in these ternary thallium chalcogenides have not been investigated both experimentally and theoretically.

In the present paper the x-ray spectroscopy method is applied for the first time to study the electron band structure of  $\text{Tl}_3\text{PS}_4$ ,  $\text{Tl}_3\text{TaS}_4$  and TAS compounds. The superposition of the x-ray spectra of the various series of all components describes the form of the electron density of states (DOS) of the compound studied and makes it possible to determine the width of the valence band, the energy gap between the filled and unfilled parts of the band, and the energy distribution of the local partial electron DOSs of various symmetries.

It is of interest to study the changes in the x-ray spectra of TAS compounds due to their crystal structure (described in detail in [2]) and chemical formula ( $\text{TlAsS}_2 \rightarrow \text{Tl}_3\text{AsS}_3 \rightarrow \text{Tl}_3\text{AsS}_4$ ). It is worthwhile recalling here the presence of the definite structural elements: the trigonal pyramids  $[\text{AsS}_3]$  in  $\text{TlAsS}_2$  and  $\text{Tl}_3\text{AsS}_3$ , as well as the coordination tetrahedra  $[\text{AsS}_4]$  in  $\text{Tl}_3\text{AsS}_4$  (and the analogous coordination tetrahedra  $[\text{PS}_4]$  in  $\text{Tl}_3\text{PS}_4$ ).

The interatomic As-S distances in these different structural elements are approximately equal to the sum of the covalent tetrahedral radii of As (1.18 Å)

and S (1.04 Å). This means that in these TAS compounds the covalent contribution to the chemical bond between As and S atoms is high. At the same time, the Tl-S distance in all the compounds studied [2] is greater than the sum of the covalent radii of the Tl (1.47 Å) and S atoms. Because of this the ionic contribution to the bond is also essential.

Until now, only  $\text{Tl}_3\text{AsSe}_3$  from the TAS compound family has been studied in detail [3] both experimentally and theoretically; the form of the x-ray photoelectron emission band was compared with the DOS calculated using the tight-binding method.

The TAS compound  $\text{Tl}_3\text{AsS}_3$  investigated in the present work has the same crystal structure as its chemical analogue  $\text{Tl}_3\text{AsSe}_3$ ; their lattice constants are very similar to each other [2], and the change from Se to S does not modify the valence band greatly. That is why it is reasonable to compare the x-ray spectra of  $\text{Tl}_3\text{AsS}_3$  that we obtained with the DOS of  $\text{Tl}_3\text{AsSe}_3$  determined in [3], taking into account the different position  $E_v$  of the peak of the valence band.

## 2. Experimental details

The fluorescent x-ray emission K bands and the absorption K spectra of sulphur and phosphorus in the compounds investigated were obtained using a DRS-2 x-ray spectrograph [4] with a resolution of 0.2 eV.

The primary  $L_{2,3}$  emission bands of S and P were obtained using an RSM-500 spectrometer [4] with a resolution of about 0.4 eV. The K and L spectra of sulphur were superimposed on a common energy scale using the S  $K\alpha_1$  line as a reference. The same procedure was used for the K and L spectra of phosphorus. To determine the common energy scale for the x-ray spectra of S and P in  $\text{Tl}_3\text{PS}_4$  the energies of the inner 2p level of S and P in this compound were measured using the x-ray electron spectrometer. Deconvolution of the K spectra has been carried out to eliminate the smearing due to the inner K level and the spectrometer window widths. The short-wave part (tail) of the corrected emission S K band curve was approximated by a straight line. The latter crosses the axis of abscissae at the energy  $E_v$ , which was taken as the zero of the energy scale; it is the top of the valence band. The experimental uncorrected x-ray spectra for S and P are shown in figures 1-3.

## 3. Results and discussion

In general the K band of sulphur represents the energy distribution of the partial S p states [4]. That is why its main maximum A (figures 1-3) for all compounds investigated determines the energy position of the principal part of these states in the valence band. The other maxima of the S K band can be explained by the hybridization of S p states and the partial states of other atoms, partners of the S atom in the compounds, showing thus the interaction of atoms in the compounds. Similar information can be obtained from the K band of phosphorus.

The S  $L_{2,3}$  band gives a direct picture of the density of the S s states [4], and its principal maximum D (figures 1-3) shows the energy position of these states in the valence band. Analogous knowledge can be obtained from the intensity profile of the  $L_{2,3}$  band of phosphorus.

