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## Combined x-ray absorption and x-ray diffraction studies of $\text{CuGaS}_2$ , $\text{CuGaSe}_2$ , $\text{CuFeS}_2$ and $\text{CuFeSe}_2$ under high pressure

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**Abstract:** I-III-VI<sub>2</sub> compounds  $\text{CuGaS}_2$ ,  $\text{CuGaSe}_2$ ,  $\text{CuFeS}_2$  and  $\text{CuFeSe}_2$  have been studied by x-ray absorption spectroscopy and x-ray diffraction as a function of pressure. The combination of both techniques allowed the complete determination of the structures in their whole stability range. The equation of state of these compounds have been determined, as well as the volume compression at the transitions. The recovered phases after a pressure cycle are identical to the initial phases.

### Introduction

Semiconductors of the I-III-VI<sub>2</sub> family with the chalcopyrite structure (fig. 1) are isoelectronic analog of the zinc-blende II-VI semiconductors where the replacement of the cationic sublattice by two different species induces: i) a tetragonal distortion,  $\epsilon = 2 - a/c$  ii) the anion displacement,  $u = 0.25 + (d^2_{\text{VI-I}} - d^2_{\text{VI-III}}) / a^2$ .

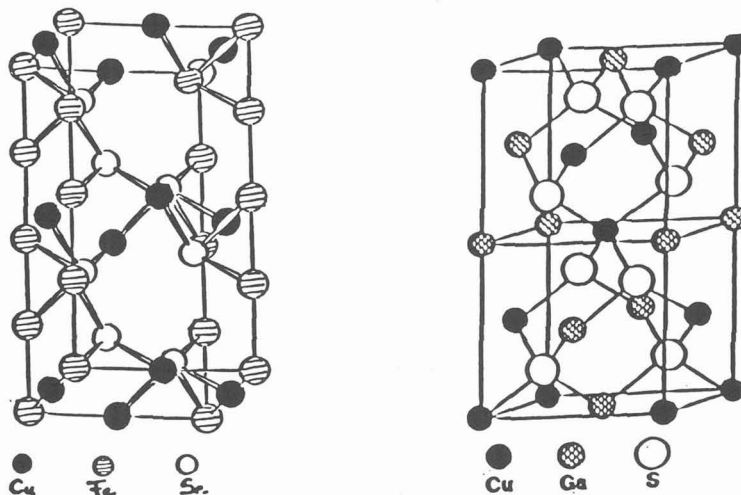


Fig. 1. Eskebornite ( $\text{CuFeSe}_2$ ) and chalcopyrite ( $\text{CuGaS}_2$ ) structures

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These compounds have been studied especially because of their optical, electrical and magnetic properties. The Cu based chalcopyrites have recently stimulated a great interest as promising materials for optoelectronic devices.  $\text{CuFeSe}_2$  is the only one which doesn't crystallize in the chalcopyrite type, but in the eskebornite structure.<sup>2</sup> (see fig.1).

The evolution with pressure of  $\text{CuGaSe}_2$ ,  $\text{CuGaS}_2$ ,  $\text{CuFeS}_2$  and of  $\text{CuFeSe}_2$  have been investigated by energy dispersive x-ray diffraction (EDX) and by x-ray absorption spectroscopy (XAS) in the dispersive mode at the Cu, Ga and Fe K edges. Combining the information on the bond length variation obtained by XAS and on the variation of the parameters  $a$  and  $c$  of the tetragonal unit cell obtained by EDX make it possible to determine the evolution of all the structural parameters:  $a$ ,  $c$ ,  $u$ , and  $\epsilon$  under quasi hydrostatic pressure.

The EXAFS spectra have been analyzed using the classical equation, in the one electron, plane waves approximation. A software written by A. San Miguel<sup>5</sup> was used to analyze the EXAFS oscillations.

### Experimental

Not intentionally doped  $\text{CuGaS}_2$  and  $\text{CuGaSe}_2$  samples were grown by iodine vapor transport method and the samples of  $\text{CuFeS}_2$  and  $\text{CuFeSe}_2$  by melt annealing.

Membrane diamond anvil cells<sup>3</sup> were used as high pressure generator. Silicon oil was the pressure transmitting medium and the pressure was determined using the linear ruby scale.

XAS experiments were performed at the energy dispersive spectrometer of the LURE (Orsay-France). The diffraction experiments took place at the energy dispersive station on the wiggler beam line of the LURE. In both cases, the samples were finely grinded. Fig. 2 shows an example of EDX spectra for the eskebornite and rocksalt phases of  $\text{CuFeSe}_2$ .

