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PHASE RELATIONS IN THE Cu-Fe-Se SYSTEM AT 900° AND 700° C **

RIASSUNTO. — Per la definizione delle relazioni fra le fasi esistenti nel sistema Cu-Fe-Se a diverse temperature sono state studiate per il momento le isoterme a 900° e 700° C mediante esperienze di quenching e analisi diffrattometriche, ottiche e termodifferenziali.

A 900° C un largo campo a un liquido ternario (L) domina la regione centrale del sistema. Al di sopra del suo limite ricco in Se esiste un campo a due liquidi non miscibili fra L e Se liquido. A questa temperatura esistono solo due fasi solide, oltre a Cu e Fe metallici: $Cu_{2-x}Se$, con $0,00 \leqslant X \leqslant 0,10$, corrispondente al minerale berzelianite ($bz_{s.s.}$) e $Fe_{1-x}Se$, con $0,00 \leqslant X \leqslant 0,25$, corrispondente al minerale achavalite ($ach_{s.s.}$). Fra questi due composti e il liquido ternario L si stabiliscono delle tie-lines che individuano due campi a due fasi: $bz_{s.s.} + L$ e $ach_{s.s.} + L$. Nella regione del ternario al di sotto del 33 % e del 50 % at. di Se, rispettivamente sui binari Cu-Se e Fe-Se, sono stati individuati i seguenti campi: due campi estremi a due fasi: $Cu_{s.s.} + bz_{s.s.}$ e $Fe_{s.s.} + ach$ e tre campi a tre fasi: $Cu_{s.s.} + bz_{s.s.} + Fe_{s.s.}$, $bz_{s.s.} + L + Fe_{s.s.}$ e $Fe_{s.s.} + L + ach$.

A 700° C il liquido ternario si ritira verso il bordo Cu-Se e verso il vertice Se del sistema. Nella regione ricca in Se si ha, pertanto, la comparsa di un largo campo a tre fasi: $Se_L + L + ach_{s.s.}$ e di uno piccolo a due: $Se_L + ach_{s.s.}$ vicino al bordo Fe-Se. A questa temperatura la punta più povera in Se del campo a un liquido ternario raggiunge quasi il 50 % at. di Se e, pertanto, nella zona centrale del sistema, compaiono un campo univariante: $bz_{s.s.} + L + ach_{s.s.}$ e uno bivariante: $bz_{s.s.} + ach_{s.s.}$. Indagini a raggi X di alta temperatura hanno permesso di stabilire che, anche a 700° C, non esistono fasi ternarie nella regione a composizione corrispondente a quella dell'eskebornite ($CuFeSe_2$) contrariamente a quanto avviene nel sistema Cu-Fe-S. La comparsa del campo bivariante: $bz_{s.s.} + ach_{s.s.}$, che proibisce la coesistenza del liquido L con $Fe_{s.s.}$, provoca la scomparsa, nella regione ricca in metalli, del campo a tre fasi: $Fe_{s.s.} + L + ach$, sostituito, vicino al bordo Fe-Se, da quello a due fasi: $Fe_{s.s.} + ach_{s.s.}$.

ABSTRACT. — As a part of a complete investigation of phase relations and properties of compounds in the Cu-Fe-Se system, the phase relations at 900° and 700° C have been investigated by silica tube quenching experiments using microscopic, differential thermal and X-ray analyses.

At 900° C a homogeneous liquid field (L) dominates the central region of the system. Above its Se-rich limit, which varies from 60 % at. on the Cu-Se border to almost 75 % at. on the Fe-Se, an extensive liquid immiscibility field spans the Se-rich portion of the system. At this temperature, apart from the solid phases on the metal system, not discussed here, only two solid phases exist: $Cu_{2-x}Se$, with $0.00 \leqslant X \leqslant 0.10$, berzelianite solid solution ($bz_{s.s.}$) and $Fe_{1-x}Se$, with $0.00 \leqslant X \leqslant 0.25$, achavalite solid solution ($ach_{s.s.}$). Between these two solid phases and the ternary liquid two two-phase fields are established: $bz_{s.s.} + L$ and $ach_{s.s.} + L$. In the region of the system below 33 % and 50 % at. Se, respectively on the Cu-Se and Fe-Se systems, the following fields were detected: Cu, with a maximum Fe-content of 2 % at. ($Cu_{s.s.}$) plus $bz_{s.s.}$ and Fe, with a maximum Cu-content of nearly 4 % at. ($Fe_{s.s.}$) plus ach, and three three-phase fields: $Cu_{s.s.} + bz_{s.s.} + Fe_{s.s.}$, $bz_{s.s.} + L + Fe_{s.s.}$ and $Fe_{s.s.} + L + ach$.

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At 700° C the large L-liquid field retreats towards the Cu-Se border together with the liquid immiscibility field, with the consequent appearance of a large three-phase field: $Se_L + ach_{s.s.} + L$ and a very small two-phase field, near the Fe-Se border: $Se_L + ach_{s.s.}$. At this temperature the Se-poor point of the L-liquid field reaches a Se-content of almost 50 % at. Therefore, in the central region of the system, an univariant field: $bz_{s.s.} + L + ach_{s.s.}$ and a divariant one: $bz_{s.s.} + ach_{s.s.}$ appear. This last field prohibits the L-liquid coexisting with $Fe_{s.s.}$. High-temperature X-ray analyses of charges with composition corresponding to that of eskebornite ($CuFeSe_2$), have permitted to establish that even at 700° C no ternary phases are present in the Cu-Fe-Se system in contrast with the situation in the Cu-Fe-S system. The appearance of the divariant field: $bz_{s.s.} + ach_{s.s.}$ causes the disappearance, in the metal rich region, of the three-phase field: $Fe_{s.s.} + L + ach$ which is substituted, near the Fe-Se border, by the two-solid-phase field: $Fe_{s.s.} + ach_{s.s.}$.

Introduction

During the last two decades systematic investigations of phase relations in sulfide systems have yelded significant information on the thermodynamic stability of sulfide minerals and on the conditions of their formation. Most of the experimental work is concerned with sulfides, arsenides and sulfo-salts while little attention has been paid to selenides and sulfo-selenides despite their importance especially for industrial application. Studies on phase relations in various selenide systems have been mainly conducted by solid-state physicists because of the semiconducting properties of Se-compounds.

In the overall interest for trace elements in ore deposits as possible indicators of geochemical conditions of mineral formation, special consideration has been given in recent literature to selenium ,especially for particular geological settings such as roll-type sandstone uranium deposits, as pointed out by Gent (1976) in his annotated bibliography of the geology of selenium and by Howard (1977) in a recent work on the geochemistry of selenium to which the reader is referred for reference of detailed geochemical studies.

The Cu-Fe-Se system was selected for study because knowledge of its phase relations is a neecssary prerequisite to the study of the phase relations in the quaternary Cu-Fe-S-Se system which could shed some light on the role played by Se in stabilizing copper-iron sulfides and on the significance of the Se/S ratio as a useful indicator of the physico-chemical environments of deposition from sulfide ore solutions. While the phase relations in the Cu-Fe-S system have been studied for a long time (Merwin & Lombard, 1937) and are to date well known, especially at high and moderate temperatures (cfr. Craig, 1974; Sugaki et al., 1975 and the bibliography therein), those in the Cu-Fe-Se system have not been investigated sistematically and only Franz (1970, 1971 a and 1975) has conducted investigations on some joins of the Cu-Fe-Se, Cu-Fe-S-Se and Cu-Fe-Sn-S-Se systems.

The final object of our study is to determine the stable assemblages in the entire Cu-Fe-Se system over a wide range of temperature. The necessity of collecting as many data as possible in order to portray the major features of the phase diagram at whatever temperature, up to now unknown, suggested studying the 900° and

700° C isotherms first as equilibrium could be attained, at these temperatures, over a relatively short period of time.

