

## The use of the FEFF8 code to calculate the XANES and electron density of states of some sulfides

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The FEFF8 was used to calculate x-ray absorption spectra (XANES) and the local partial electron density of states (LDOS) for several sulfides: InPS<sub>4</sub> (twice defective chalcopyrite), CdIn<sub>2</sub>S<sub>4</sub> (normal spinel) and Tl<sub>3</sub>AsS<sub>3</sub> (space group R3m). The calculated XANES are compared with experimental spectra. The self-consistent MT-potentials found for clusters of about 35 atoms were used to calculate XANES and LDOS for clusters of 87 atoms in the approach of full multiple scattering. In all cases the agreement of the simulated XANES and experimental ones is quite good. The theoretical LDOS agree well with the experimental x-ray emission *K*- and *L*<sub>2,3</sub>-spectra.

**Keywords:** semiconductors, LDOS, XANES, electronic structure, FEFF8.

### 1. Introduction

The ternary semiconducting compounds possess rather complicated crystal structures which makes it difficult to apply traditional methods of solid state physics such as OPW, APW, KKR, etc. to calculate their electronic energy structure. Moreover these methods can be used only for ideal crystals and do not permit to take any imperfections in the crystal lattice, the holes in the electronic shell of any of its atoms or the effect of the energy dependence of the exchange-correlation potential into account. All these are important in the calculation of x-ray absorption spectra. In the present work, the FEFF8 code (Ankudinov et al., 1998) based on the multiple scattering in real space (RSMS) theory was used. This *ab initio* code is based on a self-consistent field approach to the electron density in the real space. Muffin-tin potentials are used which take the hole in the inner ionized shell into account. It allows to consider a cluster with an arbitrary distribution of atoms. One of the advantages of the FEFF8 program compared to the previous FEFF7 code (and some other codes for XANES calculation) is that the local partial densities of electron states can be obtained not only in the empty conduction band but in the valence band as well.

### 2. Theoretical and experimental procedures

First, the self-consistent MT-potentials were determined for clusters of about 35 atoms. For the compounds investigated 10 iterations were usually enough to achieve self-consistency in the Fermi energy up to a precision in  $E_F$  of about 0.03 eV. To carry out the calculations in a reasonable time, clusters of 87 atoms were used for the full multiple scattering (FMS) calculations. In addition accurate calculations of the remaining important dominant single-scattering (SS) paths were performed using the Rehr-Albers (RA) scattering-matrix algorithm for enlarged clusters of 1000 atoms (Rehr J.J., Albers R.C., 1990).

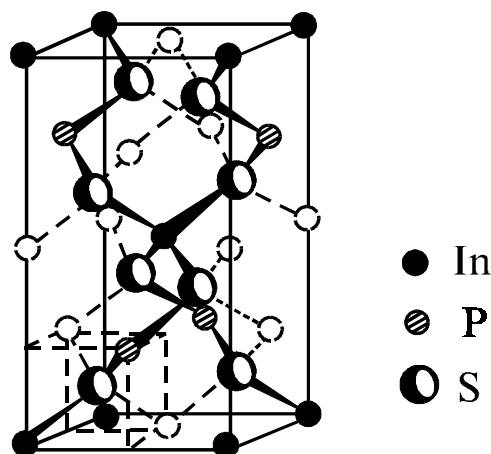


Figure 1

The elementary cell of twice defective chalcopyrite InPS<sub>4</sub>.

The compound CdIn<sub>2</sub>S<sub>4</sub> has the crystallographic diamond-like structure of a normal spinel ( $O_h^7 = Fd3m$ ). Its cubic elementary cell has the lattice parameter  $a = 1.0797 \text{ nm}$  (Rehwald, 1967) and includes 8 formula units, the parameter  $u$  of sulfur atom's displacement being supposed equal to 0.386. The sulfur atoms are located in the f.c.c. sublattice, and every S atom has the 3 nearest neighbor atoms of In in octahedral sites and one Cd atom at the tetrahedral site with the bond lengths:  $R_{(Cd-S)} = 0.2543 \text{ nm}$ ,  $R_{(In-S)} = 0.2586 \text{ nm}$ , and  $R_{(S-S)} = 0.3481 \text{ nm}$ .