### Results and Discussion

The  $a$  and  $c$  parameters have been determined for all compounds in the stability range of the low pressure phase: chalcopyrite and eskebornite. The evolution of the volumes per unit formula obtained by EDX in the low pressure phase have been fitted with a first-order Murnaghan equation of state<sup>4</sup>:

$$V = V_0 \left( 1 + \frac{B'_0 P}{B_0} \right)^{-\frac{1}{B'_0}}$$

where  $B_0$  is the bulk modulus at ambient,  $B'_0$  its pressure derivative and  $V_0$  the volume per unit formula at ambient. The various parameters deduced from the EDX experiments are shown in the Table I.  $B_0$  has been calculated with  $B'_0=4$  in the low pressure phase. The  $\epsilon$  parameter have been calculated in the stability range of the low pressure phase. Its variation with pressure is small (less than 3% in all compound. see fig. 3).

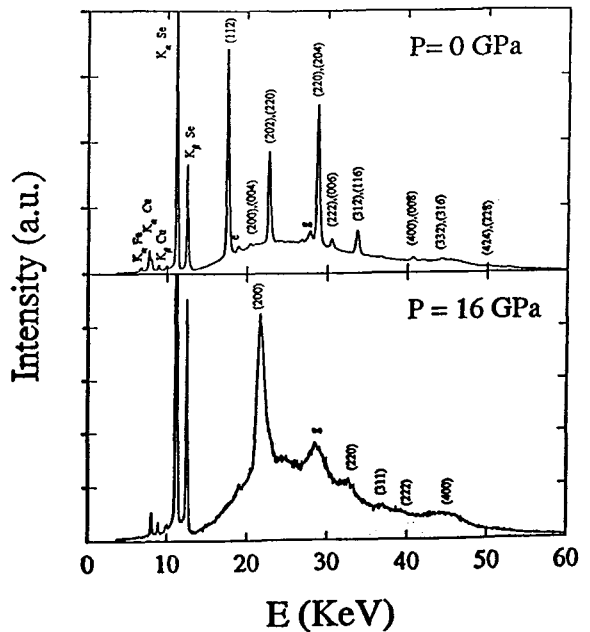


Fig. 2. Diffraction spectra in the eskebornite and NaCl phases of  $\text{CuFeSe}_2$

Phase transitions to disordered rocksalt have been observed for all the chalcopyrite samples. In the case of  $\text{CuFeSe}_2$ , a tetragonal phase appears near 2 GPa with an increase of  $\epsilon$ , and around 8 GPa a transition to a NaCl type structure takes place.

Only data of obtained at the Cu and Ga K edges for  $\text{CuGaS}_2$  and at the Cu and Fe K edges for  $\text{CuFeS}_2$  have been entirely analyzed. Since  $d_{\text{Cu-Se}}$  and  $d_{\text{Cu-Fe}}$  are very close in  $\text{CuFeSe}_2$ , the results are difficult to analyze in this compounds. The combination of EDX and XAS makes possible the complete determination of the atomic positions in the unit cell, and is therefore a substitute to the single crystal x-rays diffraction. In  $\text{CuGaS}_2$ , the Cu-S and Ga-S bond lengths have been deduced (fig. 4.) and these data used to calculate the structural parameter  $u = .25 + (d_{\text{Cu-S}}^2 - d_{\text{Ga-S}}^2)/a^2$ . The linear bulk moduli for the individual bonds have been determined and are  $B_{\text{Ga-S}} = 60$  GPa and  $B_{\text{Cu-S}} = 120$  GPa. The difference of the bonds compressibilities is expressed by the pressure dependence of  $u$ , which decreases. The parameters  $\epsilon$ , obtained from EDX, and  $u$ , obtained from EXAFS, decrease with pressure and the transition takes place when  $\epsilon = 0$  and  $u = 0.25$ . This is however not a general property in the chalcopyrite compounds: in  $\text{CuFeS}_2$   $u$  is almost independent of the pressure and therefore the value of the parameters at the transition are different of the ideal values.

There are two remarkable differences between the eskebornite and chalcopyrite compounds: the bulk modulus is three times smaller in the former than in the latter and the volume change at the transition is half the chalcopyrite values. The diffraction peaks in the first high pressure phase of  $\text{CuFeSe}_2$  could be indexed in the tetragonal structure, and it is possible that this new phase is a disordered eskebornite one, due to the increase of tetragonal distortion.

The bulk moduli of the rocksalt structures in  $\text{CuGaS}_2$  and  $\text{CuGaSe}_2$  have been studied both at upstroke and downstroke, and are slightly larger than in the chalcopyrite structure.

The recovered phases after a pressure cycle are similar to the initial phases, showing reversibility, but the peaks are much broader.