Phases and phase relations

The natural and synthetic phases present in the two binary systems Cu-Se and Fe-Se, and in the ternary Cu-Fe-Se are reported in fig. 1, while their crystallographic characteristics and thermal stabilities are summarized in table 1. No attempt has been made to include all published studies relating to these phases but rather to provide a brief summary of the most significant to the present work.

The phase relations in the Cu-Se system have been studied by HEYDING (1966), DIES (1967), BERNARDINI & CATANI (1968), BERNARDINI et al. (1972), MURRAY & HEYDING (1975) and recently reviewed by BERNARDINI et al. (1976, 1977) in their studies on the phase relations in the Cu-S-Se system. Reviews of the phase relations in the metallic system Cu-Fe may be found in HANSEN & ANDERKO's, « Constitution of binary alloys » (1958) and in ELLIOTT's (1965) and SHUNK's (1969) supplements. 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 Fe-Se system are not clearly defined, especially at low temperatures, altough, since the first work of HÄGG & KINDSTRÖM (1933), several authors (TEGNER, 1938; HARALDSEN & GRØNVOLD, 1944; HARALDSEN, 1952; HIRONE & CHIBA, 1956; TRÖFTEN & KULLERUD, 1961; KULLERUD, 1968; DUTRIZAC et al., 1968 a and b) have studied this system. Of the above mentioned works the first complete study on the Fe-Se system is that of KULLERUD (1968) who portrayed the general features of the phase diagram above 400° C using quenching and D.T.A. experiments. In the same year DUTRIZAC et al. (1968 b) worked out indipendently the phase relations in this system. The main differences are in the high-temperature Fe-rich region and in the region around the $Fe_{1-x}Se$ composition. No mention, in fact, is made by DUTRIZAC et al. (1968 b)

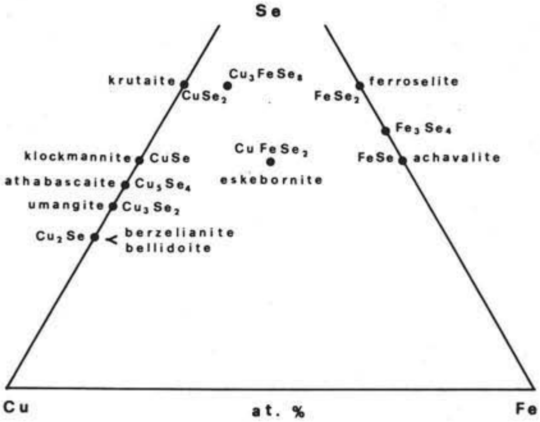


Fig. 1. — Minerals and synthetic phases in the Cu-Fe-Se system.

TABLE 1

Natural and synthetic phases in the Cu-Se, Fe-Se and Cu-Fe-Se systems

Mineral or synthetic phase	Composition	Crystallography, thermal stability and references
"Cu-Se" system		
Berzelianite	Cu_2Se	orth. $\xrightarrow{130\,^\circ C}$ cub. $\xrightarrow{1113\,^\circ C}$ liq. (1,2,3,22)
Bellidoite	Cu_2Se	tetr. (6)
Defective berzelianite	$Cu_{2-x}Se$	cub. (1,2,4,5)
Umangite	Cu_3Se_2	tetr. $\xrightarrow{142\,^\circ C}$ $Cu_{2-x}Se$ + CuSe (1,2,20,22)
Athabascaite	Cu_5Se_4	orth. (14)
Klockmannite	CuSe	low-hex. $\xrightarrow{60\,^\circ C}$ high-hex. $\xrightarrow{384\,^\circ C}$ $Cu_{2-x}Se$ + Se liq. (1,2,19)
synthetic	$CuSe_2$	orth. $< 342\,^\circ C$ (1,2,11,16,26)
Krutaïte	$CuSe_2$	cub. (15)
"Fe-Se" system		
Achavalite	FeSe *	tetr. (PbO-type) $\xrightarrow{458\,^\circ C}$ hex. (NiAs-type) + Fe (7,9,12,13,27)
synthetic	$Fe_{1-x}Se$	tetr. $\xrightarrow{380\,^\circ C}$ hex. (NiAs-type) $\xrightarrow{835-872\,^\circ C}$ α-$Fe_{1-x}Se$ $\rightarrow$ $\xrightarrow{1065\,^\circ C}$ liq. (9,13,17,27)
synthetic	Fe_7Se_8	tricl. $\xrightarrow[4C \rightarrow 3C]{240-298\,^\circ C}$ hex. (NiAs-type) $\xrightarrow[3C \rightarrow 2C \rightarrow 1C?]{320-388\,^\circ C}$ $\rightarrow$ hex. (NiAs-type) (23,24,25)
synthetic	Fe_3Se_4	monocl. $\xrightarrow{725\,^\circ C}$ (λ-type transition) hex. (NiAs-type) $\xrightarrow{600\,^\circ C}$ hex. $\xrightarrow{727\,^\circ C}$ $Fe_{1-x}Se$ + liq. (17,21,25,27)
Ferroselite	$FeSe_2$	orth. (FeS_2-m-type) $\xrightarrow{585\,^\circ C}$ $Fe_{1-x}Se$ + Se liq. $\xrightarrow{580\,^\circ C}$ Fe_3Se_4 + Se liq. (8,9,16,17,18,27,28)
"Cu-Fe-Se" system		
Eskebornite	$CuFeSe_2$	cub. $\xrightarrow{480\,^\circ C}$ $(Cu,Fe)Se_{2-x}$ + Cu_3Se_2-similar liq. $\xrightarrow{560\,^\circ C}$ $\rightarrow$ $Cu_{2-x}Se$ + $CuFeSe_{x<2}$-similar liq. (7,10,29)
synthetic	(Fe,Cu)Se	tetr. (7)
synthetic	$(Cu,Fe)Se_{2-x}$	cub. $\xrightarrow{530\,^\circ C}$ $Cu_{2-x}Se$ + $CuFeSe_{x<2}$-similar liq. (7,10)

* According with references (12) and (27) this phase has surplus iron atoms in interstitial positions.

(1) Bernardini and Catani (1968); (2) Bernardini, Corsini and Trosti (1972); (3) Boettcher, Haase and Treupel (1955); (4) Borchert (1945); (5) Borchert and Patzak (1955); (6) De Montreuil (1970); (7) Franz (1970); (8) Franz (1971 b); (9) Franz (1972); (10) Franz (1975); (11) Gattow (1965); (12) Grønvold (1968); (13) Hägg and Kindström (1933); (14) Harris, Cabri and Kaiman (1969); (15) Johan, Picot, Pierrot and Kvaček (1972); (16) Kjekshus, Rakke and Andresen (1974); (17) Kullerud (1968); (18) Kullerud and Donnay (1958); (19) Lippmann (1962); (20) Morimoto and Koto (1966); (21) Morimoto and Kullerud (1959); (22) Morimoto and Uchimizu (1967); (23) Okazaki (1959); (24) Okazaki (1961); (25) Okazaki and Hirakawa (1956); (26) Sadanaga (1966); (27) Svendsen (1972); (28) Tegner (1938); (29) Tischendorf (1960).

of the stability field of Fe_3Se_4 which, according to KULLERUD (1968), melts incongruently at 727° C into $Fe_{1-x}Se$ plus liquid. On the other hand the former authors have investigated in detail the high-temperature region only inferred by the latter. SVENDSEN (1972), in his investigation on the decomposition pressures and standard enthalphy of formation for iron selenides, reported the region of the Fe-Se system ranging from 30 % to 100 % at. Se, above 400° C. According to this author the Fe_3Se_4 phase exists only as a monoclinic deformation, derived from the increased vacancies in the Fe-strata, of the NiAs-like structure with approximate composition Fe_7Se_8. Therefore below 725° C, which is the temperature of the λ-type transition undergone by Fe_3Se_4 to change into the hexagonal high-temperature structure, the two-phase field: $Fe_{1-x}Se + Fe_3Se_4$ inferred by KULLERUD (1968), should not exist.