The compound InPS<sub>4</sub> belongs to the structural type of twice-defective chalcopyrite of the space group  $\bar{4}(S_4^2)$  and has elementary cell parameters' of  $a = 0.5623 \text{ nm}$  and  $c = 0.9058 \text{ nm}$ . The unit cell, shown in Fig.1, contains two formula units (Berga D.M. et al., 1983). This structure has a nearly close-packed distribution of S-atoms with a quarter of tetrahedral interstitials being occupied by atoms of indium and phosphorus.

The compound Tl<sub>3</sub>AsS<sub>3</sub> crystallizes as a structure of the space group R3m with the lattice parameters  $a = 0.9667 \text{ nm}$  and  $c = 0.7061 \text{ nm}$  (Berga D.M. et al., 1983). The structure is composed of trigonal pyramids [AsS<sub>3</sub>]. Three apices of each pyramid the trigonal pyramids [TlS<sub>3</sub>] are attached, so that uninterrupted chains of pyramids [AsS<sub>3</sub>] and [TlS<sub>3</sub>] are formed.

Once the coordinates of atoms within these structures were determined, the clusters centered at the absorbing atom of sulfur or phosphorus were constructed which contained up to 1000 atoms.

Experimental sulfur *K*-edge spectra of the compounds CdIn<sub>2</sub>S<sub>4</sub> (Gusatinskii A.N. et al., 1986) and Tl<sub>3</sub>AsS<sub>3</sub> (Lavrentyev A.A. et al., 1993) have been published previously but not compared with theoretical data.

The fine structures of the spectra of sulfur and phosphorus are very feature-rich because the widths of the *K*-levels of S (0.57 eV) and P (0.54 eV) (Blokhin M.A. et al., 1982) are rather small so that the broadening of the spectra is insignificant. The fluorescent *K*-edge spectra of S and P (as well as the *L*-emission spectrum of In in CdIn<sub>2</sub>S<sub>4</sub>) were obtained with the vacuum x-ray spectrograph with Johann's focusing. The quartz crystal monochromator provided a resolution of about 0.2 eV. The radius of the bent quartz crystal was 50 cm. The primary *L*<sub>2,3</sub>-bands of sulfur and phosphorus in CdIn<sub>2</sub>S<sub>4</sub>, InPS<sub>4</sub>, and Tl<sub>3</sub>AsS<sub>3</sub> were obtained using a RSM-500 spectrometer with a spherically bent diffraction grating (radius 2 m, grating with

