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Cu-Fe-S (Copper-Iron-Sulfur)

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A critical evaluation of this ternary system was carried out in 1979 by Chang et al. [1979Cha]. The highlights of this review are described in some detail below. More recent information on this system is mainly from the thermodynamic measurements of [1989Nag] and [2002Lus].

Binary Systems

There are no intermediate phases in the Cu-Fe system. A metastable liquid miscibility gap is known [Massalski2]. The Cu-S system [1983Cha] is characterized by two liquid miscibility gaps. The gap at Cu-rich compositions has a monotectic temperature of 1105 °C. $Cu_{1.76\text{-}1.79}S$ [CaF_2 type face-centered cubic (fcc); mineral name: digenite, *dg*] forms congruently at 1130 °C. Cu_2S (chalcosite, *cc*) is monoclinic below 103 °C and has the $B8_2$ type hexagonal structure between 103 and 435 °C. Above 435 °C, it has the CaF_2 type cubic structure and is continuous with digenite. CuS (*B*18 type hexagonal; mineral name: covellite, *cv*) forms peritectoidally at 507 °C. There are two intermediate phases in the Fe-S system [1982Kub]. The monosulfide $Fe_{1-x}S$ (NiAs type hexagonal; mineral name: pyrrhotite, *po*) is stable at Fe-deficient (S-rich) compositions with a range of 50-55 at.% S. $Fe_{1-x}S$ with 52 at.% S melts congruently at 1188 °C. In the Fe-FeS region, the solidification is through a eutectic reaction at 988 °C. In the FeS-S region, a monotectic reaction at 1082 °C yields $Fe_{1-x}S$ of 54.2 at.% S and a sulfur-rich liquid $(S)_l$. At 743 °C, cubic FeS_2 (pyrite, *py*) forms peritectically and undergoes a transition to the orthorhombic form (marcasite) at 425 °C. The phase relations below 350 °C in the pyrrhotite region are complex with the occurrence of several ordered forms.

Previous Review of the Ternary System

Chang et al. [1979Cha] made a critical evaluation of this ternary system and listed a number of ternary compounds. A more detailed list and description of the ternary compounds are given below primarily from the reports of [1966Yun], [1974Cra], [1979Cha] and [Pearson3]. Table 1 lists the crystal structure and the lattice parameter data. Cu_5FeS_4 (τ_1; mineral name: bornite, *bn*) has an extensive homogeneity range and exists in several crystal forms [Pearson3]. The low-temperature (LT) form is tetragonal, with $a = 1.094$ nm and $c = 2.188$ nm (Table 1). On heating to 228 °C, it changes to a cubic form with $a \approx 0.550$ nm. Superstructures

Table 1 Cu-Fe-S crystal structure and lattice parameter data

Phase	Mineral name and abbreviation	Pearson symbol	Space group	Lattice parameters, nm
Cu_5FeS_4 (τ_1) (LT)	bornite, *bn*	*tP*160	$P\bar{4}2_1c$	$a = 1.094$ $c = 2.188$
τ_2	intermediate solid solution, *iss*	*cF*12	$F\bar{4}3m$	$a = 0.536$
$CuFeS_2$ (τ_3)	chalcopyrite, *cp*	*tI*16	$I\bar{4}2d$	$a = 0.5289$ $c = 1.0423$
$Cu_5FeS_{4.05}$ (τ_4)	*x*-bornite	(a)	…	$a = 1.65$ $c = 1.10$
$CuFe_2S_3$ (τ_5)	cubanite, *cb*	*oP*24	*Pnma*	$a = 0.62336$ $b = 1.11201$ $c = 0.64679$
$Cu_{5.5}FeS_{6.5}$ (τ_6)	idaite, *id*	(b)	…	$a = 0.3782$ $c = 1.1187$
Cu_3FeS_8 (τ_7)	fukuchilite, *fk*	*cF*10	$Fm\bar{3}m$	$a = 0.560$
$Cu_9Fe_8S_{16}$ (τ_8)	talnakhite, *tal*	*cI*96	$I\bar{4}3m$	$a = 1.0605$
$Cu_9Fe_9S_{16}$ (τ_9)	mooihoekite, *mh*	*tP*34	$P\bar{4}2m$	$a = 1.0585$ $c = 0.5383$
$Cu_4Fe_5S_8$ (τ_{10})	haycockite, *hc*	*oP*204	*P*222	$a = 1.0705$ $b = 1.0734$ $c = 3.1630$
$Cu_{0.12}Fe_{0.94}S$ (τ_{11}) Cu_5FeS_6	nukundamite, *nk*	*hP*8	$P\bar{3}m1$	$a = 0.3783$ $c = 1.1195$
(a) tetragonal				
(b) hexagonal				