As concerns the phase relations in the Cu-Fe-Se system, FRANZ (1970) investigated some « combinations » at 400° C by X-ray and differential thermal analyses and found two new phases: 1) $(Cu,Fe)Se_{2-x}$, cubic pyrite-type structure, with a_o ranging from 6.061 Å for the $(Cu_{0.82}Fe_{0.18})Se_{2-x}$ composition to 6.000 Å for the $(Cu_{0.52}Fe_{0.48})Se_{2-x}$. This new phase should melt incongruently at 530° C into $Cu_{2-x}Se$ plus a $CuFeSe_2$--similar liquid; 2) (Fe,Cu)Se, tetragonal space group P4/nmm, with $a_o = 3.79$ Å and $c_o = 5.50$ Å. With increasing Cu-content the c_o of this phase decreases down to 5.30 Å. The same author in 1975 gave the powder diagram of the $(Cu,Fe)Se_{2-x}$ phase for the $(Cu_{0.74}Fe_{0.26})Se_{2-x}$ composition and established the compositional stability field of eskebornite at 400° C, which seems to have an elliptical form ranging from $Cu_{1.04}Fe_{0.96}Se_2$ to $Cu_{0.88}Fe_{1.12}Se_2$ and from $CuFeSe_{1.8}$ to $CuFeSe_{2.2}$.

Methods of experimental investigation

Experimental charges were synthesized in evacuated silica-glass capsules, as described by KULLERUD (1971), either using the single tube technique or the double tube for some charge on and near the Fe-Se border. During quenching, in fact, transitions in solid selenides caused frequent craking of the sample tubes. Reactants were pure elements as specified by supplier's analyses (Alfa Inorganics Ltd., Ventron, Beverly, Mass.). Iron powder was reduced in a stream of hydrogen at 900° C at least for four hours. Charges were heated in Nichrome wound furnaces, whose temperature was controlled within ± 3° C or better (as measured on calibrated chromel-alumel thermocouples), quenched in iced water, repeatedly ground under acetone and reheated for periods of several weeks to a maximum of four months for the 700° C isotherm. Over 120 specific compositions were prepared in this way in order to study the phase relations at 900° and 700° C.

The quenched products were investigated by visual examination trough the transparent walls of the silica tubes, in order to ascertain the presence of liquids or liquid immiscibility, by reflected light microscopy and by X-ray diffraction analyses with CoKα radiation on a Philips X-ray diffractometer. In some instances chemical composition of the phases present was determined by electron probe analyses with a Philips Norelco ARM/3 microprobe using pure elements and synthetic CuSe and Fe-rich sphalerite as standards, while some element distribution maps were taken with a Jeol Scanning Electron Microscope U/3.

Silica tube quenching experiments are not suitable for the study of unquenchable phases as frequent in selenide as in sulfide systems. To investigate such phases D.T.A. experiments were conducted, using thermocouple well tubes (BERNARDINI, 1966) and pure quartz as reference material, on a Tem-Press DT 712 with heating and cooling rate of 3° C/min. Few charges were also investigated by high-temperature X-ray analyses performed with a Rigaku-Denky Debye camera equipped with a Pt-wound furnace controlled at ± 5° C through a Pt-Pt/Rh thermocouple.

Experimental results

a) The 900° C isotherm

The phase relations in the Cu-Fe-Se system at 900° C are shown in fig. 2. The Se-rich portion of the system is occupied by a homogeneous liquid field (L) whose upper limit varies from nearly 60 % at. Se on the Cu-Se border (HEYDING, 1966) to almost 75 % at. on the Fe-Se (SVENDSEN, 1972) and by an extensive liquid immiscibility field above these limits.

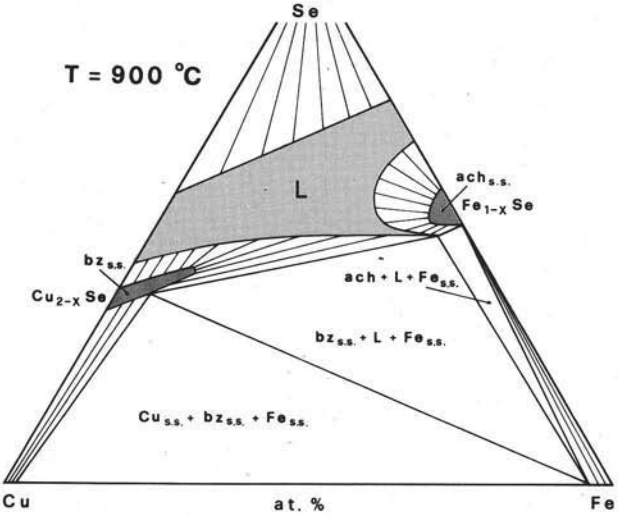


Fig. 2. — Phase relations in the Cu-Fe-Se system at 900° C. — L = ternary liquid; bz$_{s.s.}$ = berzelianite solid solution; ach$_{s.s.}$ = achavalite solid solution; Cu$_{s.s.}$ = copper solid solution; Fe$_{s.s.}$ = iron solid solution. All phases and phase assemblages coexist with vapour.

The presence of various solid phases in the X-ray diffraction patterns of the quenched charges from these two liquid fields, the results of some of which are reported in table 2, may be explained by the complicated non-equilibrium structures observed in the relative polished sections. These structures, as shown in fig. 3,

TABLE 2

Selected experimental results at 900° and 700° C

n°.	Bulk comp. atom. %			Phases detected at room temperature by X-ray and microscope studies
	Cu	Fe	Se	
902	5	20	75	{[$Fe_{1-x}Se$ + Fe_3Se_4?] + $(Cu,Fe)Se_{2-x}$}
903	16	16	68	{$(Cu,Fe)Se_{2-x}$ + CuSe + [$Fe_{1-x}Se$ + Fe_3Se_4?]}
904	5	27	68	{$(Cu,Fe)Se_{2-x}$ + [$Fe_{1-x}Se$ + Fe_3Se_4?]}
911	8	37	55	[$Fe_{1-x}Se$ + Fe_3Se_4?] + {$CuFeSe_2$ + $(Cu,Fe)Se_{2-x}$ (traces)}
916	25	25	50	{$CuFeSe_2$ + $(Cu,Fe)Se_{2-x}$ + [$Fe_{1-x}Se$ + Fe_3Se_4?]}
917	12	38	50	[$Fe_{1-x}Se$ + Fe_3Se_4?] + {$CuFeSe_2$}
918	5	45	50	FeSe + $Fe_{1-x}Se$?
920	5	48	47	{FeSe} + Fe (traces)
923	47	10	43	$Cu_{2-x}Se$ + $CuFeSe_2$ (as exsolution lamellae) + {$(Cu,Fe)Se_{2-x}$}
924	33	24	43	A-phase * + {FeSe}
927	50	10	40	A-phase + $CuFeSe_2$ (as exsolution lamellae)
933	58	5	37	A-phase
940	45	20	35	A-phase + Fe + {FeSe}
944	5	62	33	{FeSe} + Fe + A-phase (traces)
946	60	15	25	A-phase + Cu + Fe
947	35	40	25	A-phase + Fe + {FeSe}
953	20	70	10	A-phase + Fe + Cu (traces)
960	39	18	43	A-phase + $CuFeSe_2$ (as exsolution lamellae) + {FeSe}
968	32	21	47	A-phase + {$CuFeSe_2$ (also present as exsolution lamellae)}
702	5	20	75	[$Fe_{1-x}Se$ + Fe_3Se_4?] + {$(Cu,Fe)Se_{2-x}$}
703	16	16	68	{$(Cu,Fe)Se_{2-x}$ + CuSe + [$Fe_{1-x}Se$ + Fe_3Se_4?]}
704	5	27	68	[$Fe_{1-x}Se$ + Fe_3Se_4?] + {$(Cu,Fe)Se_{2-x}$}
715	40	10	50	{$(Cu,Fe)Se_{2-x}$ + $CuFeSe_2$ + $Cu_{2-x}Se$ (traces)}
716	25	25	50	[$Fe_{1-x}Se$ + Fe_3Se_4?] + $Cu_{2-x}Se$ + {$CuFeSe_2$ + $(Cu,Fe)Se_{2-x}$}
717	12	38	50	FeSe + $Cu_{2-x}Se$ + {$CuFeSe_2$ + $(Cu,Fe)Se_{2-x}$}
718	5	45	50	FeSe + $Fe_{1-x}Se$?
720	5	48	47	FeSe + Fe
723	47	10	43	$Cu_{2-x}Se$ + {$CuFeSe_2$} (also present as exsolution lamellae)
724	33	24	43	A-phase * + FeSe + Fe (traces)
727	50	10	40	A-phase + $CuFeSe_2$ (as exsolution lamellae)
733	58	5	37	A-phase
744	5	62	33	FeSe + Fe + A-phase (traces)
747	35	40	25	A-phase + Fe + FeSe
749	75	5	20	A-phase + Cu + Fe
755	15	25	60	[$Fe_{1-x}Se$ + Fe_3Se_4?] + {$(Cu,Fe)Se_{2-x}$}
757	30	20	50	{$CuFeSe_2$ + $(Cu,Fe)Se_{2-x}$} + $Cu_{2-x}Se$ (traces)
760	39	18	43	A-phase + $CuFeSe_2$ (as exsolution lamellae) + FeSe
761	45	15	40	A-phase + FeSe

