

## A MÖSSBAUER STUDY OF TERNARY COMPOSITIONS IN THE SYSTEM Cu-Fe-Se: PRELIMINARY RESULTS

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**RIASSUNTO.** — La cristallochimica del ferro nei composti ternari del sistema Cu-Fe-Se è stata studiata mediante spettroscopia Mössbauer a temperatura ambiente. L'indagine spettroscopica di due termini della soluzione solida  $(\text{Cu,Fe})\text{Se}_{2-x}$ , con rapporti leggermente diversi M/Se, ha indicato che il ferro si trova in un solo sito della struttura del tipo pirite. I valori dello spostamento isomerico (0,48 e 0,46 mm/sec., relativi a Fe metallico) suggeriscono la presenza di  $\text{Fe}^{2+}$  a basso spin nei siti ottaedrici. Composti ternari all'interno del campo della soluzione solida « Se-iss », intorno alla composizione  $\text{CuFeSe}_2$ , mostrano spettri assai complessi, che suggeriscono l'inizio di una transizione per ordinamento magnetico appena al di sotto della temperatura ambiente. Si ritiene che il ferro in queste fasi sia essenzialmente  $\text{Fe}^{2+}$  ma ancora non è stato stabilito il numero dei siti reticolari occupati. Allo scopo di risolvere questi problemi sono attualmente in corso ulteriori indagini Mössbauer a bassa temperatura.

**ABSTRACT.** — The crystal chemistry of iron of ternary compounds in the Cu-Fe-Se system has been investigated using  $^{57}\text{Fe}$  Mössbauer spectroscopy at room temperature. Spectroscopic investigation of two diselenide compositions  $(\text{Cu,Fe})\text{Se}_{2-x}$ , differing slightly in M/Se ratio, showed Fe occurring in only one site in the pyrite-like structure. Isomer shift values (0.48 and 0.46 mm/sec., relative to iron metal) support the occurrence of low-spin  $\text{Fe}^{2+}$  in the octahedral sites. All the compositions within the « Se-iss » field, in the central portion of the system (around  $\text{CuFeSe}_2$ ), show complex spectra which are believed to represent the onset of a magnetic ordering transition just below room temperature. The spectra show a dependence on relative Fe concentration which supports this interpretation. The iron in these phases is believed to be essentially high-spin  $\text{Fe}^{2+}$  but the number of Fe-containing sites has not yet been clearly established. Further spectroscopic work at low temperature is underway to solve these problems.

### Introduction

A series of ternary compositions in the system Cu-Fe-Se have been synthesized and annealed at 500° and 300° C. The syntheses were part of an investigation of phase relations in the system Cu-Fe-Se (BERNARDINI & MAZZETTI, 1979; BERNARDINI et al., 1981, 1982). All synthesized compositions, which were produced using standard sealed silica tube techniques, were investigated using reflected light microscopy, X-ray powder diffraction and electron probe methods of analysis.

A number of the samples were selected for study using  $^{57}\text{Fe}$  Mössbauer spectroscopy to investigate the crystal chemistry of iron in the system. Information on the compositions and structures of the samples studied is shown in table 1, which lists the starting compositions of the synthesized charges and the results of examination by X-ray powder diffraction and examination in polished section under the reflected light microscope. Two samples with compositions of the type  $(\text{Cu,Fe})\text{Se}_{2-x}$ , which correspond to the synthetic phase reported by FRANZ (1970) (and hereafter termed the « Franz phase »), were synthesized and annealed at 500° C and are compositionally and structurally homogeneous. The other compositions synthesized all lie within the solid solution field which centres around the composition  $\text{CuFeSe}_2$  and is referred to generally as the « Se-iss ». A series of four compositions all containing

48 % at. Se and with increasing Fe/Cu ratio were investigated (these were annealed at 500° C). Two further compositions containing 47 % at. Se were studied which were also annealed at 500° C. A series of three compositions of varying Fe/Cu ratio and 48 % at. Se but annealed at 300° C were also examined.

