

THE SYSTEM Cu-Fe-Se: RECONNAISSANCE PHASE RELATIONS BETWEEN 500 AND 700°C

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ABSTRACT

Phase relations in the system Cu-Fe-Se at 500°C have been studied in silica tube by quenching experiments whereas the assemblages up to 700°C have been established mainly through D.T.A. runs on presynthesized charges. Synthetic eskebornite reacts on heating to form Se-intermediate solid solution (Se-*iss*) and $(\text{Cu,Fe})\text{Se}_{2-x}$, followed by Se-poor *iss*, which decomposes into Cu_{2-x}Se and $\gamma\text{-Fe}_{1-x}\text{Se}$ between 635 and 640°C. Synthetic $(\text{Cu,Fe})\text{Se}_{2-x}$ on heating shows an endothermic effect at 410°C, a progressive loss of Se between 575 and 655°C and melts to a liquid of similar composition at 660°C. According to the thermal behavior of the two ternary solid solutions, the variation of phase relations at different temperatures between 500 and 700°C and consistent four-phase equilibria reactions are reported.

Keywords: Cu-Fe-Se system, phase relations, 500°C isotherm, eskebornite, Se-*iss*, diselenide solid solution, D.T.A.

SOMMAIRE

On a étudié les relations de phase dans le système Cu-Fe-Se à 500°C par synthèse suivie de trempe en tubes de silice, et à 700°C, surtout par A.T.D. sur les charges présynthétisées. L'eskebornite de synthèse se décompose par chauffage, donnant d'abord un mélange de Se-*iss* (solution solide intermédiaire) + $(\text{Cu,Fe})\text{Se}_{2-x}$, et ensuite une *iss* pauvre en Se qui se décompose en Cu_{2-x}Se et $\gamma\text{-Fe}_{1-x}\text{Se}$ entre 635 et 640°C. Le composé synthétique $(\text{Cu,Fe})\text{Se}_{2-x}$ montre un pic endothermique à 410°C et une perte progressive en Se de 575 à 655°C, et il passe par fusion à un liquide d'à peu près la même composition à 660°C. A la lumière du comportement thermique des deux solutions solides ternaires, on illustre la variation des relations de phase entre 500 et 700°C, ainsi que les réactions d'équilibre à quatre phases.

(Traduit par la Rédaction)

Mots-clés: système Cu-Fe-Se, relations de phase, isotherme à 500°C, eskébornite, Se-*iss*, diséléniure en solution solide, A.T.D.

INTRODUCTION

Phase relations in selenide systems have received considerable attention from chemists and solid-state physicists for many years. However, they have received far less from experimental petrologists and mineralogists, despite the importance of Se as a possible indicator of geochemical conditions of mineral formation, especially in particular geological settings (Gent 1976, Howard 1977). Knowledge of the phase relations in the quaternary system Cu-Fe-S-Se is a necessary prerequisite for investigation of the significance of the S/Se ratio as a possible indicator of Cu-Fe sulfide ore genesis.

The present work, part of a study in progress on Cu-Fe selenides that involves characterization of their properties and determination of phase equilibria in the system Cu-Fe-Se over a wide range of temperature, reports on the variation of phase relations between 500 and 700°C.

PREVIOUS STUDIES

The natural and synthetic phases present in the two binary systems Cu-Se and Fe-Se and in the ternary system Cu-Fe-Se are reported in Table 1, together with their crystallographic characteristics and thermal stabilities.

The phase relations in the system Cu-Se have been studied by Heyding (1966), Dies (1967), Bernardini & Catani (1968), Bernardini *et al.* (1972) and Murray & Heyding (1975); they have been reviewed by Bernardini *et al.* (1976, 1977) in their studies on the phase relations in the system Cu-S-Se. Reviews of the phase relations in the metallic system Cu-Fe may be found in Hansen & Anderko (1958) and in the supplements of Elliott (1965) and Shunk (1969). No reference to more recent literature will be given here, because the phase relations in this system are beyond the scope of this work. The phase relations in the system Fe-Se, studied by many authors since the first work

