



HAL
open science

Combined x-ray absorption and x-ray diffraction studies of CuGaS₂, CuGaSe₂, CuFeS₂ and CuFeSe₂ under high pressure

T. Tinoco, J. Itié, A. Polian, A. San Miguel, E. Moya, P. Grima, J. Gonzalez, F. Gonzalez

► To cite this version:

T. Tinoco, J. Itié, A. Polian, A. San Miguel, E. Moya, et al.. Combined x-ray absorption and x-ray diffraction studies of CuGaS₂, CuGaSe₂, CuFeS₂ and CuFeSe₂ under high pressure. Journal de Physique IV Proceedings, 1994, 04 (C9), pp.C9-151-C9-154. 10.1051/jp4:1994923 . jpa-00253484

HAL Id: jpa-00253484

<https://hal.science/jpa-00253484>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Combined x-ray absorption and x-ray diffraction studies of CuGaS_2 , CuGaSe_2 , CuFeS_2 and CuFeSe_2 under high pressure

T. Tinoco*, J.P. Itié**, A. Polian*, A. San Miguel*(1), E. Moya*, P. Grima*, J. Gonzalez*** and F. Gonzalez****

* *Physique des Milieux Condensés, Université P. & M. Curie, 4 Place Jussieu, BP. 77, 75252 Paris cedex 05, France*

** *LURE, Université Paris Sud, Bât. 209D, 91405 Orsay cedex, France*

*** *Centro de Estudios de Semiconductores, Universidad de los Andes, Merida 5101, Venezuela*

**** *Departamento de Física, Universidad Central de Venezuela, Ap. 47586, Caracas 1041A, Venezuela*

Abstract: I-III-VI₂ compounds CuGaS_2 , CuGaSe_2 , CuFeS_2 and 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-VI₂ 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, $u = 0.25 + (d^2_{\text{VI-I}} - d^2_{\text{VI-III}}) / a^2$.

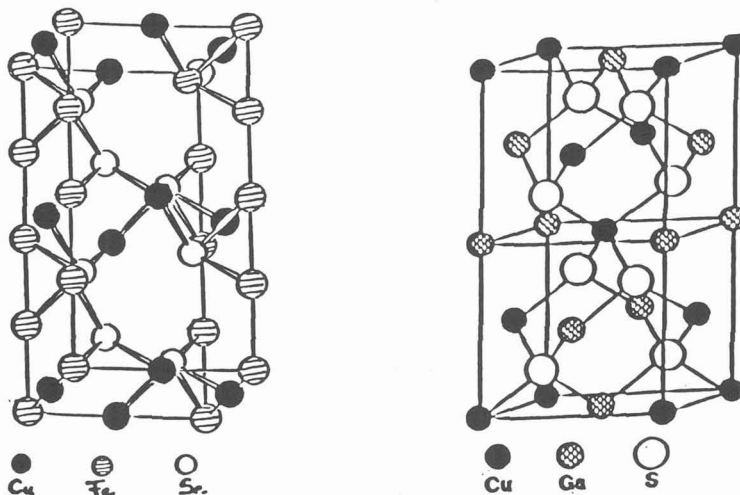


Fig. 1. Eskebornite (CuFeSe_2) and chalcopyrite (CuGaS_2) structures

(1) Present address: ESRF, BP. 220, 38043 Grenoble cedex, France

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. CuFeSe_2 is the only one which doesn't crystallize in the chalcopyrite type, but in the eskebornite structure.² (see fig.1).

The evolution with pressure of CuGaSe_2 , CuGaS_2 , CuFeS_2 and of 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 ϵ 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 Miguel⁵ was used to analyze the EXAFS oscillations.

Experimental

Not intentionally doped CuGaS_2 and CuGaSe_2 samples were grown by iodine vapor transport method and the samples of CuFeS_2 and CuFeSe_2 by melt annealing.

Membrane diamond anvil cells³ 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 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 state⁴:

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

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 ϵ 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).