### Experimental methods

The technique employed in the synthesis of samples and their examination by X-ray diffraction, electron microprobe and optical microscopy methods have been described elsewhere (BERNARDINI et al., 1981, 1982).

<sup>57</sup>Fe Mössbauer spectra were obtained from powders spread as a thin coating on adhesive tape. The equipment employed consisted of the Harwell spectrometer drive and detector system with the Inotech 5200 multichannel analyzer (1024 channels). Data were accumulated in 512 channels of the memory and output onto lineprinter and punched tape.

The source of  $\gamma$ -rays was <sup>57</sup>Co in a Pd matrix and the spectrometer calibrated using iron foil. All isomer shifts reported in this work are with respect to the center of gravity of the six-peak iron foil spectrum as zero. Data in this preliminary work were obtained with the sample only at room temperature ( $\sim 300^\circ$  K).

The data obtained were computer fitted to groups of Lorentzian peaks using a least squares iterative procedure based on the program devised by STONE (1967).

### Results and discussion

#### Franz phase (Cu,Fe)Se<sub>2-x</sub>

The phase (Cu,Fe)Se<sub>2-x</sub> is a diselenide which exhibits a range of solid solution at elevated temperature. It is reported to have a cubic structure based on that of pyrite (FRANZ, 1970, 1975) and would, therefore, contain Se-Se groups and Cu and Fe in a slightly distorted octahedral coordination.

Mössbauer spectra have been obtained at room temperature for two Franz phase compositions, both with equal atom percent Cu and Fe but the second slightly more deficient in Se (see table 1). Both spectra (see fig. 1 a, b) comprise of a single quadrupole doublet with no evidence to suggest iron occur-

TABLE 1  
Compositional data on synthetic  
Cu-Fe-Se phases

Sample No.	Formula	Atomic % starting comp'n	Results of X-ray / optical study
"Franz" phase (annealed at 500°C)			
F - 5/7	(Cu,Fe)Se <sub>2-x</sub>	Cu <sub>15.0</sub> Fe <sub>15.0</sub> Se <sub>70</sub>	CuFeSe <sub>2-x</sub> alone
503	(Cu,Fe)Se <sub>2-x</sub>	Cu <sub>16.0</sub> Fe <sub>15.0</sub> Se <sub>68</sub>	CuFeSe <sub>2-x</sub> alone
Se-iss phases (annealed at 500°C)			
1 - 5/5	~CuFeSe <sub>2</sub>	Cu <sub>27.5</sub> Fe <sub>24.5</sub> Se <sub>48</sub>	CuFeSe <sub>2</sub> alone + homogeneous
1 - 5/7	~CuFeSe <sub>2</sub>	Cu <sub>24.0</sub> Fe <sub>27.5</sub> Se <sub>48</sub>	CuFeSe <sub>2</sub> + trace Cu
1 - 5/8	~CuFeSe <sub>2</sub>	Cu <sub>23.5</sub> Fe <sub>28.5</sub> Se <sub>48</sub>	CuFeSe <sub>2</sub> + trace Cu
1 - 5/9	~CuFeSe <sub>2</sub>	Cu <sub>22.0</sub> Fe <sub>30.0</sub> Se <sub>48</sub>	CuFeSe <sub>2</sub> + trace Cu
1 - 5/10	~CuFeSe <sub>2</sub>	Cu <sub>29.0</sub> Fe <sub>24.0</sub> Se <sub>47</sub>	CuFeSe <sub>2</sub> alone + homogeneous
1 - 5/11	~CuFeSe <sub>2</sub>	Cu <sub>28.0</sub> Fe <sub>25.0</sub> Se <sub>47</sub>	CuFeSe <sub>2</sub> + trace Cu
Se-iss phases (annealed at 300°C)			
1 - 3/6	~CuFeSe <sub>2</sub>	Cu <sub>26.0</sub> Fe <sub>26.0</sub> Se <sub>48</sub>	CuFeSe <sub>2</sub> + trace Cu
1 - 3/8	~CuFeSe <sub>2</sub>	Cu <sub>23.5</sub> Fe <sub>28.5</sub> Se <sub>48</sub>	CuFeSe <sub>2</sub> + 7 trace Cu
1 - 3/9	~CuFeSe <sub>2</sub>	Cu <sub>22.0</sub> Fe <sub>30.0</sub> Se <sub>48</sub>	CuFeSe <sub>2</sub> + 7 trace Cu

ring in more than one position in the structure or to suggest any form of magnetic interaction between iron atoms in the structure at room temperature.