TABLE 1. "NATURAL AND SYNTHETIC PHASES IN THE Cu-Fe, Fe-Se AND Cu-Fe-Se SYSTEMS

Mineral or synthetic phase	Composition	Crystallography, thermal stability and references
Berzelianite	Cu ₂ Se	monocl. $\xrightarrow{123^{\circ}\text{C}}$ cub. $\xrightarrow{1113^{\circ}\text{C}}$ liq. (3,8)
Bellidoite	Cu ₂ Se	tetr. (2)
Def. berzelianite	Cu _{2-x} Se	cub. (8)
Umangite	Cu ₃ Se ₂	tetr. $\xrightarrow{113^{\circ}\text{C}}$ Cu _{2-x} Se + CuSe (8)
Athabascaite	Cu ₅ Se ₄	orth. (5)
Klockmannite	CuSe	low-hex. $\xrightarrow{50^{\circ}\text{C}}$ orth. $\xrightarrow{120^{\circ}\text{C}}$ high-hex. $\xrightarrow{379^{\circ}\text{C}}$ Cu _{2-x} Se + Se (8)
synthetic	CuSe ₂	orth. (FeS ₂ -m-type) $\xrightarrow{332^{\circ}\text{C}}$ CuSe + Se (8)
Krutaitē	CuSe ₂	cub. (FeS ₂ -py-type) (6)
Achavalite	FeSe (*)	β -tetr. (PbO-type) $\xrightarrow{457^{\circ}\text{C}}$ δ -Fe _{1-x} Se-hex. (NiAs-type) + Fe (10)
		δ -hex. (NiAs-type) $\xrightarrow{1065^{\circ}\text{C}}$ δ' -Fe _{1-x} Se $\xrightarrow{1078^{\circ}\text{C}}$ liq. (10)
synthetic	Fe _{1-x} Se	γ' -monocl. $\xrightarrow{\lambda\text{-type tr.}}$ δ -Fe _{1-x} Se (10)
		γ -monocl. 2C $\xrightarrow{728^{\circ}\text{C}}$ δ -Fe _{1-x} Se + liq. (10)
synthetic	Fe ₇ Se ₈	tricl. $\xrightarrow[4\text{C}]{240-298^{\circ}\text{C}}$ hex. (NiAs-type) $\xrightarrow[3\text{C}-2\text{C}-1\text{C}]{320-450^{\circ}\text{C}}$ hex. (NiAs-type) (9)
synthetic	Fe ₃ Se ₄	monocl. $\xrightarrow{725^{\circ}\text{C} (\lambda\text{-type tr.})}$ hex. (NiAs-type) (11)
		T > 600°C hex. $\xrightarrow{727^{\circ}\text{C}}$ Fe _{1-x} Se + liq. (7)
Ferroselite	FeSe ₂	orth. (FeS ₂ -m-type) $\xrightarrow{585^{\circ}\text{C}}$ γ -Fe _{1-x} Se + liq. (10)
Eskebornite	CuFeSe ₂	cub. $\xrightarrow[500^{\circ}\text{C}]{545^{\circ}\text{C}}$ (Cu,Fe)Se _{2-x} + CuFeSe _{2-x} $\xrightarrow{635^{\circ}\text{C}, 617^{\circ}\text{C}}$
synthetic	(Fe,Cu)Se	tetr. (4)
synthetic	(Cu,Fe)Se _{2-x}	cub. $\xrightarrow{580^{\circ}\text{C}}$ Cu-selenides + Se (12)

(*) according to reference (10) the tetragonal monoselenide has a Fe_{1+x}Se composition.

1- Bernardini & Mazzetti (1979b). 2- De Montreuil (1975). 3- Dies (1967). 4- Franz (1970). 5- Harris et al. (1970). 6- Johan et al. (1972). 7- Kullerud (1968). 8- Murray & Heyding (1975). 9- Okazaki (1961). 10- Schuster et al. (1979). 11- Svendsen (1972). 12- Wang (1980).

of Hägg & Kindström (1933) (e.g., Tengnér 1938, Haraldsen & Grønvold 1944, Haraldsen 1952, Hirone & Chiba 1956, Tröften & Kullerud 1961, Kullerud 1968, Dutrizac *et al.* 1968a, b, Svendsen 1972), were not clearly defined until the recent work of Schuster *et al.* (1979). These investigators established the Fe-Se diagram from 20 to 66 at. % Se between 623 and 1373 K by thermoanalytical and isopiestic methods and by X-ray analyses. In particular, they clarified the region between 51.5 and 58.5 at. % Se by identifying two monoclinic structures (γ and γ') derived from the distortion of the NiAs-related phase of Fe_{1-x}Se composition. They also confirmed the presence of a two-phase field between these two phases, found independently by Kamimura & Iwata (1978) and by Tsuji *et al.* (1979). Regarding the phase relations in the system Cu-Fe-Se, Franz (1970) investigated some "combinations" at 400°C by X-ray and differential-thermal analyses and found two new phases: (1) (Cu,Fe)Se_{2-x}, a cubic pyrite-type structure, and (2) (Fe,Cu)Se, tetragonal, space group P4/nmm. Franz (1975) also gave the powder diagram of the diselenide phase of the (Cu_{0.74}Fe_{0.26})Se_{2-x} composition and established the stability field of eskebornite at 400°C.

Bernardini & Mazzetti (1979a, b) recently determined the phase relations in the system Cu-Fe-Se at 900 and 700°C by means of silica-tube quenching experiments and studied the thermal behavior of synthetic eskebornite using D.T.A. and high-temperature X-ray analysis. More recently, Wang (1980) detected two types of recrystallized eskebornite in a sample annealed at 600°C for one week. Both Bernardini & Mazzetti (1979b) and Wang (1980) detected small amounts of Franz's (Cu,Fe)Se_{2-x} phase as a disintegration product of synthetic eskebornite heated at 500 and 550°C.