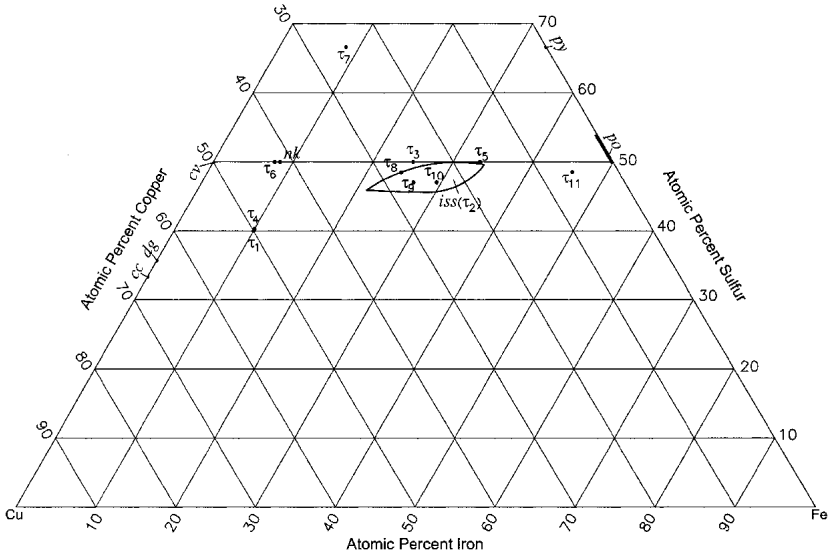

Fig. 1 Cu-Fe-S composition of the ternary compounds

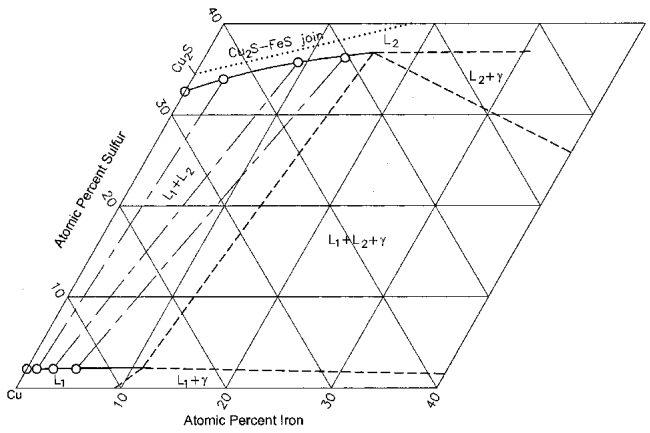

Fig. 2 Cu-Fe-S partial isothermal section at 1200 °C [2001Men]