Computer fitting of the spectra gave good fits in both cases to a pair of Lorentzian peaks and the parameters obtained in each case are listed in table 2. The isomer shift values of 0.48 and 0.46 mm/sec. respectively are somewhat greater than the value for the marcasite structure binary phase FeSe<sub>2</sub> (0.39 mm/sec.) but this can be accounted for in terms of both the difference in crystal structure and increase in cell parameters and inferred M-Se distance which results from replacement of Fe by Cu. Ferroselite is reported diamagnetic and both the magnetic and Mössbauer data indicate that the iron is low-spin Fe<sup>2+</sup>. Comparison of the isomer shift data for the two Franz phase compositions with data for FeSe<sub>2</sub> and the marcasite and pyrite structure forms of FeS<sub>2</sub>, indicates that these Franz phase diselenides also contain low-spin Fe<sup>2+</sup> in the octahedral sites of this pyrite structure material. (Note also that when the iron in the pyrite structure is in the high-spin state, the isomer shift value is much greater e.g. 0.83 mm/sec. for high-spin Fe<sup>2+</sup> in (Mn,Fe)S<sub>2</sub> reported by BARGERON et al., 1971).

The quadrupole splitting values for the two Franz phase compositions are very small (0.31 and 0.29 mm/sec. respectively) compared even to that of pyrite (0.61 mm/sec.)

TABLE 2  
Mössbauer parameters of diselenides and related phases

Sample or mineral	Composition	Structure type	Spectrum temperature (°K)	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Reference
F - 5/7	Cu <sub>15</sub> Fe <sub>15</sub> Se <sub>70</sub>	? pyrite	300	0.48	0.31	(1)
503	Cu <sub>16</sub> Fe <sub>16</sub> Se <sub>68</sub>	? pyrite	300	0.46	0.29	(1)
Ferroselite	FeSe <sub>2</sub>	marcasite	300	0.39	0.58	(2)
Synthetic	FeSe <sub>1.75</sub>	unknown	300	0.43	0.60	(3)
Pyrite	FeS <sub>2</sub>	pyrite	300	0.31	0.61	(2)
Marcasite	FeS <sub>2</sub>	marcasite	300	0.27	0.51	(2)
Synthetic	(Mn,Fe)S <sub>2</sub>	pyrite	300	0.83	1.50	(4)

(1) This work; (2) TEMPERLY & LEFEVRE (1966); (3) REDDY & CHETTY (1975); (4) BARGERON et al. (1971).

and further support the assignment of oxidation and spin states to low-spin Fe<sup>2+</sup>. The quadrupole splitting observed in pyrite is a consequence of the slight trigonal distortion of the octahedral site. In the (Cu,Fe)Se<sub>2-x</sub> phases this distortion must be offset in part by the substitution of Cu and perhaps by having Se as the anion which should lead to a more delocalized valence electron distribution.

The small differences in isomer shift and quadrupole splitting values between the two synthetic phases (F-5/7 and 503) which amount to only approximately 4 % and 6 % variation respectively, must arise from the different M/Se ratios of the two phases.