No attempt has been made to include all published studies relating to these systems, but rather to provide a brief summary of those most significant to the present work.

EXPERIMENTAL METHODS

The phase relations in the system Cu-Fe-Se at 500°C were studied by means of quenching experiments, whereas their variation between 500 and 700°C was established mainly through D.T.A. experiments on presynthesized individual compounds. Experimental charges of 600 mg were prepared by the conventional silica-tube

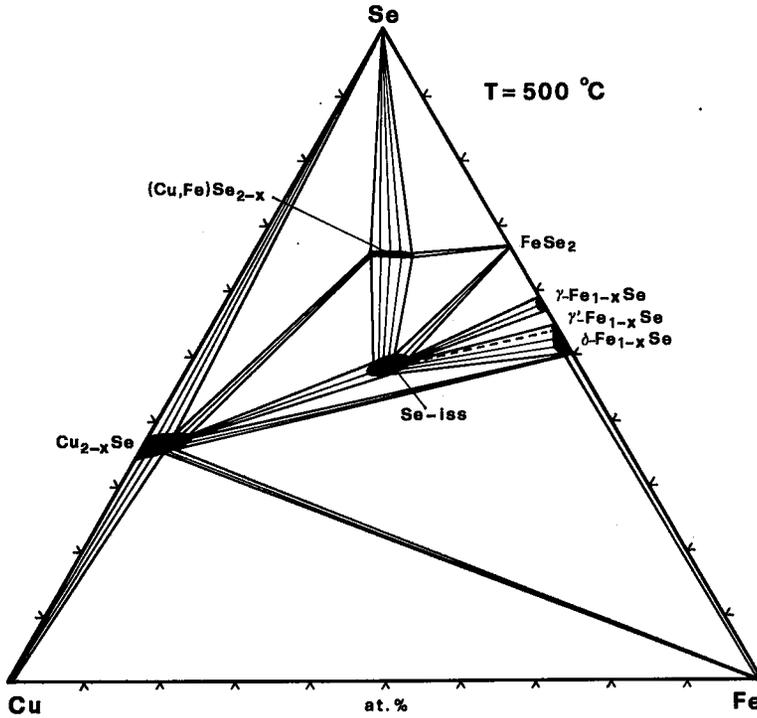


Fig. 1. Isothermal section of the condensed phase relations in the system Cu-Fe-Se at 500°C. The dashed tieline points to the Se-rich boundary of the δ -Fe_{1-x}Se phase (Schuster *et al.* 1979).

TABLE 2. SELECTED EXPERIMENTAL DATA AT 500°C

Charge number	Bulk composition (at.%)			Phases detected at room temperature (tr. = traces)
	Cu	Fe	Se	
501	10.0	10.0	80.0	(Cu,Fe)Se _{2-x} + Se
503	16.0	16.0	68.0	(Cu,Fe)Se _{2-x} + Se tr.
504	5.0	27.0	68.0	(Cu,Fe)Se _{2-x} + FeSe ₂ + Se tr.
563	25.0	8.3	66.6	(Cu,Fe)Se _{2-x} + Cu _{2-x} Se + Cu ₃ Se ₂ ? + Se tr.
564	25.0	15.0	60.0	(Cu,Fe)Se _{2-x} + Cu _{2-x} Se + Se-iss (*)
555	15.0	25.0	60.0	Se-iss + (Cu,Fe)Se _{2-x} + FeSe ₂
508	8.0	32.0	60.0	Se-iss + FeSe ₂ + γ -Fe _{1-x} Se
511	8.0	37.0	55.0	γ -Fe _{1-x} Se + Se-iss
566	8.0	39.0	53.0	Se-iss + γ' -Fe _{1-x} Se + γ -Fe _{1-x} Se
512	5.0	42.0	53.0	δ -Fe _{1-x} Se + Se-iss
516	25.0	25.0	50.0	Se-iss
517	12.0	38.0	50.0	Se-iss + δ -Fe _{1-x} Se + FeSe
568	32.0	21.0	47.0	Se-iss + A-phase (*)
559	26.5	26.5	47.0	Se-iss
569	20.0	33.0	47.0	Se-iss + FeSe + A-phase tr.
522	13.0	42.0	45.0	FeSe + A-phase + α -Cu ₂ Se tr. + Fe tr.
523	47.0	10.0	43.0	Cu _{2-x} Se + Se-iss + (Cu,Fe)Se _{2-x} tr.
561	45.0	15.0	40.0	A-phase + α -Cu ₂ Se + FeSe + Se-iss
533	58.0	5.0	37.0	A-phase
539	55.0	10.0	35.0	A-phase + α -Cu ₂ Se + Fe tr. + FeSe tr.
553	20.0	70.0	10.0	Fe + Cu + A-phase + α -Cu ₂ Se

(*) see text.

technique (Kullerud 1971), using the same high-purity elements and the same procedure employed in a previous study (Bernardini & Mazzetti 1979a). The charges were heated in Ni-chrome-wound furnaces controlled to $\pm 3^\circ\text{C}$, quenched in ice water, repeatedly ground under acetone and reheated at 500°C for periods up to a maximum of six months. The final quenched products were examined by X-ray-diffraction analyses, with Co $K\alpha$ radiation on a Philips diffractometer, and by reflected-light microscopy. The D.T.A. were run on a Tempres D.T. 712 using thermocouple-well tubes (Kullerud 1971) and a heating-and-cooling rate of $3^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The phase relations in the system Cu-Fe-Se at 500°C are summarized in Figure 1, whereas selected representative data used to define the assemblages are reported in Table 2.