* See text for explanation. { } Phases obtained from quenched liquids. [ ] Iron selenides derived from quenched $ach_{s.s.}$ terms.

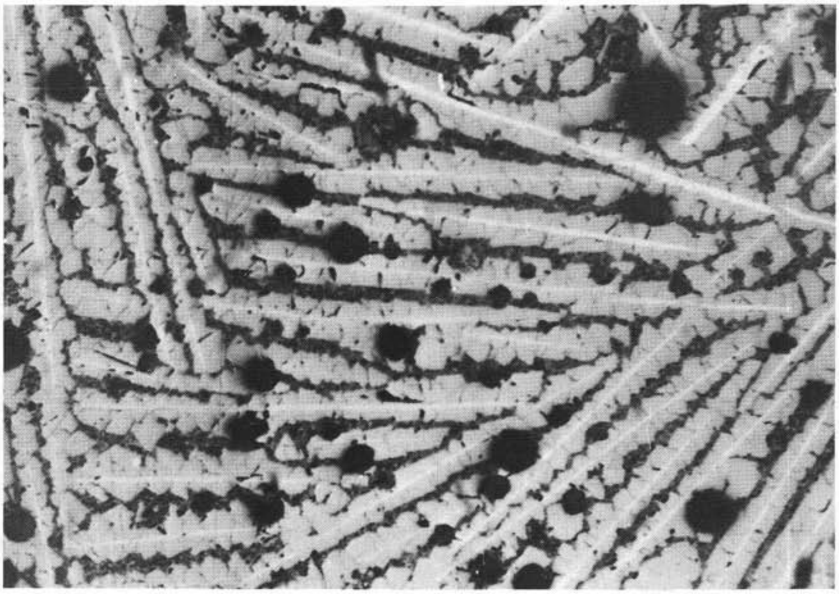


Fig. 3. — Photomicrograph of charge n. 903 (oil immersion, parallel nicols, 300 x). Remnants of elongated primary phase (white) sorrounded by perytetically-formed dendrites (greyish white) and melt (dark grey).

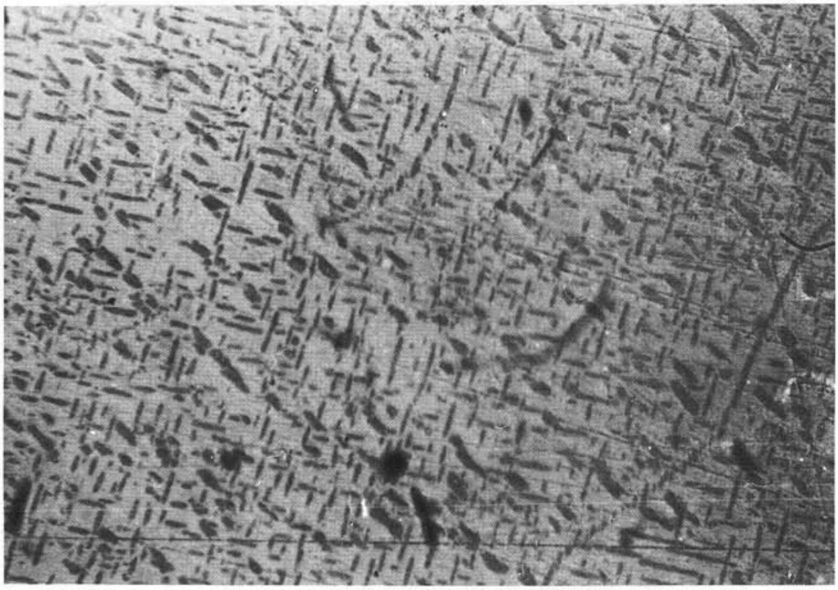


Fig. 4. — Photomicrograph of charge n. 927 (oil immersion, parallel nicols, 300 x). A-phase grain with oriented exsolution lamellae of eskebornite.

prove that the solid phases present in the quenched products are caused by subsequent solidification processes such as synthetic or perythectic reactions. At the reaction temperature, in fact, apart from the solid phases present on the Cu-Fe metal system (not discussed here), only two solid phases exist: the berzelianite solid solution ($Cu_{2-x}Se$, with $0.00 \leqslant x \leqslant 0.10$) and the achavalite solid solution ($Fe_{1-x}Se$, with $0.00 \leqslant x \leqslant 0.25$). The berzelianiite solid solution ($bz_{s.s.}$) extends through a considerable distance into the ternary system, the maximum solid solution of this phase reaching 10 % at. Fe, while the achavalite solid solution ($ach_{s.s.}$) dissolves a maximum Cu-content of nearly 5 % at.

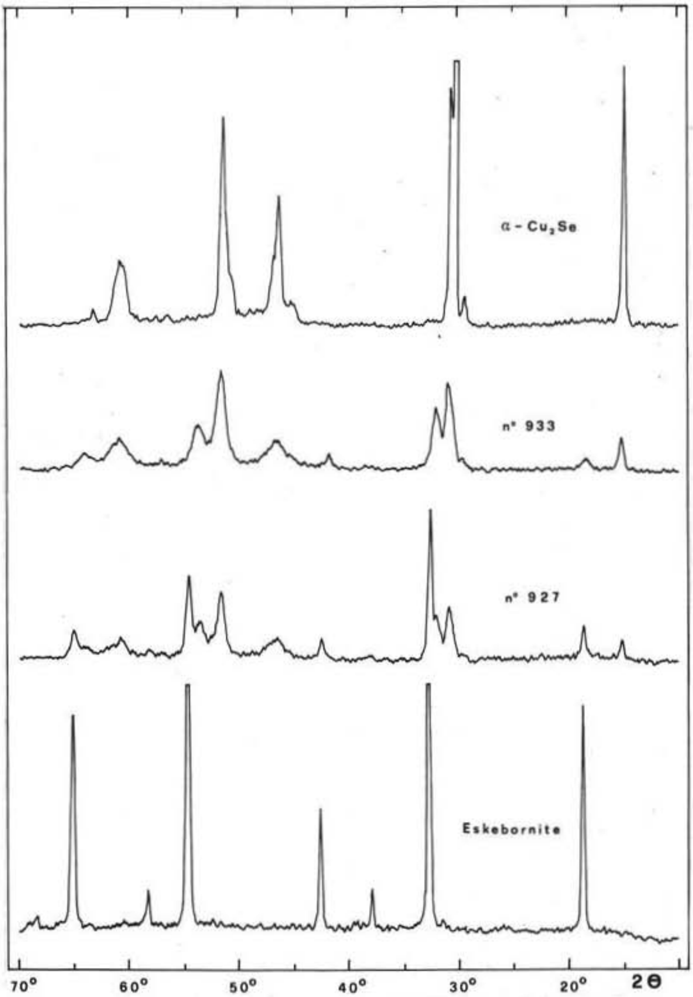


Fig. 5. — X-ray powder diffraction patterns of charges nn. 933 and 927 compared with those of pure α-Cu_2Se and eskebornite (Fe-filtered CoKα radiation).