For the compound  $\text{Tl}_3\text{PS}_4$  studied in the present work, one can see the similarity between the corresponding x-ray spectra for S and P (figure 1). The analysis of these

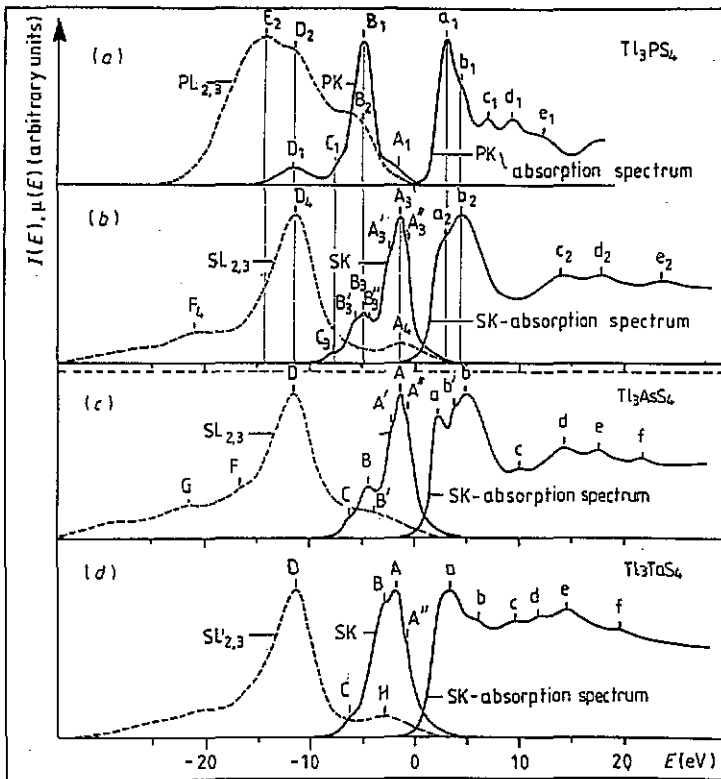


Figure 1. X-ray spectra for the  $Tl_3MS_4$ -type compounds ( $M \equiv P, As, Ta$ ): (a) x-ray primary P  $L_{2,3}$  band, fluorescent P K band and P K absorption spectrum for  $Tl_3PS_4$ ; (b)–(d) x-ray primary S  $L_{2,3}$  band, fluorescent S K band and S K absorption spectrum for (b)  $Tl_3PS_4$ , (c)  $Tl_3AsS_4$  and (d)  $Tl_3TaS_4$ .  $E_v$  is chosen as the zero energy.

spectra shows that the top of the valence band in  $Tl_3PS_4$  is formed from S p states (maximum  $A_3$  of the S K band), and the electron p states of P (maximum  $B_1$  of the P K band) situated at the approximate energy 3.5 eV. The lower part of the valence band in  $Tl_3PS_4$  is formed from the electron s states of S (maximum  $D_4$  of the S  $L_{2,3}$  band) and P (maximum  $E_2$  of the P  $L_{2,3}$  band). The electron s states of P are situated 2.5 eV deeper than the S s states and form the bottom of the valence band. The energy positions of the subbands of P and S in  $Tl_3PS_4$  may be explained by the atomic genesis of these subbands, taking into account the greater electronegativity of the S atoms in comparison with the P atoms. So the coupling of the atoms P and S in  $Tl_3PS_4$  is essentially ionic. A distinct feature of the S K band in  $Tl_3PS_4$  is the long-wavelength maximum  $B_3$ . Its energy coincides with the binding energy of the main maximum  $B_1$  of the P K band. This coincidence reveals the admixture of the S p states and the P p states in  $Tl_3PS_4$ . The correspondence of the principal and the essentially intense additional maxima of the various curves for  $Tl_3PS_4$  (figure 1) indicates the significant degree of atomic and interatomic hybridization of the electron states and the covalent contribution to the P–S bonding.

The forms of the x-ray spectra and DOS of isoelectronic compounds with the same type of crystal structure are nearly always alike. This is confirmed by comparison of the x-ray K and L spectra of S in  $Tl_3PS_4$  and  $Tl_3AsS_4$  (figures 1(b) and 1(c)). The

features of the S K absorption spectra in both components which coincide reveal the similarity in the surroundings of the S atom (including the second or the third coordination sphere) in these compounds. Using the analysis made above for  $\text{Tl}_3\text{PS}_4$ , one can interpret the maximum B of the S K band in  $\text{Tl}_3\text{AsS}_4$  as the result of the admixture of the S p states and the As p states. At the same time, as is evident from figure 1(a), the P p states are strictly localized to a definite binding energy; only a small amount of these states are admixed with the S s and p states.