At 500°C two ternary solid-solutions exist: (1) CuFeSe_2 , hereafter indicated as Se-*iss*, by analogy with the *iss* term used by many authors (Mukaiyama & Izawa 1970, Cabri 1973, Barton 1973, Sugaki *et al.* 1975) to describe the extensive solid-solution field existing in the central part of the system Cu-Fe-S; (2) $(\text{Cu,Fe})\text{Se}_{2-x}$, in the Se-rich region of the system. These solid solutions correspond, respectively, to the mineral eskebornite and to $(\text{Cu,Fe})\text{Se}_{2-x}$, the synthetic phase of Franz (1970). The accurate compositional limits of the two solid-solution fields, which vary both in Se content and in Cu/Fe ratio, are presently under investigation.

In the Se-rich portion of the system, $(\text{Cu,Fe})\text{Se}_{2-x}$ coexists with Se and Cu_{2-x}Se on one side and with Se and FeSe_2 on the other. These two univariant fields are separated by a divariant field: $(\text{Cu,Fe})\text{Se}_{2-x} + \text{Se}$. Between the two ternary solid-solutions, one two-phase field [$(\text{Cu,Fe})\text{Se}_{2-x} + \text{Se-iss}$] and two three-phase fields [$(\text{Cu,Fe})\text{Se}_{2-x} + \text{Se-iss} + \text{Cu}_{2-x}\text{Se}$ and $(\text{Cu,Fe})\text{Se}_{2-x} + \text{Se-iss} + \text{FeSe}_2$] are established.

According to Schuster *et al.* (1979), the following phases are stable at 500°C on the Fe-Se border: (1) hexagonal $\delta\text{-Fe}_{1-x}\text{Se}$, from 50 to almost 54 at. % Se; (2) monoclinic $\gamma'\text{-Fe}_{1-x}\text{Se}$, in the range between 53.8 and 54.2 at. % Se; (3) monoclinic $\gamma\text{-Fe}_{1-x}\text{Se}$, from 56.4 to 58.7 at. % Se, with double *c* axis with respect to $\gamma'\text{-Fe}_{1-x}\text{Se}$; (4) orthorhombic $\epsilon\text{-FeSe}_2$ at 66.6 at. % Se. In the X-ray patterns of the 500°C quenched products of the ternary charges pointing towards the Fe-Se border, the γ and γ' phases could be easily distinguished from the

hexagonal δ by the splitting of strong reflections due to monoclinic distortion. Moreover, in perfect agreement with Schuster *et al.* (1979), the presence of tetragonal $\beta\text{-FeSe}$ as a product of quenching was revealed in the 500°C quenched products of charges with a Se content equal to and less than 50 at. %. According to the results reported in Table 2, therefore, tielines could be drawn between Se-*iss* and the different Fe_{1-x}Se phases on one side, and between Se-*iss* and Cu_{2-x}Se on the other.

The Se-poor limit of the univariant field, $\text{Cu}_{2-x}\text{Se} + \gamma\text{-Fe}_{1-x}\text{Se} + \text{Se-iss}$, varies from nearly 35 at. % Se towards the Cu-Se border to almost 50 at. % Se on the Fe-Se border. In the Se-deficient portion below this tieline, the general topology of the system is the same as that portrayed for the 700°C isotherm by Bernardini & Mazzetti (1979a). These authors identified, in the quenched product of the charge with a bulk composition of 58 at. % Cu, 5 at. % Fe and 37 at. % Se, an optically and chemically homogeneous phase. The compositional formula determined by electron-microprobe analysis, $\text{Cu}_{59.5}\text{Fe}_{3.9}\text{Se}_{36.5}$, corresponds to a hypothetical $\text{Cu}_{6.6}\text{Fe}_{0.4}\text{Se}_{4.0}$ compound. The X-ray pattern of this new phase, indicated as the *A*-phase, in which the metal/selenium ratio is of the same order as that established by Morimoto & Gyobu (1971) for Fe-stabilized digenite, shows, in addition to poorly resolved reflections similar to those of monoclinic $\alpha\text{-Cu}_2\text{Se}$, some very weak lines never reported for the latter. Its optical characteristics in air (creamy-white color, reflection pleocroism not observable, weakly anisotropic from grey to greenish-grey) are very similar to those of bellidoite (de Montreuil 1975). If a situation similar to that found by Morimoto & Gyobu (1971) may be proposed for the system Cu-Fe-Se at room temperature, the presence of the *A*-phase in the 500°C quenched products (Table 2) may be ascribed to an exsolution process during the quenching.