In the quenched products of $bz_{s.s.}$ terms, depending on the x value, either the α-Cu_2Se orthorombic phase or the cubic $Cu_{2-x}Se$ were detected being the β-Cu_2Se cubic high-temperature form unquenchable (BERNARDINI et al., 1976). The quenched product of charge n. 933, with 5 % at. Fe, proved to be formed by an optically and chemically homogeneous phase with a compositional formula, as determined by electron probe analysis, of $Cu_{59.5}Fe_{3.9}Se_{36.5}$ which corresponds to a hypothetical $Cu_{6.6}Fe_{0.4}Se_{4.0}$ compound in which the metals to selenium ratio is of the same order as the one established by MORIMOTO & GYOBU (1971) for the iron-stabilized digenite at room temperature. The X-ray pattern of this phase, reported in fig. 5, shows, in addition to poorly crystallized reflections similar to those of the orthorombic α-Cu_2Se, some very weak reflections not reported for this phase. While a situation similar to the one found by MORIMOTO & GYOBU (1971) may be inferred for the Cu-Fe-Se system at room temperature, studies on the crystallographic characteristics of this new phase, from now on indicated as A-phase, are in progress.

The approximate boundary of the $bz_{s.s.}$ field, towards the central portion of the system, has been determined on the basis of the appearance of solid phases coming from the quenched L-liquid such as e.g. the $(Cu,Fe)Se_{2-x}$ compound in charge n. 923. On the contrary no evidence of a liquid phase, present at the reaction temperature, was observed in the polished section of charge n. 927 which has the same Fe-content and a lower Se-content. The exsolution lamellae in the A-phase grains of this charge, shown in fig. 4, proved to be eskebornite as a result of unmixing processes during the quenching mechanism. The diffraction patterns of the quenched products of charges nn. 933 and 927 are compared in fig. 5 with those of pure α-Cu_2Se and eskebornite. The minimum Cu/Fe ratio of $bz_{s.s.}$ terms is smaller than the of the Se-analogous of bornite which is never been detected either in synthetic or natural products.

The quenched products of $ach_{s.s.}$ terms are made of one or two iron selenides the relations of which are not clearly defined, as already mentioned. As in the case of $bz_{s.s.}$, therefore, the approximate boundary of the $ach_{s.s.}$ field has been mainly inferred by comparing the textural relationship of the assemblages observed in the polished sections of the charges with a Cu-content to a maximum of 8 % at. with their X-ray diffraction results (cfr. e.g. run n. 918).

Between the $bz_{s.s.}$ and the ternary liquid L and between the $ach_{s.s.}$ and the same liquid, two two-phase fields are established, as revealed by the assemblages detected in the quenched products of charges nn. 960 and 911. Fig. 6 shows the assemblage observed in this last charge where grains of $Fe_{1-x}Se$, with exsolution lamellae of probable Fe_3Se_4, sorrounded by a microcrystalline matrix derived from the ternary liquid, are observable. The boundaries of the two two-phase fields ($bz_{s.s.} + L$ and $ach_{s.s.} + L$) were determined by the interpretation of the different solid phases observed at room temperature in numerous charges. The liquid-phase limits are dictated by the assemblages observed e.g. in the quenched products of charges nn. 917 and 968 respectively for the $ach_{s.s.} + L$ and $bz_{s.s.} + L$ fields. The metal-rich limit points to a liquid of nearly FeSe-composition as revealed by the analysis of the 924 quenched product. Fig. 7 shows the relative assemblage made of large grains of A-phase with star-like inclusions and borders of a microcrystalline matrix derived from a FeSe-similar liquid as determined by the SEM element distribution maps and by the line carried out at the electron microprobe.

In the metal-rich region of the system the following fields were detected: two extreme two-solid-phase fields: Cu, with a maximum Fe-content of nearly 2% at. (HANSEN & ANDERKO, 1958 and supplements) indicated as $Cu_{s.s.}$, plus $bz_{s.s.}$ and Fe, with a maximum Cu-content of nearly 4% at. (cfr. above reference) indicated as $Fe_{s.s.}$, plus achavalite, and three three-phase fields: $Cu_{s.s.} + bz_{s.s.} + Fe_{s.s.}$, $bz_{s.s.} + L + Fe_{s.s.}$ and $L + ach + Fe_{s.s.}$. The boundary between the first two univariant fields has been drawn on the basis of the presence of Cu contemporary with the absence of the FeSe-similar liquid and viceversa in numerous runs (cfr. e.g. runs nn. 953 and 940). Figs. 8 and 9 show the assemblages observed in the polished sections of these charges respectively characteristics of the first and second field. No exsolution lamellae of eskebornite were ever observed in the A-phase grains of all these charges, thus making it possible to differentiate them from those present in the quenched products of the $bz_{s.s.} + L$ divariant field. In the A-phase grains of run n. 940 skeletal inclusions derived from the quenched liquid of nearly FeSe-composition, as already shown in fig. 7, are clearly visible. In the 953 polished section the absence of such a liquid is accompanied by the appearance of Cu traces. How far the poor Se-content prong of the FeSe-similar liquid has retreated from the Fe-Se border at 900° C, was inferred by comparing the results of runs nn. 920 and 944 which have the same amount of Cu (5% at.) and different Fe/Se ratio.