#### Se-iss phase

The «Se-iss» is a field of solid solution in the central portion of the Cu-Fe-Se system, the compositional limits of which have been defined at 500° C (BERNARDINI et al., 1981) and at 300° C (BERNARDINI et al., 1982). All the phases synthesized and quenched from these temperatures have structures based on the sphalerite cell with metals and sulfur in regular tetrahedral coordination. Although in the synthetic studies undertaken at 300° C, two kinds of «Se-iss» product were reported which differed in optical properties — one being optically isotropic the other anisotropic — no differences were observed in the X-ray powder diffraction patterns. All

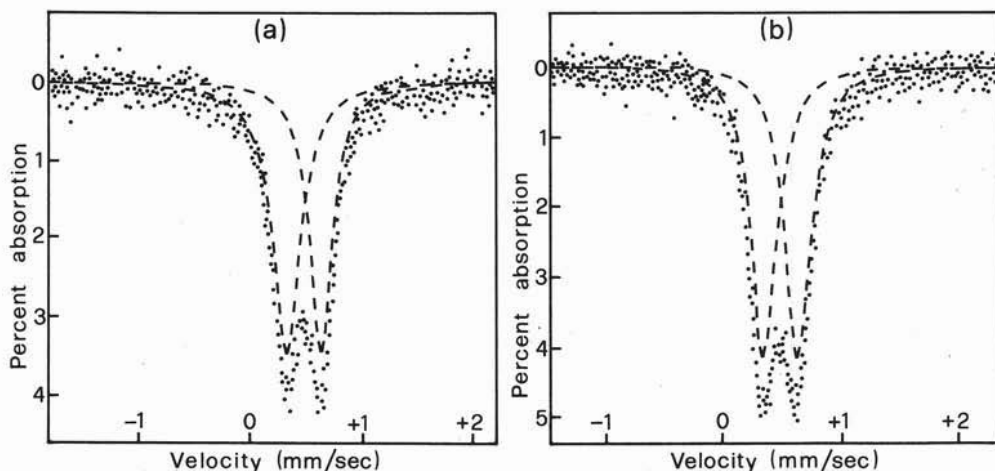


Fig. 1. — Mössbauer spectra of «Franz phase» diselenides at 300° K: (a) synthetic Cu<sub>15.0</sub>Fe<sub>15.0</sub>Se<sub>70</sub>; (b) synthetic Cu<sub>18.0</sub>Fe<sub>18.0</sub>Se<sub>68</sub>.