On the basis of the thermal effects shown in the D.T.A. curves of many Se-*iss* and $(\text{Cu,Fe})\text{Se}_{2-x}$ presynthesized charges, several quenching experiments were performed on the same charges. These were sealed in evacuated silica-glass vials, heated at temperatures higher than those of the D.T.A. peaks, quenched in ice water and immediately investigated by X-ray analysis and reflected-light microscopy.

The D.T.A. traces of a stoichiometric CuFeSe_2 charge, the $\text{CuFeSe}_{1.85}$ composition of Se-*iss* and the $(\text{Cu}_{0.5}\text{Fe}_{0.5})\text{Se}_2$ composition of $(\text{Cu,Fe})\text{Se}_{2-x}$ are shown in Figure 2. The thermal peak tem-

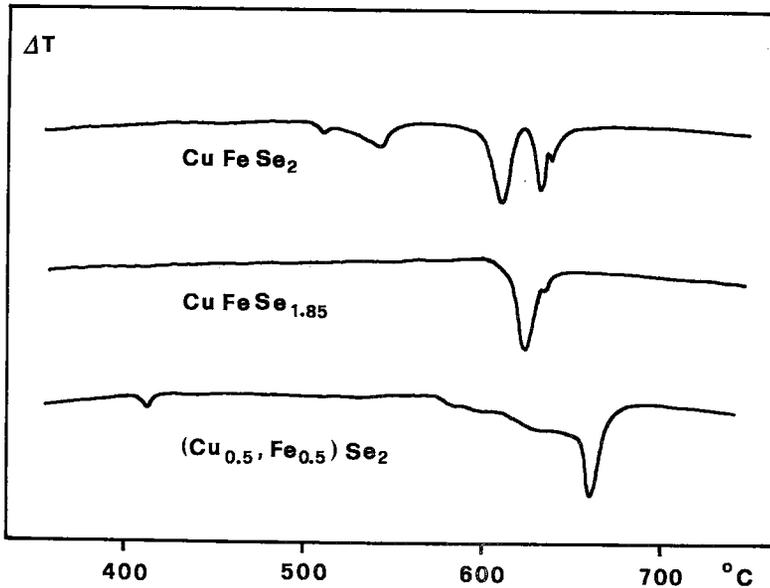


FIG. 2. D.T.A. curves of ternary solid solutions.

TABLE 3. THERMAL BEHAVIOR OF INDIVIDUAL COMPOUNDS

Composition	Tp. ($\pm 3^\circ\text{C}$)	Tq. ($\pm 3^\circ\text{C}$)	Phases detected at room temperature
CuFeSe ₂	515		
	545		
		575	Se-iss + (Cu,Fe)Se _{2-x} tr.
		625	Se-iss + γ -Fe _{1-x} Se + Cu _{2-x} Se
	635 - 640	700	Cu _{2-x} Se + γ -Fe _{1-x} Se + [Se-iss + (Cu,Fe)Se _{2-x}]
CuFeSe _{1.85}	625 - 635	700	Cu _{2-x} Se + γ -Fe _{1-x} Se
		300	(Cu,Fe)Se _{2-x} + CuSe ₂ tr. + Se tr.
(Cu _{0.5} Fe _{0.5})Se ₂		500	(Cu,Fe)Se _{2-x}
	410	625	(Cu,Fe)Se _{2-x} -type phase + Cu-selenides + Se tr.
	575 - 655		
	660	700	[(Cu,Fe)Se _{2-x} + CuSe + γ -Fe _{1-x} Se]

Tp. = D.T.A. peak temperature; Tq. = quenching temperature; tr. = traces
 [] phases obtained from quenched liquids.

peratures are reported in Table 3 together with the results of the relative quenching experiments. These D.T.A. curves may be compared with those of Franz (1970) run in N₂ atmosphere on synthetic CuFeSe₂ and (Cu,Fe)Se_{2-x} obtained at 400°C.

According to Franz (1970), the first two peaks in the CuFeSe₂ curve at 525 and 600°C are due, respectively, to its incongruent melting into (Cu,Fe)Se_{2-x} plus a Cu₃Se₂-similar liquid, and to the incongruent melting of the resulting (Cu,Fe)Se_{2-x} into Cu_{2-x}Se plus a CuFeSe_{<2}-similar liquid. Franz gives no explanation for

the endothermic peak at 630°C, whereas the large endothermic reaction starting at 730°C is attributed to a final release of Se.