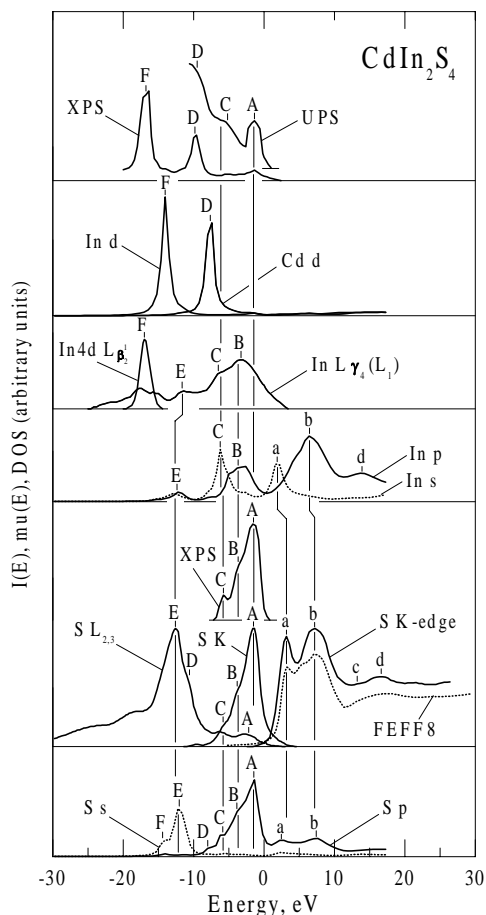


Figure 2

The calculated LDOS in  $\text{CdIn}_2\text{S}_4$  and experimental x-ray emission and absorption spectra of sulfur and indium, XPS-spectrum (Ihara, H. et al., 1978), and UPS-spectrum (Cerrina, F. et al., 1980). All curves are shown in the unified energy scale, zero of which corresponds to the top of the valence band.

600 lines per mm). The *K*-edge spectra of S were deconvoluted to the inner level and the spectrometer's window widths. The position of the top of the valence band was determined and assumed to be the energy zero. Nevertheless, in Fig.2-4 the uncorrected experimental x-ray spectra are presented.

### 3. Results and discussion

From the comparison of the theoretical LDOS and XANES and experimental x-ray and XPS spectra shown in Fig.2-4 for  $\text{CdIn}_2\text{S}_4$ ,  $\text{InPS}_4$ , and  $\text{Tl}_3\text{AsS}_3$  it follows that the top of the valence band in these compounds is formed by p-states of sulfur (maximum A of the theoretical LDOS of S p-states and S *K*-emission band). In the same region, the p-states of metals are located: In in  $\text{InPS}_4$ , Tl in  $\text{Tl}_3\text{AsS}_3$ , and Cd in  $\text{CdIn}_2\text{S}_4$ . About 3eV deeper are the p-states of the nonmetals: P in  $\text{InPS}_4$  and As in  $\text{Tl}_3\text{AsS}_3$  and likewise p-states of In in  $\text{CdIn}_2\text{S}_4$ . They are visible as maximum B in the experimental P *K*-band in  $\text{InPS}_4$  and In *L*<sub>1</sub>-band in  $\text{CdIn}_2\text{S}_4$  as well as by maximum B on the corresponding theoretical LDOS curves. Maximum C is connected with s-states of In in  $\text{InPS}_4$  and  $\text{CdIn}_2\text{S}_4$ , and of Tl in  $\text{Tl}_3\text{AsS}_3$ .

The bottom of the valence band in the semiconductors studied is formed of s-states of S (maxima D in  $\text{InPS}_4$  and E in  $\text{CdIn}_2\text{S}_4$  and

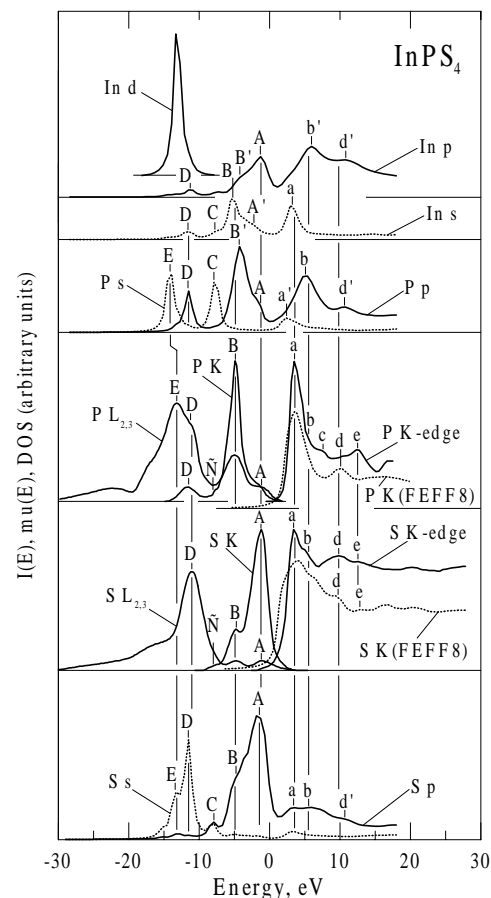


Figure 3

The theoretical LDOS in  $\text{InPS}_4$  compared with the experimental emission and absorption spectra of S and P.