with the lattice parameter as multiples of 0.550 nm are known. Bornite forms an extensive solid solution, especially with respect to the Cu/Fe ratio. Above ~335 °C, it merges with the binary phase digenite (*dg*) and extends up to 15 at.% Fe. At 700 °C, the composition of bornite includes $Cu_{1.8}S$ (*dg*), Cu_2S (*cc*), and Cu_5FeS_4. $Cu_5FeS_{4.05}$ (τ_4) is a S-rich bornite called *x*-bornite or anomalous bornite. It is tetragonal and has an upper temperature of stability of 125 °C. Above 500 °C, the intermediate solid solution (*iss*; τ_2) is a dominant ternary phase of the system. It has the disordered sphalerite-type fcc structure and varies in composition over a wide range to include the compositions of τ_5, τ_8, τ_9, and τ_{10} (see below). The upper temperature range of stability of *iss* is 960 °C. The low-temperature decomposition of *iss* is not well understood; a part of the *iss* field transforms on quenching to a primitive cubic phase that is stable in the range of 20-200 °C. $CuFeS_2$ (chalcopyrite, *cp*; τ_3) is a well-known copper-iron sulfide. It has an ordered tetragonal structure and decomposes above 557 °C to *py* + *iss*. $CuFe_2S_3$ (cubanite, *cb*; τ_5) is stable below 200-210 °C and has orthorhombic symmetry. $Cu_{5.5}FeS_{6.5}$ (idaite, *id*, also called orange bornite; τ_6) is stable below 501 °C and has a primitive hexagonal lattice. Cu_3FeS_8 (fukuchilite, *fk*; τ_7) is cubic and is stable below ~200 °C. $Cu_9Fe_8S_{16}$ (talnakhite, *tal*; τ_8) is cubic and transforms at 186 and 230 °C to other polymorphs. It finally transforms to *iss* above ~500 °C. $Cu_9Fe_9S_{16}$ (mooihoekite, *mh*; τ_9) is tetragonal and is stable below 167 °C and transforms to phase A between 167 and 236 °C and then to *iss* on further heating. $Cu_4Fe_5S_8$ (haycockite, *hc*; τ_{10}) is orthorhombic and is stable only at low temperatures. An unconfirmed compound is $Cu_{0.12}Fe_{0.94}S$ (τ_{11}). [Pearson3] lists a phase Cu_5FeS_6 (mineral name: nukundamite, *nk*), as reported by [1981Sug]. It has a composition close to idaite ($Cu_{5.5}FeS_{6.5}$) and has the same formation temperature (~500 °C) and crystal symmetry and lattice parameters as idaite. [1985Koj] report only nukundamite (and not idaite) in the temperature range of 500-300 °C. For a detailed discussion on the two minerals, see [1979Ric] and [1981Sug]. The location of the ternary phases on the Gibbs triangle is shown in Fig. 1.

The liquidus projection presented by [1979Cha] is based primarily on the work of [1952Sch]. The prominent feature is the presence of a liquid miscibility gap in the metal-rich region. The gap, which is extensive at 1350 °C, shrinks as the temperature decreases. Limited new data on the liquidus surface were reported by [1985Bys]. A number of isothermal sections were redrawn by [1979Cha], after adjusting the literature data for consistency with the binaries adopted by them. The sections are from [1969Kul] (1100 and 1000 °C), [1976Cha] (840 °C), [1973Cab] (600 °C), and [1975Sug] (350 °C). In addition, two isothermal sections at 1350 and 1200 °C for metal-rich compositions, depicting the isoactivity lines for S, Cu, and Fe were given by [1979Cha]. The phase relationships near the Cu corner at 1200 °C were redetermined recently by [2001Men]. This section and the section of [1979Cha] at 1200 °C are shown for comparison

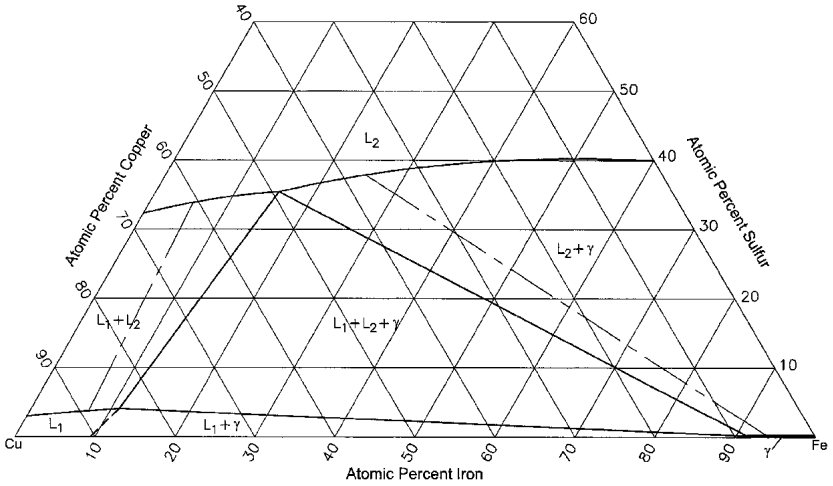

Fig. 3 Cu-Fe-S isothermal section at 1200 °C [1979Cha]

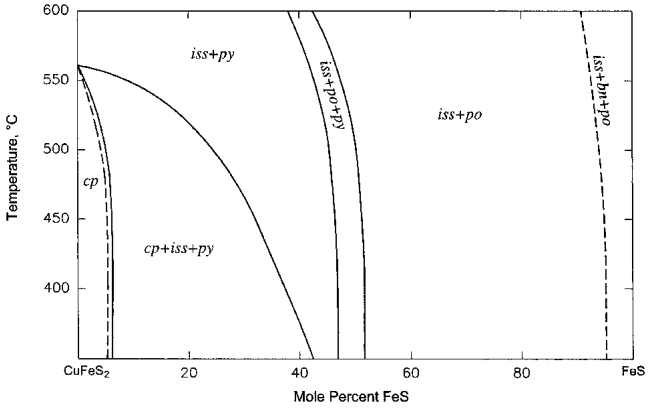

Fig. 4 Cu-Fe-S vertical section along the $CuFeS_2$-FeS join [1980Uen]