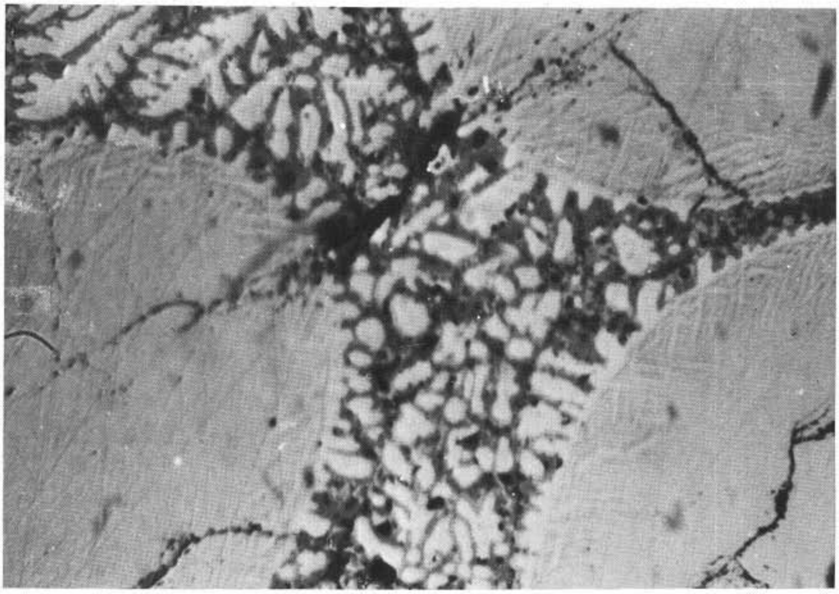
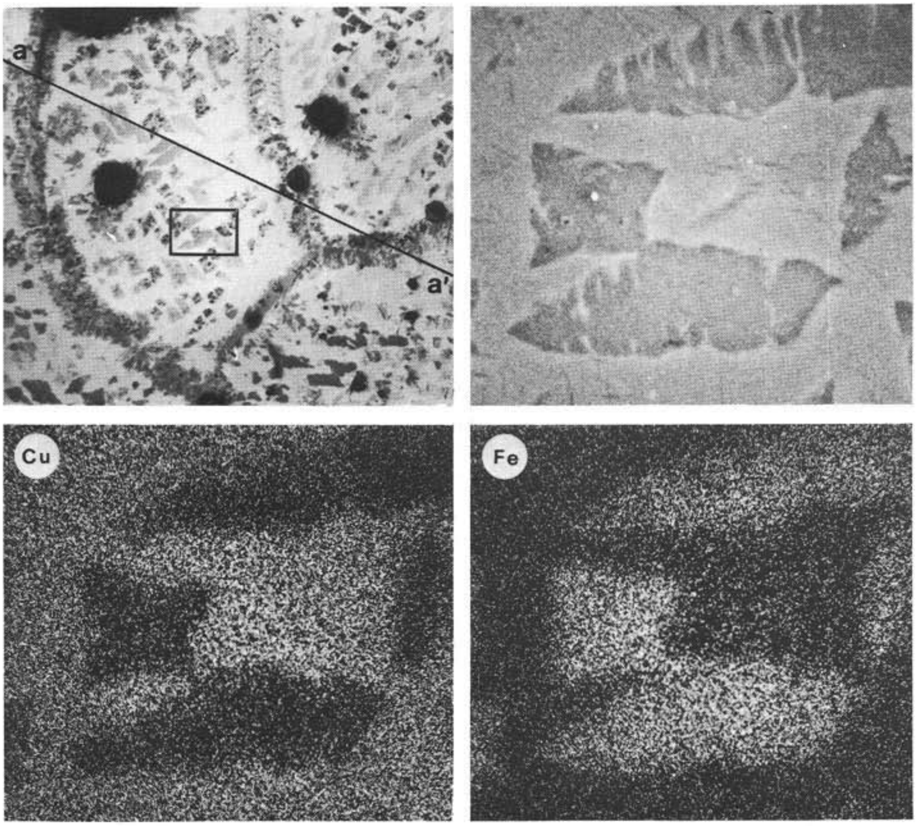


Fig. 6. — Photomicrograph of charge n. 911 (oil immersion, parallel nicols, 300 x). Grains of $ach_{s.s.}$, with exsolution lamellae of probable Fe_3Se_4, sorrounded by a microcrystalline aggregate of $CuFeSe_2$ and $(Cu,Fe)Se_{2-x}$ crystallized from L-liquid.



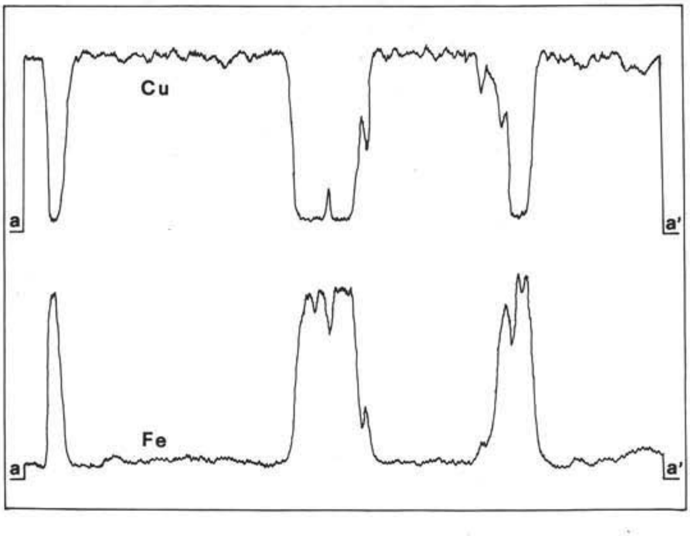


Fig. 7. — Polished section of charge n. 924. Top: reflected light photomicrograph (oil immersion, parallel nicols, 300 x) and scanning electron image (3000 x) of the particular in the black square Grains of A-phase with intergranular borders and star-like inclusions crystallized from a FeSe-similar liquid. Center: characteristic X-ray scanning pictures. Bottom: traces of linear scans along the *a-a'* line.

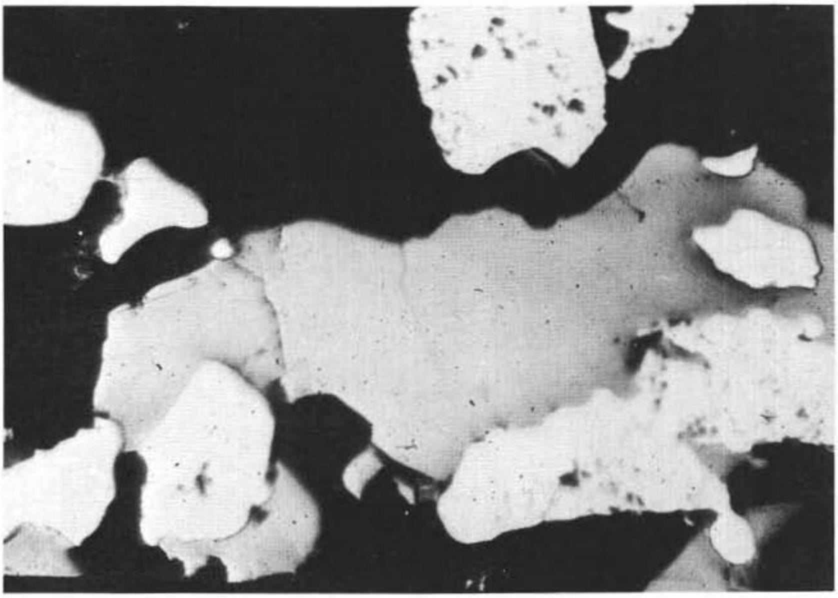


Fig. 8. — Photomicrograph of charge n. 953 (oil immersion, parallel nicols, 300 x). Simple intergrowth of A-phase grains (grey) and Cu- and Fe-grains (white).

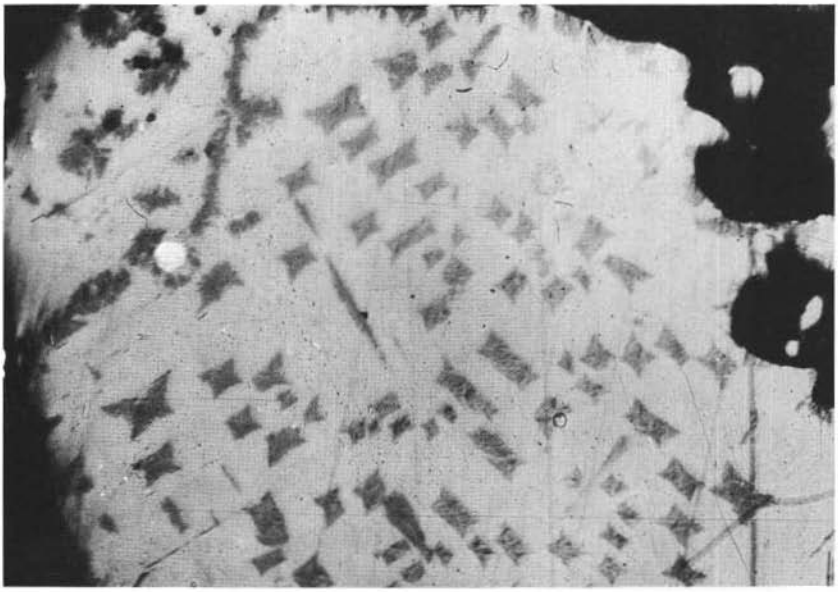


Fig. 9. — Photomicrograph of charge n. 940 (oil immersion, parallel nicols, 300 x). Grain of $bz_{s.s.}$, with intergranular border and star-like inclusions crystallized from a FeSe-similar liquid, and small intergranular Fe-grain (white).