The chemical formulae of the compounds  $\text{Tl}_3\text{AsS}_4$  and  $\text{Tl}_3\text{TaS}_4$  are nearly the same, but their crystal lattices are different [2], which results in different forms of the x-ray K absorption spectra of S in  $\text{Tl}_3\text{TaS}_4$  and  $\text{Tl}_3\text{AsS}_4$  (figure 1). Nevertheless, the basic structural unit of  $\text{Tl}_3\text{TaS}_4$  is the coordination tetrahedron  $[\text{TaS}_4]$  which plays the same role as  $[\text{AsS}_4]$  in  $\text{Tl}_3\text{AsS}_4$ . This makes it possible to construct a model of the chemical bonding in  $\text{Tl}_3\text{TaS}_4$  in the same way as for  $\text{Tl}_3\text{AsS}_4$ .

The replacement of the atoms As and P by Ta in the compounds  $\text{Tl}_3\text{MS}_4$  ( $M \equiv \text{P}$ , As, Ta) results in a change in both the form of the S K absorption spectra (due to the modification of the crystal lattice mainly) and the form of the S K emission bands. The hybridization of the Ta d and s states in  $\text{Tl}_3\text{TaS}_4$  takes place. The shoulder B of the S K band is formed from the admixed S p states. Consequently, there is a covalent contribution to the Ta-S bond, which is consistent with the increase in the electron density between Ta and S atoms found by the x-ray diffraction method [5]. The Tl-S distance in  $\text{Tl}_3\text{TaS}_4$  is greater than the sum of the covalent tetrahedral radii of Tl and S [2]; therefore the ionic contribution to the Tl-S bond prevails. However, the S K band in  $\text{Tl}_3\text{TaS}_4$  (figure 1) has a noticeable shoulder C with an energy of 6.3 eV (table 1); this can be explained by the admixture of S p states and the Tl sp hybridized states. Thus, the covalent contribution to the Tl-S bond in  $\text{Tl}_3\text{TaS}_4$  must not be excluded.

Table 1. Characteristic peak energies of the band spectra obtained by x-ray emission spectroscopy (XES) of the compounds investigated and the spectrum obtained by x-ray photoelectron spectroscopy (XPS) for  $\text{Tl}_3\text{AsSe}_3$  [3].  $E_v$  is chosen as the zero energy.

Compound	Peak energy (eV)					
	A''	A	B	C	E	D
XES	S p	S p	S p	S p	—	S s
$\text{TlAsS}_2$	0.9	1.6	4.0	6.0	—	11.5
$\text{Tl}_3\text{AsS}_3$	0.8	1.5	4.0	6.0	—	11.3
$\text{Tl}_3\text{AsS}_4$	0.8	1.5	4.5	6.4	—	11.6
$\text{Tl}_3\text{PS}_4$	0.8	1.5	5.0	7.0	—	11.5
$\text{Tl}_3\text{TaS}_4$	0.7	1.7	3.0	6.3	—	11.4
XPS						
$\text{Tl}_3\text{AsSe}_3$	0.9	1.7	4.0	6.5	10.0	—

The change in the crystal structure in the compound sequence  $\text{TlAsS}_2 \rightarrow \text{Tl}_3\text{AsS}_3 \rightarrow \text{Tl}_3\text{AsS}_4$  causes, as one can see in figure 2, an alteration in the K spectra of S which is due to the different atomic neighbourhoods of the atom S in the compounds in question.

The 'humps' B of the S K band in  $\text{TlAsS}_2$  and  $\text{Tl}_3\text{AsS}_3$  have almost the same binding energies (about 4.0 eV; table 1) and are near the position of the maximum B of the S K band of  $\text{Tl}_3\text{AsS}_4$  (about 4.5 eV). A permanent increase in the intensity