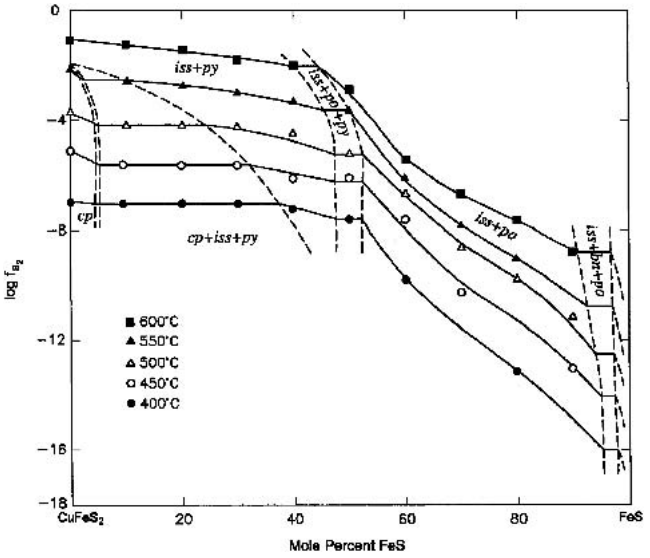

Fig. 5 Cu-Fe-S sulfur fugacity curves along the $CuFeS_2$-FeS join [1980Uen]

in Fig. 2 and 3, respectively. The composition at the metallic end of the tie-line in [1979Cha] (Fig. 3) is appreciably shifted toward higher Fe contents as compared with the tie-lines in Fig. 2.

Subsequent to the review of [1979Cha], [1980Uen] measured the phase distribution along the $CuFeS_2$-FeS join between 600 and 400 °C and constructed a vertical section shown in Fig. 4. Chalacopyrite (*cp*) has a small homogeneity range and coexists with *iss* and *py*. The two-phase field of *iss* and hexagonal *po* is wide and a small three-phase field of *iss* + *po* + *bn* appears close to the FeS end. The fugacity of sulfur (f_{S2}) was measured by [1980Uen] by the pyrrhotite indicator method of [1964Tou] for the above composition and temperature range and is shown in Fig. 5.

Recent Thermodynamic Measurements

The partial pressure of sulfur over Cu-Fe-S ternary mattes was measured at 1200 °C by [1989Nag], employing H_2S-H_2 gas mixtures. Based on their results and the literature data, [1989Nag] developed a lengthy empirical equation for calculating the partial pressure of S over the entire ternary matte composition from the Cu-S to the Fe-S side. Calculated curves of the partial pressure of S_2 at different Cu/Fe ratios shown in Fig. 6 are in good agreement with the experimental results of [1957Kri], [1970Nag], and [1976Bal]. Also, [1989Nag] used the Gibbs-Duhem integration to calculate the Raoultian activities of Cu_2S and FeS in the metal-saturated mattes.

Lusk and Bray [2002Lus] used the Ag/AgI/$Ag_{2+x}S$, $f_{S2(g)}$ electrochemical cell developed by Schneeberg [1973Sch] to study seven ternary reactions in this system in the temperature range of 460-185 °C. Cell voltage measurements and the derived sulfur fugacities were listed and plotted as a function of temperature for the following reactions:

