The Cu-S (Copper-Sulfur) System

63.546 32.06

By D. J. Chakrabarti and D. E. Laughlin
Carnegie-Mellon University

Equilibrium Diagram

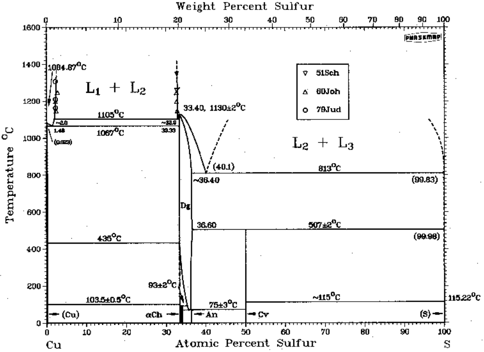
The equilibrium phases of the Cu-S system shown in Fig. 1 are:

- The liquid, L, that manifests two miscibility gaps, namely (*a*) between the liquids L_1 and L_2 above 1105 °C at Cu-rich compositions and (*b*) between the liquids L_2 and L_3 above 813 °C at higher S compositions
- The fcc terminal solid solution based on Cu, with restricted solubility of S amounting to 0.023 at.% at 1067 °C
- The orthorhombic terminal solid solution based on S, stable up to ~115 °C and with presumably negligible solubility of Cu
- The monoclinic low-chalcocite (αCh), stable up to 103.5 ± 0.5 °C at stoichiometric composition Cu_2S, and up to 90 ± 2 °C at 33.41 at.% S
- The hexagonal high-chalcocite (βCh), stable from 103.5 ± 0.5 °C at the Cu-rich limit of stoichiometric Cu_2S, and from 90 ± 2 °C at 33.44 at.% S to 435 °C at 33.34 at.% S
- The fcc digenite (Dg) with a broad phase field, whose Cu-rich boundary is approximately at Cu_2S stoichiometry between 435 and 1130 ± 2 °C; the Cu-deficient boundary extends to form the defect compound $Cu_{2-\delta}S$, which is stable up to 507 ± 2 °C at 36.60 at.% S and down to 72 ± 3 °C at 35.65 at.% S
- The orthorhombic djurleite (Dj) of nominal composition $Cu_{1.96}S$, stable up to 72 ± 3 °C at $Cu_{1.934}S$ and up to 93 ± 2 °C at 33.99 at.% S
- The orthorhombic compound anilite (An) of stoichiometry $Cu_{1.75}S$ (36.36 at.% S), stable up to 75 ± 3 °C
- The hexagonal compound covellite (Cv) of stoichiometry CuS, stable up to 507 ± 2 °C

Numerous studies have been reported on the Cu-S binary system. Uncertainty, however, persists regarding phase equilibria, because of a strong tendency for forming several metastable phases in this system. The phases formed often possess X-ray diffraction and optical properties similar to those of equilibrium phases, making phase identification difficult. Marked thermomechanical history dependence is exhibited by many of the phases. Extreme sensitivity to applied pressure has been known to cause a phase transformation during specimen preparation by grinding.

The crystal structures of the intermediate phases and compounds in this system are characterized by either hexagonal or cubic close-packing of S atoms, with Cu atoms positioned at the interstices. The transformation involving rearrangement of S atoms from cubic to hexagonal close-packing, or vice-versa, is extremely sluggish (particularly at low temperatures). This has been primarily responsible for the large number of metastable phases in

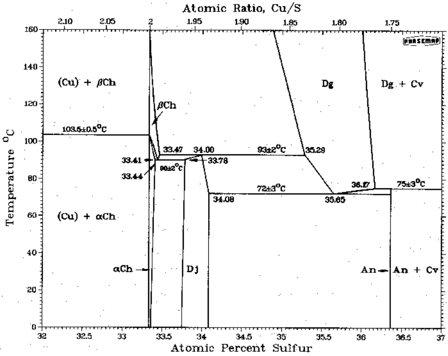
Fig. 1 Cu-S Equilibrium Phase Diagram



Compositions in parentheses are calculated values by [80Sha]. See Table 1 for references to other data.

D. J. Chakrabarti and D. E. Laughlin, 1983.

Fig. 2 Enlarged View of Cu-S Equilibrium Diagram from 0 to 160 °C and from Cu:S Ratio 1.7 to 2.1 (32 to 37 at.% S)



After Potter [77Pot]. D. J. Chakrabarti and D. E. Laughlin, 1983.

this system. In contrast, a transformation that does not require rearrangement of S atoms can be extremely rapid, and the resulting phase cannot be retained by quenching from high temperatures, necessitating in-situ studies, such as X-ray and metallography, at high temperatures.

Certain binary nonequilibrium phases are also stabilized in this system by impurities in amounts often present in naturally-occurring minerals, or that are introduced in laboratory specimens during experimental work. Thus, one such metastable phase is stabilized at room temperature by the presence of iron and another by the presence of oxygen. Most of the early studies were conducted in an open atmosphere. This resulted not only in contamination by oxygen but also in changes of composition of the samples, such as conversion of chalcocite (Ch) to higher S-containing digenite (Dg), observed on heating samples in air by [41Bue1, 42Bue2]. Even at ambient conditions, such gradual shift of composition to higher S levels occurs continuously. Thus, in natural minerals exposed to atmosphere, Ch is often found to be replaced by minerals of higher S content.