While, in fact, the exact composition of this liquid is still uncertain, the presence of A-phase traces in charge n. 944 and their absence in n. 920 suggests that the FeSe-similar liquid cannot have a Cu-content lower than 5 % at.

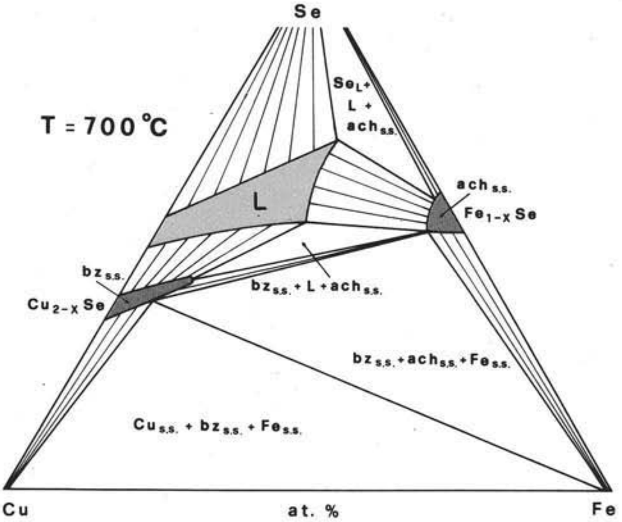


Fig. 10. — Phase relations in the Cu-Fe-Se system at 700° C (abbreviations as in fig. 2). All phases and phase assemblages coexist with vapour.

b) The 700° C isotherm

At 700° C the large L-liquid field retreats, as shown in fig. 10, towards the Cu-Se border together with the liquid immiscibility field, as evidenced by the comparison of the results of runs nn. 702, 703 and 704, reported in table 2, with those of the same composition at 900° C. Consequently a three-phase field: $Se_L + L + ach_{s.s.}$ and a very narrow two-phase field: $Se_L + ach_{s.s.}$ appear near the Fe-Se border. The problem of the solid phase present in these fields,

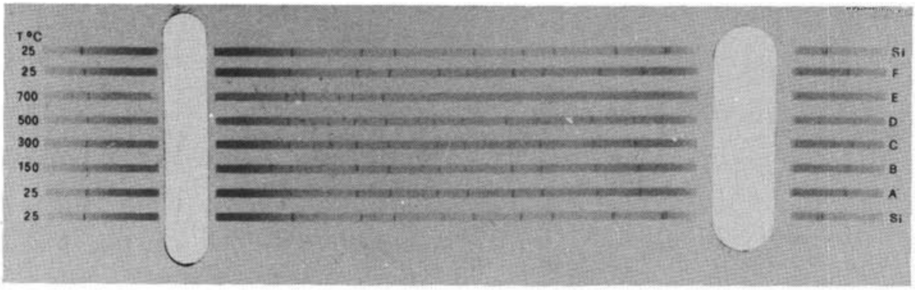
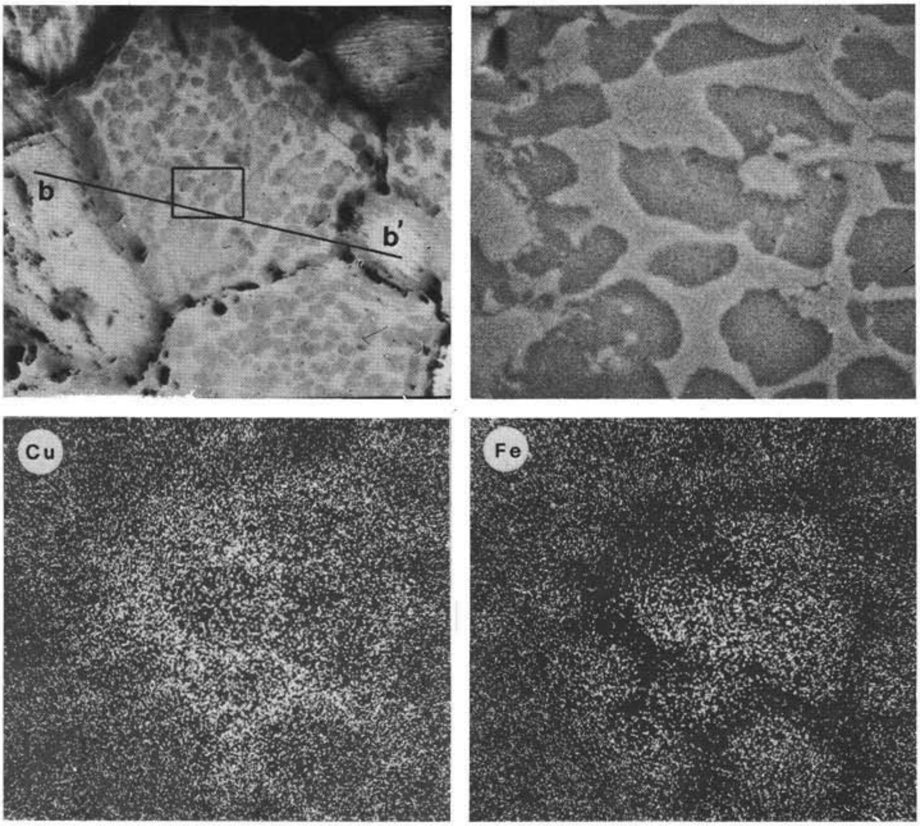


Fig. 11. — High-temperature powder diffraction patterns of synthetic eskebornite: A, B, C, D and F = $CuFeSe_2$; E = $Cu_{2-x}Se + Fe_{1-x}Se$ (film cassette ∅ 90 mm; Fe-filtered CoKα radiation).

which could be the Fe_3Se_4, is still open as already mentioned. In the quenched products of the charges of the univariant field, Fe_3Se_4 is present as exsolution lamellae in the grains of $Fe_{1-x}Se$ which are sorrounded by a microcrystalline matrix produced by the quenched liquids. The L-liquid field retreats also towards the Se-apex, its metal-rich border reaching a Se-content slightly lower than 50 % at. (cfr. run n. 757). A three-phase field: $bz_{s.s.} + L + ach_{s.s.}$ appears, therefore, in the region with a Se-content variable between 43 % and 50 % at. which includes the theoretical composition of eskebornite ($CuFeSe_2$). The high-temperature X-ray analysis of eskebornite synthesized at 300° C from pure elements (fig. 11) proves that at 700° C $CuFeSe_2$ breaks into $Cu_{2-x}Se$ and $Fe_{1-x}Se$. Moreover the D.T.A. run of eskebornite shows, in fairly good agreement with FRANZ's data (1970), an endothermic peak at 540-550° C, probably due to the incongruent melting of $CuFeSe_2$ into $CuFeSe_{2-x}$ plus selenium liquid, followed by another large peak at 600-630° C which might be explained by the decomposition of $CuFeSe_{2-x}$ into $Cu_{2-x}Se$ plus $Fe_{1-x}Se$ and a ternary liquid of composition approaching that of $(Cu,Fe)Se_{2-x}$. The possible existence of $CuFeSe_{2-x}$, which might have a cubic symmetry similar to that of $i_{s.s.}$ in the Cu-Fe-S system (CABRI, 1973), and its stability field below 700° C, might be ascertained by successive investigation at lower temperatures.

Fig. 12 shows the assemblage observed in the quenched product of run n. 716, with stoichiometric $CuFeSe_2$ composition, where grains of $Fe_{1-x}Se$, with exsolution lamellae of probable Fe_3Se_4, and grains of $Cu_{2-x}Se$, with inclusions of a microcrystalline matrix derived from the quenched liquid, are evident. The relative electron probe investigation, carried out along the line b-b′, and the element distribution maps, shown in the same figure, confirm the presence of the phases detected at room temperature.