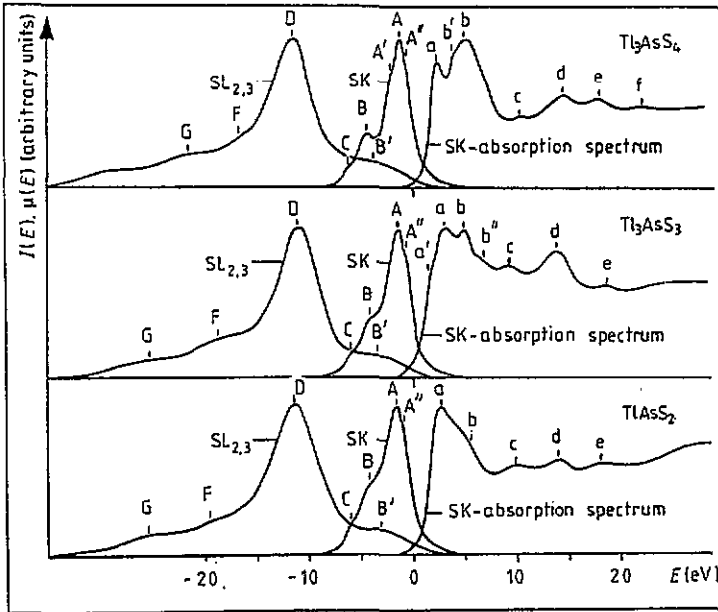


Figure 2. Results for the TAS compounds: x-ray primary S  $L_{2,3}$  band, fluorescent S K band and S K absorption spectrum. The energy scale zero corresponds to  $E_v$ .

of the maximum B (in relation to the maximum A of the S K band), i.e.  $I_B/I_A$ , is observed along the sequence  $Tl_3AsS_4 \rightarrow Tl_3AsS_3 \rightarrow TlAsS_2$ . We have interpreted above the peculiarities of the x-ray band structure of S in  $Tl_3AsS_4$ . The maximum B was explained by hybridization of the S p states and As p states. Because of this the hump B of the S K band in  $TlAsS_2$  and  $Tl_3AsS_3$  can be interpreted in the same way as the addition ('contamination') of the S p states to the As p states in spite of the slight decrease in the binding energy of As p states in these compounds.

The ionicity of the Tl-S bond is greater than that of the As-S bond; consequently, the binding energy of the hybridized Tl sp states must be higher than that of the As p states. That is why the hump C of the S K band of the compounds  $TlAsS_2$  and  $Tl_3AsS_3$  (figure 2) corresponds to the binding energy of 6.0 eV (see table 1) and may be explained by admixture of the S p states and the Tl sp states, localized in the same energy range.

Comparison (figure 3) of the x-ray spectra of sulphur in  $Tl_3AsS_3$  obtained in the present study with spectra obtained by XPS and the DOS curve for  $Tl_3AsSe_3$  (isostructural to  $Tl_3AsS_3$ ) taken from [3] leads to the conclusion that the upper part of the valence band in TAS compounds (see figure 2 also) is formed of S p states mainly, since the principal maximum A of the S K band in  $Tl_3AsS_3$  coincides with the XPS maximum  $A_1$  in  $Tl_3AsSe_3$ . Moreover, the XPS curve and the S K band for  $Tl_3AsS_3$  reveal other similar details in their form (figure 3); the maxima  $B_1$  and  $C_1$  of the XPS spectrum correspond to the features B and C of the S K band. This means that in the energy range of the maxima B and C there are some other electron states besides the S p states. As was shown above, they are the As p states (B hump range) and Tl sp states (C hump range).

The S s states in all the compounds investigated in the present work are localized

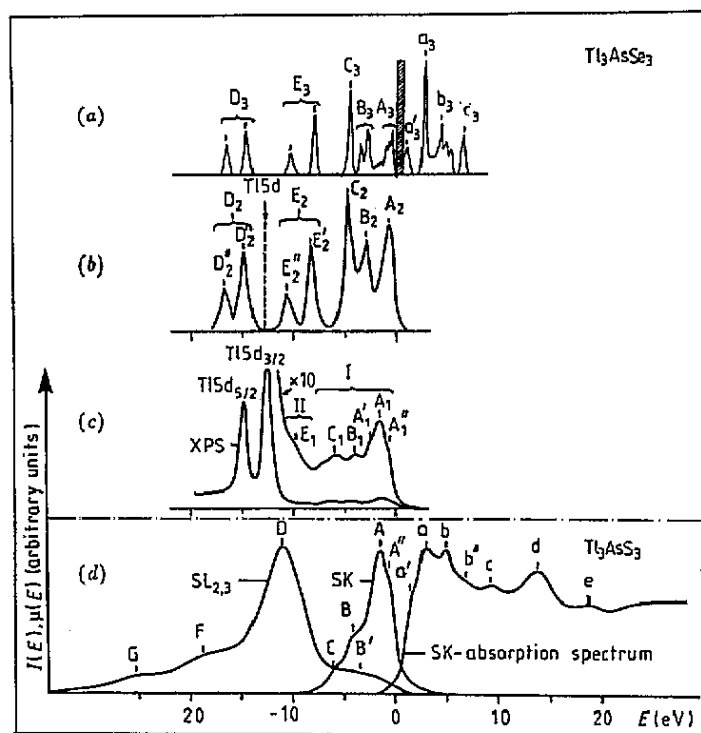


Figure 3. Results for the compounds  $Tl_3AsS_3$  and  $Tl_3AsSe_3$ : (a) unsmearred theoretical total electron DOS for  $Tl_3AsSe_3$  [3]; (b) theoretical total electron DOS convoluted with the window shape of the electron spectrometer for  $Tl_3AsSe_3$  [3]; (c) xps for  $Tl_3AsSe_3$  [3]; (d) x-ray primary S  $L_{2,3}$  band, fluorescent S K band and S K absorption spectrum for  $Tl_3AsS_3$ . The energy scale zero corresponds to  $E_v$ .