The D.T.A. curve of the CuFeSe₂ charge run in the present study always shows a sluggish base-line between the first two small endothermic peaks, with maxima, respectively, at 515 and 545°C, suggesting a reaction or reactions occurring in sequential steps over the entire range of temperatures. No attempt was made to perform quenching experiments between the two maxima. The presence of Se-iss with a different Se content from the CuFeSe₂ product quenched

from 575°C, as well as from the product quenched after the 610°C peak, was revealed by definite shifts of the reflections in the X-ray pattern of eskebornite. This suggests, in contrast to Franz's (1970) interpretation, a successive decomposition of CuFeSe_2 with increasing temperature, producing an *iss* phase poorer in Se. The amount of $(\text{Cu,Fe})\text{Se}_{2-x}$ formed after the 515 and 545°C peaks seems to be very small, as in the case of pyrite formed at 560°C from CuFeSe_2 (Dutrizac 1976). Therefore, whereas one of the two peaks detected at 515 and 545°C may be ascribed to the decomposition reaction $\text{CuFeSe}_2 \rightarrow \text{Se-iss} + (\text{Cu,Fe})\text{Se}_{2-x}$, the overall heat-effect cannot be justified by this process. Either a low-high temperature inversion of eskebornite, similar to the so-called tetragonal-cubic "transition" in chalcopyrite (Yund & Kullerud 1966, Pankratz & King 1970, Cabri 1973, Barton 1973), or the formation of two types of recrystallized eskebornite (Wang 1980) could account for the total amount of the heat involved; however, neither of these two possible explanations could be confirmed. No evidence of a transition, in fact, could be found as no weak lines, indicating a possible reordering of Cu and Fe in the X-ray pattern of the CuFeSe_2 charge quenched from 500°C, were detected. On the other hand, no different types of recrystallized eskebornite were revealed in the 575°C quenched product. The discrepancy between this and Wang's (1980) observation may be due to the different quenching temperatures and procedures used. Whereas Wang quenched the synthetic material from 600°C after melting it completely at 700°C and annealing it at 600°C for one week, the CuFeSe_2 charge prepared in the present work was heated at 575°C and quenched after only a few days. On the other hand, in disagreement with Wang's (1980) observation, no endothermic peak in the range between 545 and 555°C was detected in the D.T.A. curve of the $\text{CuFeSe}_{1.85}$ composition in the present study. The nature of the 515–545°C transformation in the CuFeSe_2 is, therefore, still unknown; only accurate high-temperature X-ray analysis using a single-crystal technique could possibly solve this problem. The broad, pronounced endothermic effect with a maximum at 610°C resulted, in some runs, in a sluggish doublet with maxima at 610 and 615°C, previously not detected by Bernardini & Mazzetti (1979b). Owing to the proximity of these two temperatures, no quenching experiments between these two peaks were attempted, but the following two four-phase equilibria reactions: $\text{Se-iss} + (\text{Cu,Fe})\text{Se}_{2-x}$ -type phase $\rightleftharpoons L + \gamma\text{-Fe}_{1-x}\text{Se}$

and $\text{Se-iss} + L \rightleftharpoons \text{Cu}_{2-x}\text{Se} + \gamma\text{-Fe}_{1-x}\text{Se}$, based on the results of quenching experiments performed at 625°C, may account for such a doublet. The exact composition of the *Se-iss* phases involved in these reactions was not determined. The final decomposition of the Se-poorest *iss* into Cu_{2-x}Se and $\gamma\text{-Fe}_{1-x}\text{Se}$ at 640°C is confirmed by the X-ray analysis of the $\text{CuFeSe}_{1.85}$ charge quenched from 700°C, in perfect agreement with the high-temperature X-ray analysis performed by Bernardini & Mazzetti (1979a). Although no explanation was found for the small shoulder in this decomposition peak, its consistent presence may suggest that decomposition occurs, in sequential steps, over a very narrow range of temperatures.

No different quenching zones, similar to those of Cabri's *iss* (1973) in the system Cu–Fe–S, have yet been discerned in the system Cu–Fe–Se. Moreover, the absence of any ferroselite-type phase in the *Se-iss* quenched product confirms that, at 545°C, CuFeSe_2 does not react to *Se-iss* and FeSe_2 but to *Se-iss* and $(\text{Cu,Fe})\text{Se}_{2-x}$, which is stable up to 660°C. In contrast, the fuku-chilite-type phase in the system Cu–Fe–S, synthesized under hydrothermal conditions and preserved metastably below 275°C, decomposes quickly and completely above this temperature into pyrite, covellite and sulfur liquid (Shimazaki & Clark 1970).

In the $(\text{Cu,Fe})\text{Se}_{2-x}$ D.T.A. curve of Franz (1970), the flexus at 490°C and the peak at 530°C were attributed, respectively, to a first loss of Se and to the incongruent melting of the resulting Se-poorer $(\text{Cu,Fe})\text{Se}_{2-x}$ -type phase into Cu_{2-x}Se plus a $\text{CuFeSe}_{x < 2}$ -similar liquid. No explanation was given for the small peak at 590°C, which does not appear in the $(\text{Cu}_{0.5}\text{Fe}_{0.5})\text{Se}_2$ curve in the present study; on the contrary, this study shows a well-defined small peak at 410°C. This low-temperature peak was not detected by Franz (1970) or Wang (1980), possibly because their charges were prepared at 400 and 500°C, respectively. In the product of $(\text{Cu}_{0.5}\text{Fe}_{0.5})\text{Se}_2$, quenched from 300°C and reported in Table 3, traces of CuSe_2 and Se were detected in addition to the diselenide solid solution, which is Se-deficient, as noted by Franz (1970) and Wang (1980). In the product of the same charge quenched from 500°C, on the other hand, only the presence of the $(\text{Cu,Fe})\text{Se}_{2-x}$ phase was observed, in agreement with its Cu–Fe compositional limits found by Wang (1980). More complicated phase relations in the Se-rich portion of the system are to be expected at temperatures below 500°C, because of the appearance of new phases on the Cu–Se