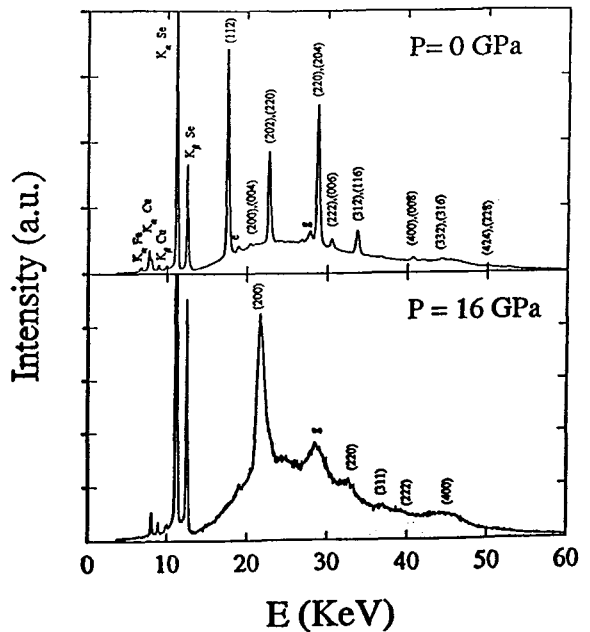


Fig. 2. Diffraction spectra in the eskebornite and NaCl phases of CuFeSe_2

Phase transitions to disordered rocksalt have been observed for all the chalcopyrite samples. In the case of CuFeSe_2 , a tetragonal phase appears near 2 GPa with an increase of ϵ , 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 CuGaS_2 and at the Cu and Fe K edges for CuFeS_2 have been entirely analyzed. Since $d_{\text{Cu-Se}}$ and $d_{\text{Cu-Fe}}$ are very close in 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 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 ϵ , 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 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 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 CuGaS_2 and 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-VI₂ and in the binary analogs II-VI compounds. In ZnS and ZnSe the transition to a rocksalt structure occur at 15 GPa and 13 GPa⁶, 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 CuGaS_2 . The mechanical properties of both compounds, which differ only by the cationic sublattice, are extremely similar.

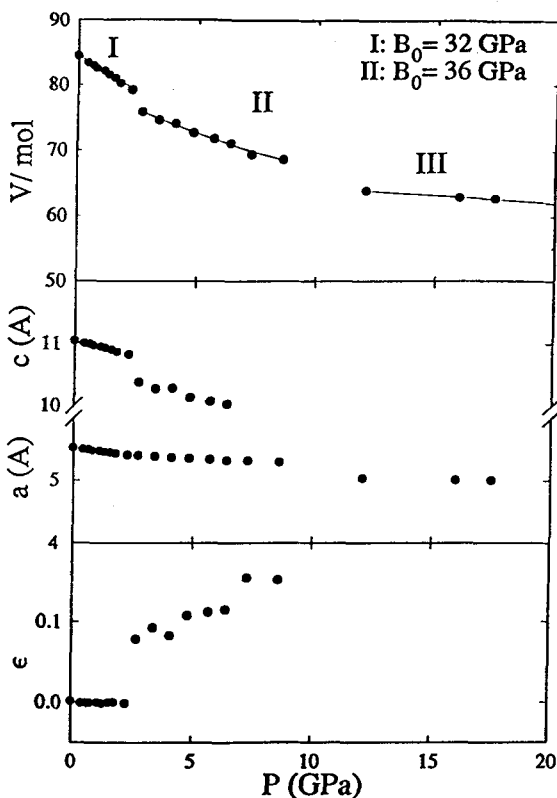


Fig. 3. Structural parameters of CuFeSe_2 as a function of pressure.

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 ϵ and u parameters decrease under pressure, to attain ideal values at the transition, but it is not the case in the other samples.

References

1. J. Jaffe and A. Zunger, *Phys. Rev. B* **29**, 1882 (1984).
2. J. Lazameres, F. Gonzalez-Jimenez, E. Jaimes, L. D'Onofrio, R. Iraldi, G. Sanchez-Porras, J. Gonzalez, J.C. Wolley and G. Lamarche, *J. Mag. and Magn. Mat.* **104-107**, 997 (1992).
3. R. LeToullec, J. P. Pinceaux and P. Loubeyre, *High Press. Res* **1**,77 (1988).
4. F. D. Murnaghan, *Am. J. Math.* **49**, 235 (1937)
5. A. San Miguel, Thèse, Université P. et M. Curie (1993).
6. S. Ves, U. Schwarz, N.E. Christensen, K. Syassen and M. Cardona, *Phys. Rev. B* **42**, 9113 (1990).

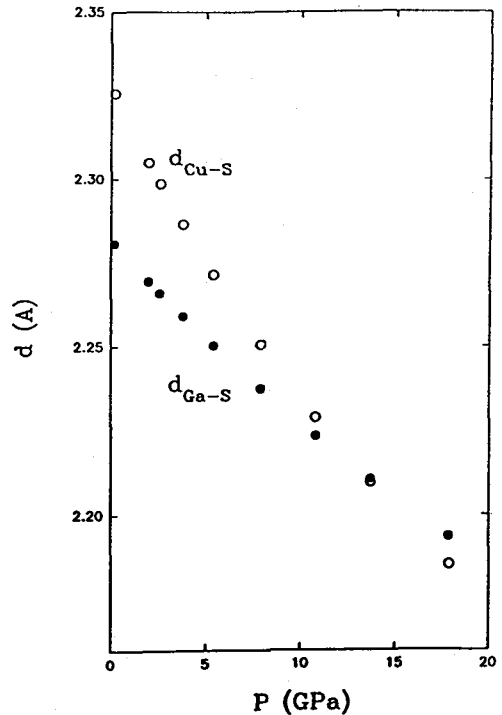


Fig. 4. First neighbours distances in CuGaS₂