near the bottom of the valence band; this is confirmed by the existence of the maximum D of the S  $L_{2,3}$  bands (figures 1–3). It is important to note that the S s states hardly take part in the bonding. There is only a slight admixture of the S s states and the valence states in the upper part of the valence band. We mean here the hump B of the S  $L_{2,3}$  bands, which is explained by the admixture of S s states and S p and As p states, which are situated in the same energy region.

According to calculations in [3], the maxima  $D_2'$  and  $D_2''$  (figure 3) of the theoretical DOS curve for  $Tl_3AsSe_3$  are attributed to the electron s states of Se, located near the bottom of the valence band. However, the calculated binding energies of these states (about 15–17 eV from  $E_v$ ) seem to be overestimated, since the maximum of the density of S s states in TAS compounds according to data in our present x-ray spectroscopy investigation is situated near the energy 11.5 eV from  $E_v$  (see table 1).

The maximum  $E_2''$  in the theoretical DOS curve, which corresponds to nearly the same binding energy as the feature  $E_1$  of XPS (see figure 3) has been associated [3] with As s states; this does not contradict the results of our x-ray spectroscopy study of TAS compounds. However, the neighbouring maximum  $E_2'$  explained in [3] as the contribution from Se 4p states cannot be understood in this way as this maximum is situated in the energy region where these states are apparently absent because the intensity of the S K band in this energy region is negligible. The maximum  $E_2'$  of the

DOS is more probably related to As *s* states.

In summary, the analysis of theoretical and experimental curves shown in figure 3 makes it possible to state that the maximum  $A_2$  of the calculated electron DOS of  $Tl_3AsSe_3$  corresponds to Se 4*p* states,  $B_2$  to As 4*p* states,  $C_2$  to the hybridized Tl *sp* states,  $E'_2$  and  $E''_2$  to As 4*s* states and, finally,  $D'_2$  and  $D''_2$  to Se 4*s* states.

#### 4. Estimation of the forbidden energy band widths of the compounds studied with the x-ray spectroscopy method

For the compounds investigated, we have estimated the forbidden band width  $E_g$  using the corrected S K spectra with experimental errors of 0.2 eV. This is shown in table 2 which gives the results obtained in this work and those from the literature.

Table 2. Comparison of energy discontinuity  $\Delta E$  between the emission edge and the absorption edge for the corrected S K spectra with the  $E_g$ -value from the literature.

	Value (eV) for the following compounds					Reference
	$TlAsS_2$	$Tl_3AsS_3$	$Tl_3AsS_4$	$Tl_3PS_4$	$Tl_3TaS_4$	
$\Delta E$	1.7	1.3	1.8	2.0	1.8	This work
$E_g$	2.15, 2.22				2.18, 2.7	[6]
$E_g$	1.9	1.5	2.0	2.2		[1]

As is evident from table 2, in most cases the values of  $\Delta E$  obtained with an accuracy of 0.2 eV are in good agreement with the  $E_g$  value taken from the literature. This means that the S *p* states give a noticeable contribution to the DOS near the top of the valence band, as well as at the bottom of the conduction band of the semiconducting compounds studied in the present work.

#### 5. Conclusion

Unfortunately, in many cases the x-ray bands—the spectra connected with the transition of the electron from the valence band to the inner atomic level (core level) and vice versa—are impossible to obtain for all components of the compounds in question. The reasons for these difficulties are the low intensity of the x-ray bands, the significant smearing of the band due to the inner level width, and the overlapping of the x-ray bands with other x-ray lines. Nevertheless, the fine structure of the x-ray emission band of one component (e.g. sulphur) or two components (e.g. sulphur and phosphorus) can be used to obtain information about the DOS of the components of the compounds in the same way as was done earlier [7, 8] for other compounds. This is possible by comparison of the x-ray and the photoelectron spectra of isoelectronic analogous compounds with the same crystal structure, such as  $Tl_3PS_4$  and  $Tl_3AsS_4$ , or  $Tl_3AsS_3$  and  $Tl_3AsSe_3$ .



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