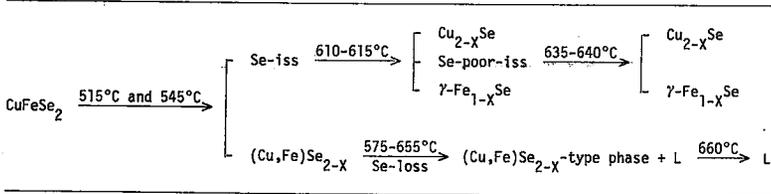


FIG. 3. Scheme of the thermal behavior of synthetic CuFeSe₂.

border (Murray & Heyding 1975). However, the 410°C peak detected in the D.T.A. curve of the (Cu_{0.5}Fe_{0.5})Se₂ charge may be ascribed to a passage from a three-phase to a one-phase field. The reconnaissance of the phase relations at 300°C should make it possible to clarify this problem completely, but it may already be in-

ferred that the compositional limits of the diselenide solid solution at 300°C must be narrower than those established by Wang (1980) at 500°C. At 575°C, (Cu,Fe)Se_{2-x} begins to break down incongruently, losing Se and giving off a ternary liquid extending from the Cu-Se border, on which it appears at 523°C (Murray

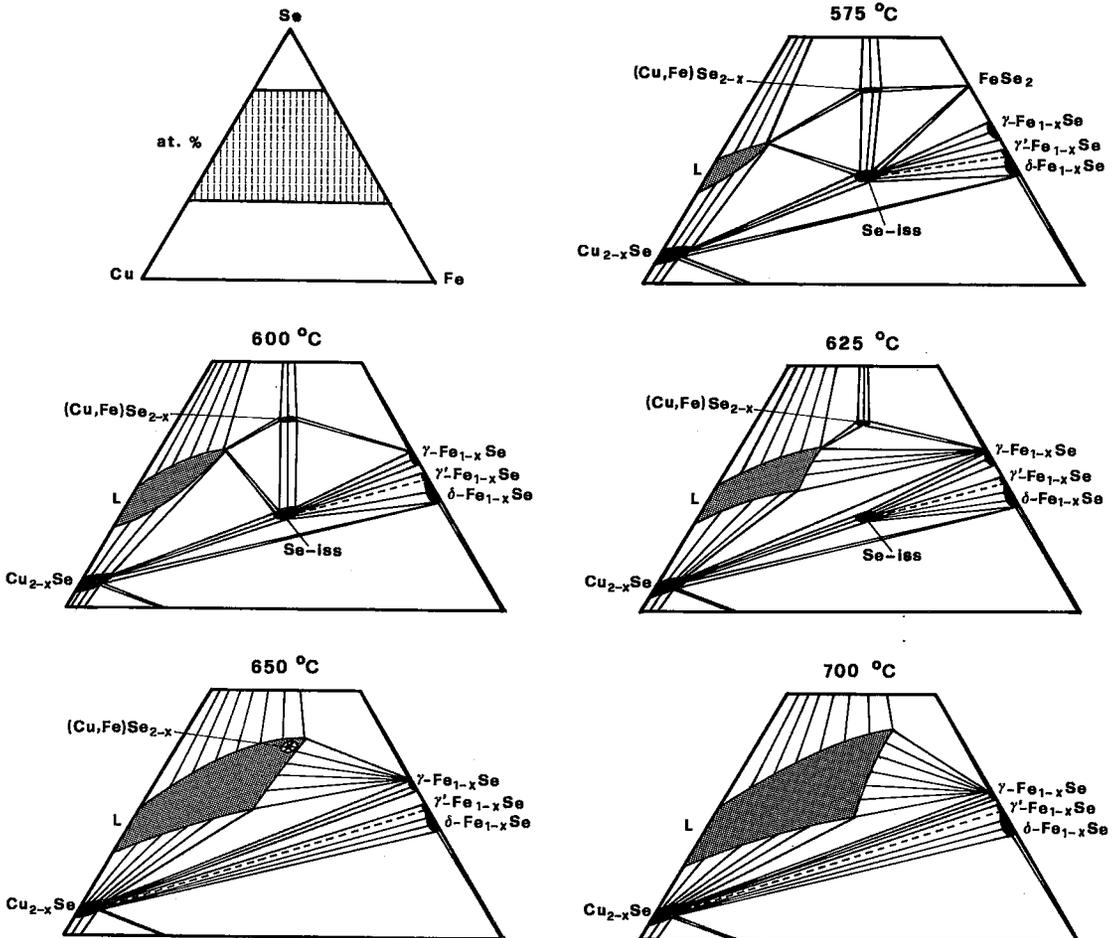


FIG. 4. Phase relations in the central region of the system Cu-Fe-Se at different temperatures between 575 and 700°C. Dashed line as in Figure 1.

