ELECTRONIC STRUCTURE FROM X-RAY K-EDGES IN ZnS:Fe AND CuFeS₂

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RESUME Les structures des seuils K de Zn, Fe, Cu et S dans la blende (ZnS:Fe) et dans la chalcopryrite apportent des informations sur leur structure électronique. Une énergie de référence commune a été déterminée pour tous les seuils. La relation XANES distance-énergie est applicable aux différents éléments à partir de cette énergie de référence. La comparaison avec les calculs de structure de bande de CuFeS₂ est satisfaisante.

ABSTRACT Information about the electronic structures of natural ZnS:Fe (zinc-blende) and CuFeS₂ (chalcopryrite) has been obtained from K-edge absorption structure of Zn, Fe, Cu and S. The features in the edges of the different atoms have been used to place these spectra on a common energy scale. The inverse distance-energy relationship is consistent with the positions of shape resonances in the metal cation spectra, referenced to the same zero energy. A good agreement has been found with band structure calculations for CuFeS₂.

INTRODUCTION

Sphalerite (ZnS), also known as zinc-blende, and chalcopryrite (CuFeS₂) are important metal sulfide minerals in which all elements are tetrahedrally coordinated. They are also prototypes of wide structural families containing semiconductors of fundamental interest. Their electronic properties and band structures are strongly dependent on the composition and the presence of minor components. In pure sphalerite, zinc and sulfur atoms build fcc lattices related by the translation vector (1/4, 1/4, 1/4). The zinc-blende structure has space group symmetry F43m (T₂²_d). Iron is often present at a few percent concentration and replaces zinc atoms. In this structure iron is known to be in the 2+ valence state and in high-spin configuration (1). The chalcopryrite structure may be derived from the zinc-blende structure by ordering the two cations Cu and Fe alternately on the cation sublattice. This confers to the chalcopryrite structure the space group symmetry I42d (D¹²_{2d}).

In both structures, all cations are 4-fold coordinated, at the centers of regular or nearly regular tetrahedra of sulfur. Sulfur atoms occupy regular tetrahedra of zinc atoms in ZnS and are in distorted tetrahedra of two copper atoms and two iron atoms in CuFeS₂ (2).

Pure ZnS is an insulating material with a band gap value of 3.8 eV (1,5). The presence of iron narrows the gap to 0.4 eV, due to d-d transitions in iron. CuFeS₂ is a semi-conductor with a narrow band gap of 0.7 eV (6). Its electronic structure is not completely understood. The many different experimental approaches used generally indicate monovalent copper and trivalent iron. Nevertheless the magnetic moment of iron atoms is 3.85 B (1), which is neither the expected value for Fe³⁺ nor for Fe²⁺. The electronic structures of pure ZnS in its cubic and hexagonal phases and of CuFeS₂ have been calculated using both the SCF-X method and first principles band structure calculations (3-7).

This study examines the near edge fine structure at the K-edges of all cations and of sulfur in sphalerite and chalcopyrite as probes of the local densities of empty states. EXAFS at the K-edge of iron in two different ferrous sphalerites confirmed that iron is 4-fold coordinated, occupying the sites of zinc atoms, and showed that cation-anion distance is the same as ZnS distance in pure sphalerite.

EXPERIMENTAL

The K-edges of iron, copper and zinc (at 7111 eV, 8980 eV and 9650 eV respectively) were measured using the synchrotron radiation of LURE-DCI (Orsay) (Figure 1 and 2). The spectra were recorded by the transmission method using a silicon (400) "channel-cut" single crystal monochromator. The overall energy resolution for the final states, which results from the convolution of the core level width and of the

The K-edges of sulfur (2470 eV) were recorded at LURE-ACO on the soft X-ray EXAFS line using a Ge(111) double-crystal monochromator. The absorption coefficient was determined from the total photoelectron yield with a "channeltron" detector. The energies of the K-edges were calibrated with a reliability of ≈ 0.2 eV for different spectra relative to the same element.

CATION EDGES

The iron K-edge spectra in ZnS:Fe containing iron at different concentration levels are superposed in figure 1b, 1c. It is noticeable that the local electronic state of iron is dependent on the iron concentration in the energy range corresponding to metal 4p-states. This effect is more evident in figure 3 where the two iron K-edges are superimposed. The electronic density of empty 4p-states is larger in the mineral containing iron at a higher concentration, while the spectra are strictly identical in the energy range of 1s-3d transitions. The local density of 4p states in iron increases with Fe concentration possibly because of the presence of other Fe atoms as second neighbours, which enhances p electron delocalization. In contrast, the pre-edge features in both cases are identical in amplitude due to the very localized nature of the 1s-3d transition. The zinc spectrum (figure 1a) for pure ZnS exhibits a large peak in the energy range of 4p density of states.

The spectrum of iron in CuFeS₂ (figure 2b) can be compared directly to iron spectra in ZnS:Fe. The first maxima after the main absorption edge (4p electronic density of states) occur at the same energy. Comparison of their "pre-edges", corresponding to 1s-3d transitions, is of interest (figure 4). In CuFeS₂, the position of the maximum, which is 1 eV higher than for ZnS:Fe, is consistent with the trivalent character of Fe in chalcopyrite. Moreover the unusually high amplitude of the "pre-edge" in chalcopyrite can be understood in terms of the especially short Fe-S distance (2.25 Å). This distance would favor a large covalency of the bonding and a strong hybridization of the iron 3d-states with the sulfur 3p-states. The copper spectrum (figure 2a) exhibits a "pre-edge" feature, "A", which is unexpected with the hypothesis of monovalent copper in CuFeS₂ (3d¹⁰). The maximum of absorption is similar to zinc and it corresponds to high local electronic density of 4p-states.