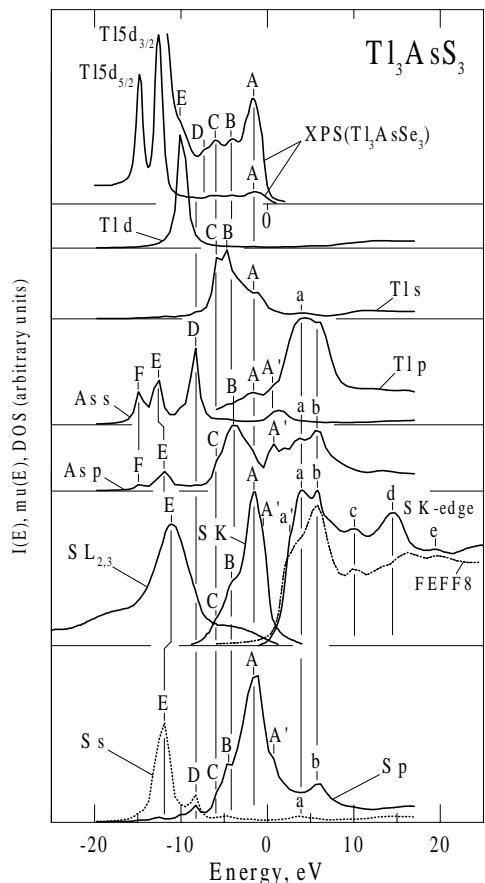
$\text{Tl}_3\text{AsS}_3$  on the S *L*<sub>2,3</sub>-band and DOS of S s-states) and s-states of As in  $\text{Tl}_3\text{AsS}_3$  and P in  $\text{InPS}_4$ . See also maxima E and F of the As s-states in  $\text{Tl}_3\text{AsS}_3$  and E on the P s-states in  $\text{InPS}_4$ .

Significant mixing of electron states takes place, as can be seen from the coincidence of energy positions of various features of the LDOS of different elements of the same compound. It proves the high degree of the covalence of chemical bonds.

In general, a good correspondence between the theoretical, calculated curves and their experimental analogues can be observed. The only exception is the energy positions of the calculated levels lying deep within the valence band d-states of the metals, these are at about 3eV lower energy compared to XPS data taken from the literature.

One can see this in Fig.2 for the XPS spectrum of  $\text{CdIn}_2\text{S}_4$  (Ihara H. et al., 1978), where peaks D (Cd 4d-states) and F (In 4d-states) do not coincide with analogous maxima in the calculated curves. A similar situation applies to the Tl5d-states in the isoelectronic  $\text{Tl}_3\text{AsSe}_3$ , as one can see in Fig.4, where the XPS spectrum (Ewbank, M.D. et al., 1981) is compared with the calculated LDOS of Tl d-states.

The calculated *K*-absorption spectra of sulfur and phosphorus in  $\text{CdIn}_2\text{S}_4$ ,  $\text{InPS}_4$ , and  $\text{Tl}_3\text{AsS}_3$  are presented in Fig.2-4 as dashed lines



**Figure 4**

The calculated LDOS of Tl, As, and S in  $Tl_3AsS_3$  together with experimental  $L_{2,3}$ -emission and  $K$ -absorption spectra of sulfur. For comparison XPS-spectrum of  $Tl_3AsSe_3$  is shown.

below their experimental analogues. Especially good agreement for the form and energy position of the main maxima has been obtained for  $CdIn_2S_4$  (Fig.2). It is worse for  $InPS_4$  (Fig.3) and  $Tl_3AsS_3$  (Fig.4).

In general, one can state that the correspondence between theory and experiment is quite good, taking into account the complicated structure of the compounds studied, for which the application of the muffin-tin scheme is not necessarily reliable.

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