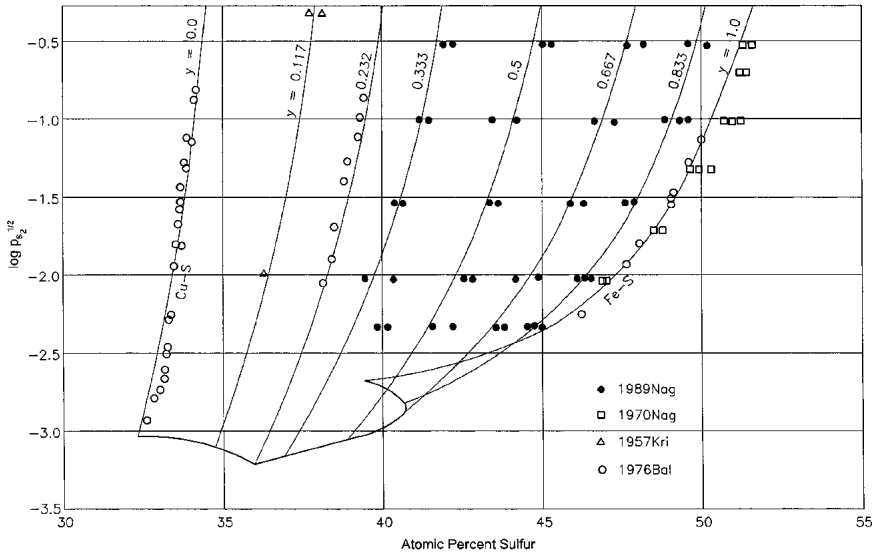

Fig. 6 Cu-Fe-S sulfur partial pressure versus composition over mattes at 1200 °C

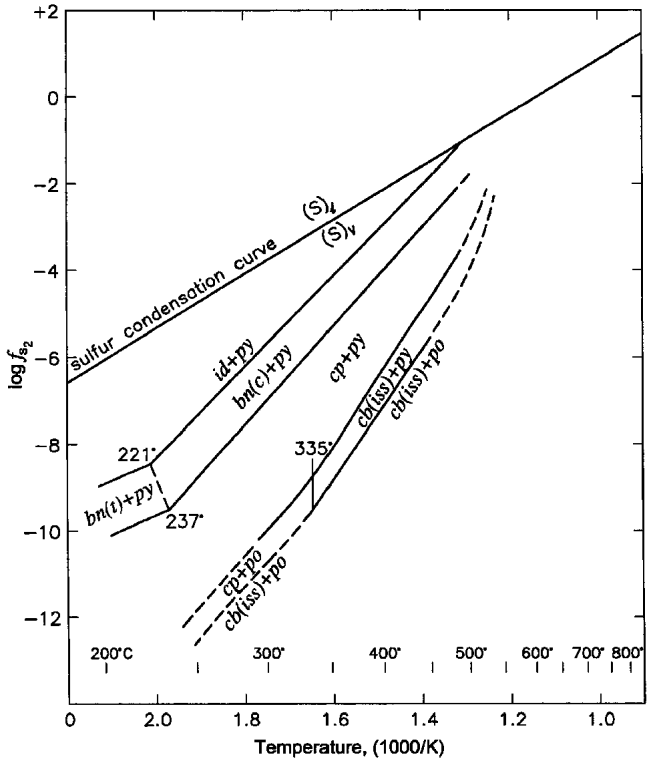

Fig. 7 Cu-Fe-S log f_{S2} versus (1000/T(K)) for selected reactions [2002Lus]

$$py + id = bn + (S)_v \quad (1)$$

$$py + bn = cp + (S)_v \quad (2)$$

$$py + cp = iss + (S)_v \quad (3)$$

$$po + cp = cb\ (iss) + (S)_v \quad (4)$$

$$py + cb\ (iss) = po + cb\ (iss) + (S)_v \quad (5)$$

$$py + cp = po + cp + (S)_v \quad (6)$$

and

$$py = po + (S)_v \quad (7)$$

The LT phase cubanite (*cb*), stable at 200-210 °C [1974Cra], transforms to the intermediate solid solution (*iss*) on heating and is denoted as *cb* (*iss*) in the above reactions. Figure 5 shows the plot of log f_{S2} versus 1/T(K) for reactions 1-6. Reaction 7 (not shown in Fig. 5) pertains to the Fe-S binary system. At 335 °C, an invariant four-phase equilibrium prevails among *cp*, *py*, *po*, and *cb* (*iss*) and a U-type transition reaction *py* + *cb* (*iss*) ↔ *cp* + *po* occurs on cooling. At 221 °C, sulfur-rich bornite transforms from cubic to tetragonal form [*bn*(c) → *bn*(t)] on cooling; sulfur-poor bornite undergoes this structural transition at 237 °C. Sulfur activities were also measured for several of these reactions by [1973Bar], using the pyrrhotite indicator method of [1964Tou]. [1985Ale] measured the S vapor pressure over Cu rich alloys of this system in the temperature range of 1250-900 °C.

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