In order to determine the metal-rich boundary of the univariant field: $bz_{s.s.} + L + ach_{s.s.}$, numerous runs were performed in the region with a Se-content variable between 37 % and 50 % at. In charges nn. 761 and 724, with 50 % and 43 % at. Se respectively, only two solid phases were detected: A-phase and FeSe, plus probable Fe traces in the second. The A-phase grains observed in the polished section of charge n. 761 did not show exsolution lamellae of eskebornite, thus suggesting the $bz_{s.s.} — ach_{s.s.}$ join pointing to a $bz_{s.s.}$ term of pure A-phase composition. On the other hand the probable Fe traces in charge n. 724 may suggest this join pointing to a compound with a metal to selenium ratio = 1/1, towards the Fe-Se border. A very narrow divariant field: $bz_{s.s.} + ach_{s.s.}$ is, therefore, established below the univariant field: $bz_{s.s.} + L + ach_{s.s.}$. Its Se-rich limit varies from almost 43 % at. in the $bz_{s.s.}$ region, as proved by the exsolution lamellae of eskebornite observed in the A-phase grains of run n. 760 with this Se-content, to nearly 50 % at. close to the Fe-Se border; the Se-poor limit goes from 37 % at. in the $bz_{s.s.}$ region to the same 50 % at., as accounted for by the results of charge n. 717 which, with this last Se-content and with 12 % at. Cu and 38 % at. Fe, is



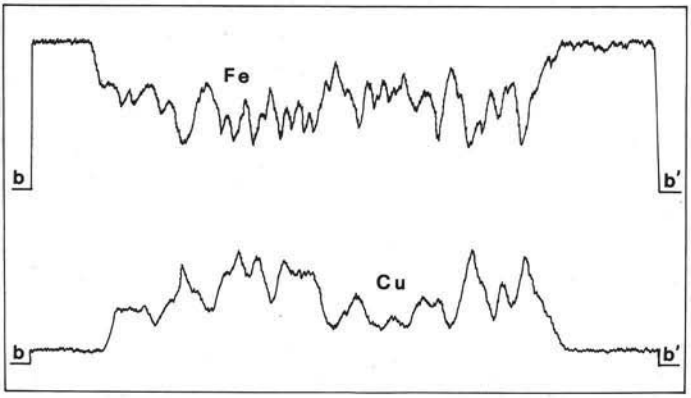


Fig. 12. — Polished section of charge n. 716. Top: reflected light photomicrograph (oil immersion, parallel nicols, 300 x) and scanning electron image (3000 x) of the particular in the black square. Intergrowth of ach$_{s.s.}$ grains (whitish), with exolution lamellae of probable Fe_3Se_4, and bz$_{s.s.}$ grains (grey) with buck-shot inclusions (darkish grey) crystallized from a $CuFeSe_2$-similar liquid. Center: characteristic X-ray scanning pictures. Bottom: traces of linear scans along the *b-b'* line.

located in the univariant field: bz$_{s.s.}$ + L + ach$_{s.s.}$. The establishement of the divariant field between bz$_{s.s.}$ and ach$_{s.s.}$ causes the disappearance of the small three-phase field: L + ach + Fe$_{s.s.}$, close to the Fe-Se border present at 900° C, which is substituted by a two-solid-phase field: ach$_{s.s.}$ + Fe$_{s.s.}$ (cfr. run n. 720 and fig. 13).

The inner boundaries of the two extreme two-solid-solution fields: $bz_{s.s.} + Cu_{s.s.}$ and $ach_{s.s.} + Fe_{s.s.}$ are dictated by the Fe- and Cu-content that Cu and Fe can respectively dissolve at 700° C (Hansen & Anderko, 1958 and supplements) and by the results of the experiments performed in the region below the $bz_{s.s.} + ach_{s.s.}$ divariant field (cfr. e.g. runs nn. 744 and 749).

No variation in the position of the boundary between the two three-solid-phase fields: $Cu_{s.s.} + bz_{s.s.} + Fe_{s.s.}$ and $bz_{s.s.} + ach_{s.s.} + Fe_{s.s.}$ was observed with respect to the one portrayed between $Cu_{s.s.} + bz_{s.s.} + Fe_{s.s.}$ and $bz_{s.s.} + L + Fe_{s.s.}$ at 900° C (cfr. e.g. run n. 747). The appearance at 700° C of the divariant field: $bz_{s.s.} + ach_{s.s.}$, in fact, has only prohibited the L-liquid coexisting with $Fe_{s.s.}$.

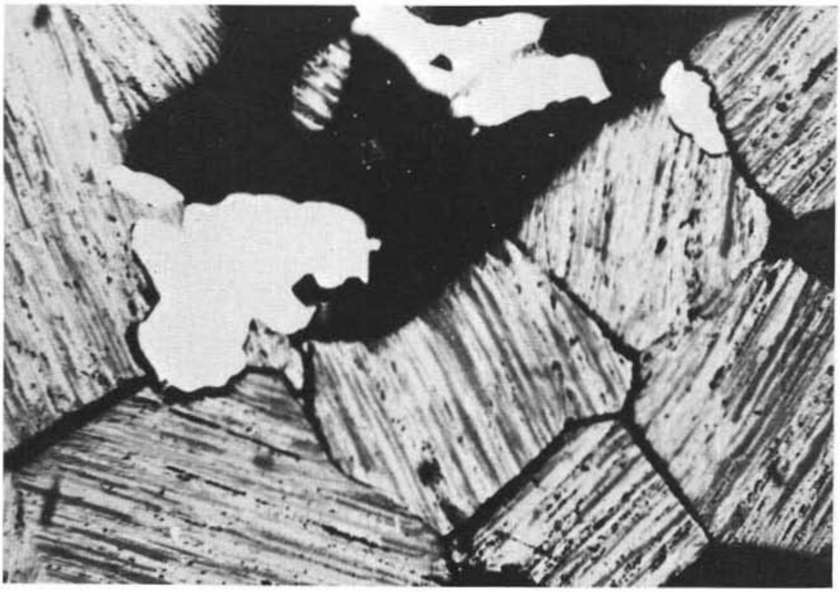


Fig. 13. — Photomicrograph of charge n. 720 (oil immersion, parallel nicols, 300 x). Simple intergrowth of $ach_{s.s.}$ grains (whithish grey), with prominent twin lamellae (grey), and Fe grains (white).

Conclusions

The phase relations in the Cu-Fe-Se system at 900° and 700° C have been defined accurately by quenching experiments. At 900° C a large ternary liquid field dominates the central portion of the system and only two solid phases, apart from those on the Cu-Fe border, were detected. At 700° C the only difference with the tie-lines pattern depicted for the 900° C isothermal section is the appearance, in the central region of the system, of an univariant field: $bz_{s.s.} + L + ach_{s.s.}$, with the liquid apex at almost 50 % at. Se. No ternary phases were detected either at 900° or at 700° C in contrast with the situation in the Cu-Fe-S system at the same temperatures.

According to YUND & KULLERUD (1966) and to KULLERUD et al. (1969), in fact, at both these temperatures the central area of the Cu-Fe-S system is characterized respectively by a small and a larger solid solution field, successively indicated as $i_{s.s.}$ field (BARTON, 1973; CABRI, 1973). While the boundaries of this field are very variable both in the Cu/Fe ratio and in the S-content, the latter is always lower than that of stoichiometric $CuFeS_2$.

In the Cu-Fe-Se system even for compositions corresponding to those of mooihockite and haycockite (CABRI & HALL, 1972), or between the two, no solid ternary phase was detected. Owing to the much lower temperature limits of the stability fields of the different phases in the two binary systems Cu-Se and Fe-Se with respect to the corresponding sulfur systems, a situation similar to that of the Cu-Fe-S system at 900° and 700° C, should occur in the Cu-Fe-Se system at lower temperatures. More complicated phase relations, therefore, are to be expected in this system at 500° and 300° C where more changes in the tie-lines configuration should occur owing to the appearance of new solid phases and separation of high--temperature solid solutions.

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