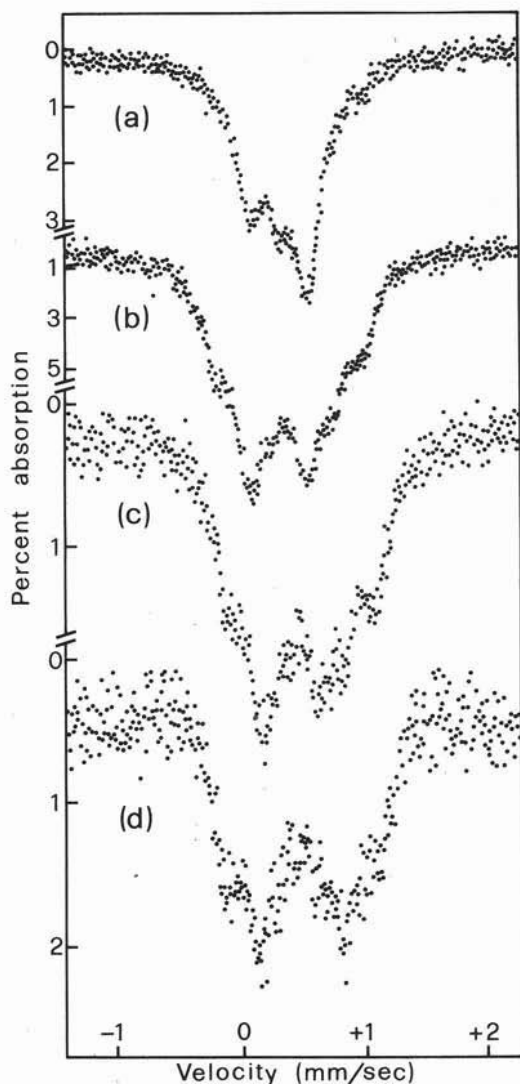


Fig. 2. — Mössbauer spectra of a series of « Se-iss » selenides annealed at 500° C (spectra obtained at 300° K): (a)  $\text{Cu}_{27.5}\text{Fe}_{24.5}\text{Se}_{48}$ ; (b)  $\text{Cu}_{24.5}\text{Fe}_{27.5}\text{Se}_{48}$ ; (c)  $\text{Cu}_{23.5}\text{Fe}_{28.5}\text{Se}_{48}$ ; (d)  $\text{Cu}_{22.0}\text{Fe}_{30.0}\text{Se}_{48}$ .

of the synthetic materials have powder patterns the same as that of eskebornite ( $\text{CuFeSe}_2$  with cubic  $\text{Pm}\bar{3}\text{m}$  structure) and the possibility of a tetragonal chalcopyrite-type structure occurring in some of these phases remains unresolved (BERNARDINI et al., 1982).

Room temperature Mössbauer spectra were obtained for six samples quenched from 500° C, four of these were phases with a

fixed ratio of M/Se (of 52/48) and varying Cu/Fe ratio (table 1). The spectra obtained for these samples are shown in fig. 2 *a-d* starting with the lowest iron content (24.5% at. Fe) in fig. 2 *a* and extending to the highest iron content (30% at. Fe). These complex spectra show a clear dependence with regard to their shape on the iron content of the samples. (It is also notable that apart from the sample with lowest iron content, the other three samples showed minor Cu impurity suggesting Fe/Cu ratios even higher than the starting compositions). Particularly in the later spectra (fig. 2 *c, d*) the formation of the type of six-peak spectrum characteristic of magnetically ordered material can be discerned. An alternative interpretation is of overlapping quadrupole doublets arising from Fe in different sites without the additional complexity of magnetic ordering. However, the values of quadrupole splittings which would be obtained according only to this last interpretation (e.g.  $\sim 2.98$  mm/sec. for outermost peaks in fig. 2 *d*), are very unlikely. By analogy with  $\text{CuFeS}_2$  (chalcopyrite), for which formal oxidation states on the cations are now well established as  $\text{Cu}^+\text{Fe}^{3+}\text{S}_2^-$  (TOSSELL et al., 1982), the iron is expected to be high-spin  $\text{Fe}^{3+}$ . Mössbauer parameters for the iron in chalcopyrite (at 300° K) are generally reported as: isomer shift = 0.20 mm/sec.; quadrupole splitting = 0 (VAUGHAN & BURNS, 1972) in a material which is antiferromagnetically ordered at room temperature (hyperfine magnetic field at the nucleus = 350 Kgauss at 300° K, VAUGHAN & BURNS, 1972). Taking estimated values of the centre of gravity of « pairs » of peaks in the spectra of fig. 2, yields approximate isomer shift values in the range 0.25-0.50 mm/sec. supporting the occurrence of iron as high-spin  $\text{Fe}^{3+}$  (cf. tetrahedrally coordinated high-spin  $\text{Fe}^{3+}$  isomer shift values for sulfides with bornite = 0.39 mm/sec., germanite = 0.34 mm/sec.).

On the basis, therefore, of the room temperature spectra, we suggest that these « Se-iss » samples contain high-spin  $\text{Fe}^{3+}$  which is involved in a magnetic coupling interaction, the ordering temperature of which is probably a little below room temperature. In accordance with this interpretation, the magnetic hyperfine spectrum is better deve-