It is interesting to compare the transition pressure and the bulk moduli in the I-III-VI<sub>2</sub> and in the binary analogs II-VI compounds. In ZnS and ZnSe the transition to a rocksalt structure occur at 15 GPa and 13 GPa<sup>6</sup>, respectively, very close to the values in the chalcopyrite analogs. The bulks moduli are 103.6 GPa ( $B' = 4$ ) in ZnS and 97 GPa in  $\text{CuGaS}_2$ . The mechanical properties of both compounds, which differ only by the cationic sublattice, are extremely similar.

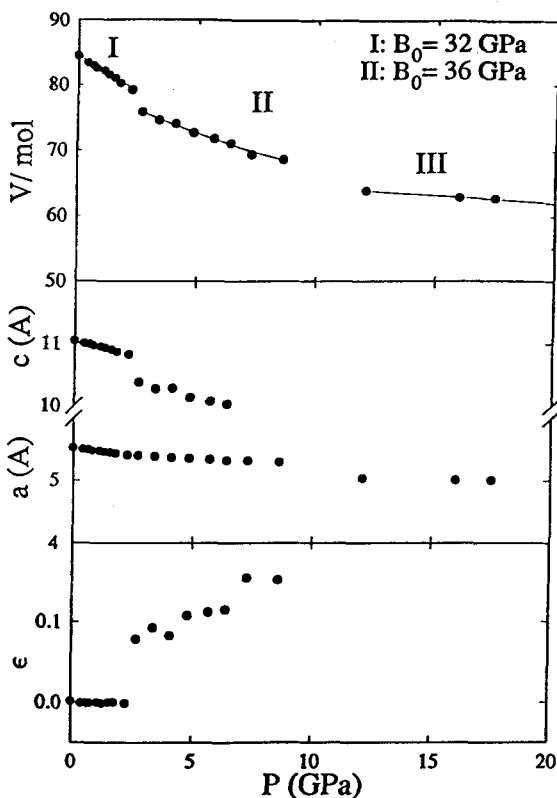


Fig. 3. Structural parameters of  $\text{CuFeSe}_2$  as a function of pressure.

Table I. Summary of the structural data obtained with EDX.

Compound	Pressure range (GPa)	Transition pressure (GPa)	Structure	Volume change	Bulk Modulus (GPa)	B'₀
CuGaS₂	0-16	15	chalcopyrite rocksalt	14%	97	4
	16-37				105	3
CuGaSe₂	0-13	13	chalcopyrite rocksalt	13%	102	4
	13-33				113	3
CuFeS₂	0-7	7	chalcopyrite rocksalt	10%	91	4
	7-10				-	-
CuFeSe₂	0-2	2.5	eskebornite tetragonal rocksalt	6% 7%	32	4
	2-10	10			36	4
	10-20	-			-	-

### Conclusion

The combination of EXAFS and EDX has allowed the complete determination of the crystalline structure of CuGaS₂ and CuFeS₂. In the chalcopyrite and eskebornite samples, a transition to a disordered rocksalt phase has been observed at high pressure. The bulk moduli and volume changes are different in the eskebornite structure (36 GPa and 7%), whereas it is 97-102 GPa and 13% for the chalcopyrites structure. The recovered phases after decompression are similar to the initial phases. In CuGaS₂ the  $\epsilon$  and  $u$  parameters decrease under pressure, to attain ideal values at the transition, but it is not the case in the other samples.

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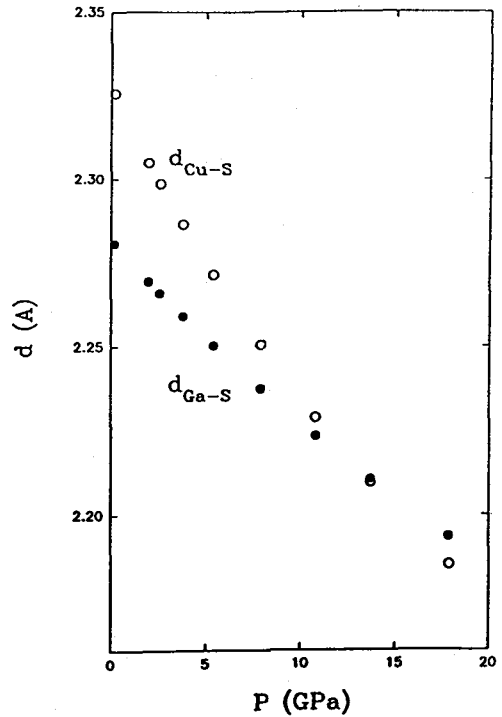


Fig. 4. First neighbours distances in CuGaS₂