& Heyding 1975), ultimately to melt at 660°C to a liquid of similar composition. The analyses of the product quenched from 625°C reveal the presence of a solid $(\text{Cu,Fe})\text{Se}_{2-x}$ -type phase and Cu-selenides exsolved from a quenched liquid. The product quenched from 700°C, however, contains only phases exsolved from a quenched liquid of higher Se content than Franz's (1970) CuFeSe_x $<_2$ -similar liquid. On the basis of the results of the quenching experiments, performed on many CuFeSe_2 and $(\text{Cu}_{0.5}\text{Fe}_{0.5})\text{Se}_2$ charges, the thermal effects in the relative D.T.A. curves may be explained by the series of reactions shown in Figure 3.

CONCLUSIONS

In accordance with the thermal behavior of synthetic Se-*iss* and $(\text{Cu,Fe})\text{Se}_{2-x}$, the probable phase relations in the system Cu-Fe-Se between 500 and 700°C are portrayed in Figures 1 and 4. Between 515 and 545°C stoichiometric CuFeSe_2 reacts to Se-*iss*, poorer in Se, and to $(\text{Cu,Fe})\text{Se}_{2-x}$. The latter, in turn, upon

breakdown to a $(\text{Cu,Fe})\text{Se}_{2-x}$ -type phase (poorer in Se) plus liquid, melts at 660°C to a liquid of similar composition. At 575°C tielines may be established between Se-*iss* and the ternary liquid extending from the Cu-Se border. According to Schuster *et al.* (1979), FeSe_2 melts incongruently at 585°C into $\gamma\text{-Fe}_{1-x}\text{Se}$ plus Se. Therefore, at this temperature the invariant reaction $\text{FeSe}_2 + \text{Se-iss} \rightleftharpoons \gamma\text{-Fe}_{1-x}\text{Se} + (\text{Cu,Fe})\text{Se}_{2-x}$ should occur in order to establish the $\gamma\text{-Fe}_{1-x}\text{Se} + (\text{Cu,Fe})\text{Se}_{2-x}$ tieline. From 600 to 625°C, two four-phase equilibria reactions, depicted as dashed lines in Figure 5, occur in such a narrow range of temperatures that the resulting effects in the D.T.A. curve of CuFeSe_2 may coalesce in a single peak, as noted above. At 625°C, tielines may be established between the ternary liquid (L) and $\gamma\text{-Fe}_{1-x}\text{Se}$, and between this last phase and Cu_{2-x}Se . At 635–640°C, Se-*iss* decomposes into Cu_{2-x}Se and $\gamma\text{-Fe}_{1-x}\text{Se}$, so that $(\text{Cu,Fe})\text{Se}_{2-x}$ is the only ternary solid phase remaining in the system at 650°C. At 660°C, $(\text{Cu,Fe})\text{Se}_{2-x}$ melts so that no ternary solid phases remain at 700°C. In the central region of the system, therefore, a three-phase field appears between Cu_{2-x}Se , $\gamma\text{-Fe}_{1-x}\text{Se}$ and the ternary liquid, whose composition approaches that of CuFeSe_2 with increasing temperature (Bernardini & Mazzetti 1979a).

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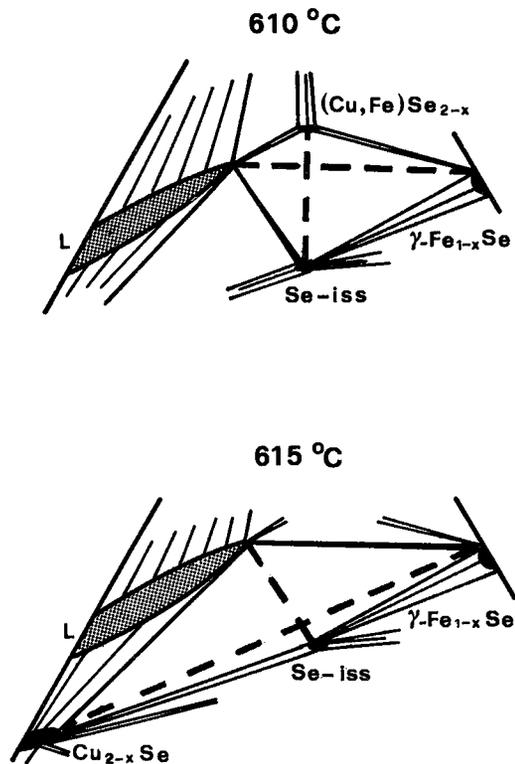


FIG. 5. Schematic drawing of phase equilibria in the system Cu-Fe-Se at 610 and 615°C.

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