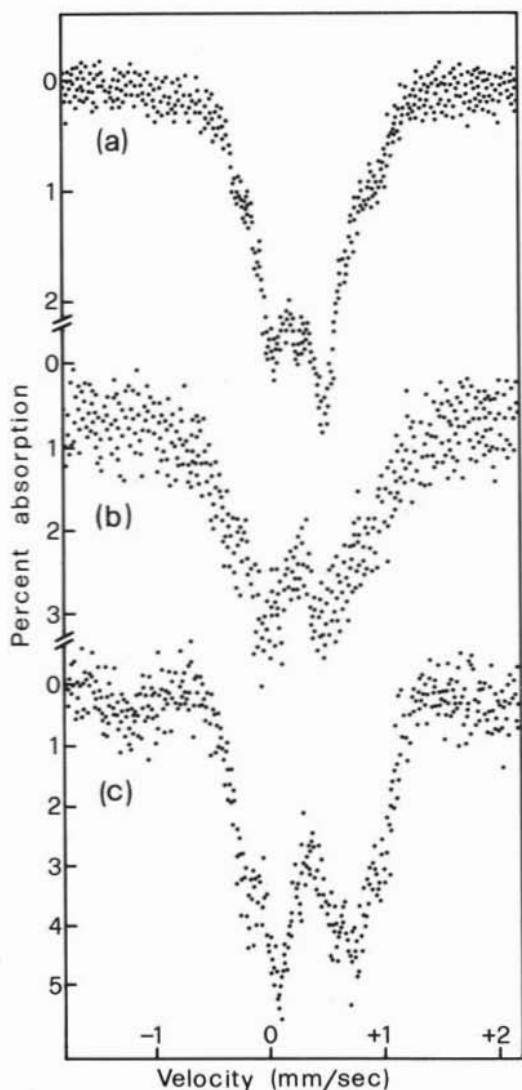


Fig. 3. — Mössbauer spectra of a series of « Se-iss » selenides annealed at 300°C (spectra obtained at 300°K): (a)  $\text{Cu}_{20.0}\text{Fe}_{20.0}\text{Se}_{40}$ ; (b)  $\text{Cu}_{20.0}\text{Fe}_{20.0}\text{Se}_{40}$ ; (c)  $\text{Cu}_{22.0}\text{Fe}_{20.0}\text{Se}_{48}$ .

loped in samples containing more iron (fig. 2 c, d).

The same general observations apply to the two samples annealed at 500°C with M/Se ratio of 53/47 and to the three samples annealed at 300°C with M/Se ratios of 52/48 (see table 1). In fig. 3 a-c the spectra obtained for the samples annealed at 300°C are shown. Again we see the appearance of magnetic hyperfine splitting

which is itself dependent on iron content (which again increases for samples with high iron contents). Not surprisingly, the spectra of samples I-3/8 and I-3/9 are very similar to those of samples I-5/8 and I-5/9, compositions being identical and only annealing temperature being different. This further supports the view that variations in the spectra with Fe/Cu are real and reproducible.

Clearly most (perhaps all?) of the  $\text{Fe}^{3+}$  in these  $\sim \text{CuFeSe}_2$  compositions is in tetrahedral cation sites of the type found in sphalerite. However, not only are all of the compositions studied metal-rich but in nearly all cases the iron is less than, or in excess of, the copper content. There is no clear evidence from the Mössbauer spectra (fig. 2 and 3) of iron occupying more than one type of crystallographic site in the structure, assuming that the complexities observed arise from incipient magnetic ordering. However, the complex room temperature spectra are too poorly resolved to enable this possibility to be properly discussed. It may well be that study of spectra at lower temperatures will reveal the presence of more than one magnetic hyperfine sub-spectrum.

### Concluding remarks

The study of ternary phases in the system Cu-Fe-Se by  $^{57}\text{Fe}$  Mössbauer spectroscopy indicates that the phase  $(\text{Cu,Fe})\text{Se}_{2-x}$  or « Franz » phase contains only one type of iron in the structure which is probably octahedrally coordinated low-spin ferrous iron. Phases in the « Se-iss », which centre around compositions  $\sim \text{CuFeSe}_2$ , exhibit complex spectra believed to represent the onset of a magnetic ordering transition just below room temperature. The iron in these phases is believed to be essentially high-spin  $\text{Fe}^{3+}$  but the number of iron-containing sites has not yet been clearly established. Further low temperature work is underway to resolve these problems.

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