Fig. 1- K-edges spectra and their derivatives for zinc in ZnS and iron in ZnS:Fe. (a- 5 wt% iron, b-13 wt% iron).

Fig. 2- K-edges spectra and their derivatives for copper and iron in CuFeS₂.

To correlate edge information with the electronic structures of these two compounds, it is necessary to find a common zero reference energy, relative to the cations of a given material. This zero energy is chosen to be the level of the upper valence band. In this way, it can be assumed that the 4p-peaks, corresponding to delocalised electronic states, are roughly at the same energy above the zero reference. A relative positioning for both cations in both compounds can then be obtained.

Specification of the zero energy for iron spectra (figure 1b, 1c) will determine the zero energy for Zn in blends and Cu in chalcopyrite. The "pre-edges" of the three iron spectra feature 3d-3d localised transitions. Data available from optical absorption measurements indicate that these 3d-3d transitions have an energy of ≈ 0.4 eV in ZnS:Fe and ≈ 0.7 eV in CuFeS₂. This procedure results in the energy scale reported in the five spectra of figures 1 and 2.

Fig. 3- K-edges spectra of iron in ZnS:Fe. (dotted line: 13 wt% Fe, dashed line: 5 wt% Fe)

Fig. 4-Iron k-edges: dotted line: ZnS:Fe (13 wt% Fe), dashed line CuFeS₂.

All five spectra present a maximum of absorption in the energy range of 30-40 eV which can be attributed to a resonance in the continuum. An energy-distance relationship has been shown to apply when a given atomic species is present in environments of similar geometries in different compounds (8). In this relationship $(E - E_0)d^2 = Cst$, where E is the energy of the resonance and d the distance from the absorbing atom to its first neighbours; E_0 is generally taken as a bound state resonance. This implies that the scattering of the photoelectron is localised within the coordination atomic shell. This relationship holds for the resonances "Y" in the iron spectra in ZnS:Fe and in CuFeS₂, E_0 being the zero energy previously assigned. In this case the relationship can be applied for different cations (Fe, Cu, Zn) because of the common reference energy E_0 (Table 1). An identical relationship is valid for "X" resonances on the copper and iron spectra of CuFeS₂. In ZnS:Fe "X" resonances are not clearly defined in Zn or in Fe spectra.

TABLE I

	CuFeS ₂		ZnS : Fe	
	Fe	Cu	Fe	Zn
$d(\text{\AA})$	2,26	2,30	2,34	2,34
$E_x - E_0$ (eV)	35,28	34,04	33,04	33,04
$(E_x - E_0) d^2$	180,2	180,1	180,9	180,9
$E_x - E_0$ (eV)	26,17	23,18		
$(E_x - E_0) d^2$	123,1	122,8		

SULFUR EDGES

The sulfur K-edge spectra in ZnS and in CuFeS₂ are reported in figure 5. The sulfur edge in ZnS exhibits a high absorption peak as it has also been observed in other metal sulfides. In contrast, the sulfur K-edge in CuFeS₂ presents an unusual structure, the first absorption maxima consisting of two sharp features preceding the broad maximum. This splitting can be understood in terms of the sulfur coordination, which consists of a tetrahedron of two iron and two copper at slightly different distances; the large mixing of orbitals related to S-Fe and S-Cu bonding also contributes to this

Fig. 5-Sulfure K-edges: dotted line: ZnS, full line: CuFeS₂.

splitting. These two peaks correspond to the 3d transition "pre-edges" of copper and iron edge spectra. However, they are separated by 2.2 eV while the relative positions of copper and iron spectra (figure 2a, 2b) give about 1 eV between the 3d features. It may be inferred that the larger energy separation between the two initial peaks in the sulfur spectrum of chalcopyrite results from the mixing of the Cu and Fe orbitals with S orbitals and the consequent additional splitting.

DISCUSSION

In the case of chalcopyrite the results reported here can be compared to the local densities of states given by Hamajima et al (6) based on SCF- $K\alpha$ band structure calculation. The atomic contents of the eigenfunction at the Γ point are reproduced in figure 6 and they are superimposed with the three experimental spectra of CuFeS_2 . The Fermi level of the calculation has been chosen as to correspond with the zero energy determined above. The small difference between the actual Fermi level and the top of the valence band, (certainly less than 0.4 eV) does not modify significantly the comparison. These calculations indicate that the pre-edge features for Fe and Cu in chalcopyrite correspond to narrow d-states in the lowest portion of the conduction band. This result contrasts with the normal assignment of Fe, Ti, V etc... in oxides to a localized bound state. The calculation reproduces many features of the experimental spectra. In the copper and iron spectra the 3d peaks as well as the large 4p resonances in the 10-13 eV range coincide quite well. As for the sulfur the broad maximum at 7-9 eV is also reproduced by the calculation. The splitting between the two first peaks in the spectrum is not predicted well by the calculation.

Because none of the band structure calculations on ZnS report local densities of states for Zn, Fe and S atoms separately in the appropriate energy range, no detailed analysis of the Zn, Fe or S spectra of zinc-blende is possible at present.

Fig. 6-K-edges spectra of iron, copper and sulfur in CuFeS_2 . Eigenvalues and atomic contents of the eigenfunctions (at the Γ point) are represented by proportional vertical lines.

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