The Cu-S system is characterized by the occurrence of miscibility gaps in the liquidus at two ranges of composition. Also occurring are the intermediate phases Dg, stable over a wide composition range; αCh, βCh, and Dj, with narrow phase fields; and stoichiometric compounds An (Cu_7S_4) and Cv (CuS). Dj is in equilibrium with An at room temperature [77Pot] and not with the low-digenite phase, considered for a long time as the low-temperature equilibrium modification of Dg. Earlier observations of Dg at room temperature could be related to the effect of impurities such as Fe [71Mor] or to the conversion of An to Dg during specimen grinding [70Mor]. Cv is in equilibrium with the terminal solid solution of Cu in S, (S), indicating the absence of further intermediate phases at >50 at.% S [64Gat].

The provisionally evaluated Cu-S equilibrium diagram is presented in Fig. 1. An enlarged diagram between 0 and 160 °C, and between Cu:S atomic ratios 1.7 and 2.1 (37 to 32 at.% S), based largely on the very detailed studies by Potter [77Pot], is presented in Fig. 2. The work was based on the electromotive force (emf) measurement with aqueous electrolyte. The investigator utilized high-purity materials (99.999% spectrographic-grade S, 99.975% Cu containing 100 ppm Fe and 100 ppm Ni as major impurities) and took precautions against contamination by oxygen. Information on much of the solidus and liquidus, apart from the miscibility gaps, is derived from Cook [72Coo], and that on the Dg and Ch boundaries largely from Roseboom [66Ros] and Cook [72Coo]. The experimental methods employed were X-ray at high temperatures by [66Ros] and X-ray, differential thermal analysis (DTA), and high-temperature phase equilibration by metal whiskers growth by [72Coo]. The purity of the materials used by both authors was similar to or better (e.g., 99.999% Cu by [72Coo]) than that of [77Pot], and precautions against contamination by oxygen at high temperatures also were taken.

The equilibrium temperatures, compositions, and coexisting phases for the different invariant reactions, according to different authors, are presented in Table 1. The accepted data are shown in boldface type.

Liquidus and Solidus

As previously stated, the Cu-S system is characterized by the presence of two large regions of liquid immiscibility.

Table 1 Transformation Temperatures and Compositions in the Cu-S System

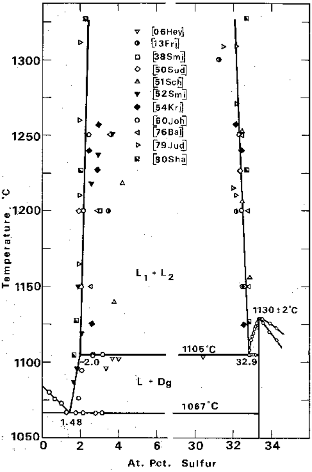
Transformation mode and phase	Composition, at.% S ⟨Cu/S⟩	Composition reference(a)	Temperature, °C Reference(b)					
			[Hansen]	[72Coo]	[66Ros]	[77Pot]	[60Joh]	[47Jen]
Congruent L ⇌ Dg	⟨**1.994**⟩, **33.40-33.49**	[72Coo]	1129	**1130 ± 2**	···	···	1129	1129
	···, 33.46	[47Jen]						
	···, 33.32	[60Joh]						
	···, 33.40-33.49	[15Pos]	1130 ± 1 [15Pos]					
	···, 33.45	(c)	1131(c)					
Monotectic $L_2 \rightleftharpoons L_1$ + Dg	**32.9**, ~**2.0**, ···	[60Joh]	**1105**	1104	···	···	**1105**	**1105**
	32.9, 2.9, ···	[47Jen], [Hansen], ···						
	···, ···, ⟨**2.002**⟩	[72Coo]						
	···, 2.6, ···	[79Mou]						
	32.82, 1.7, 33.35	(c)	**1105**(c)					
Eutectic L ⇌ (Cu) + Dg	**1.48**, ···, ⟨**2.00025**⟩	[60Joh], ···, [72Coo]	**1067**	···	···	···	**1067**	1066 [47Jen, 79Mou]
	1.5, ···, ···	[Hansen]						
	1.52, **0.0225**, 33.35	(c)	**1067**(c)					
Monotectic $L_2 \rightleftharpoons$ Dg + L_3	41, ~**36.4**, ···	[71Van](d), [67Rau, 74Rau], ···	···	812	···	···	795 [67Rau, 71Van]	**813** [74Rau, 60Kul1, 60Kul2]
	···, ~36.3, ···	[72Coo]						
	···, ~38.5, ···	[71Van]						
	40.09, 36.29, **99.83**	(c)	812(c)					
Peritectoid (Cu) + βCh ⇌ αCh	~0, ~**33.33 ± 0.02**, ~**33.33 ± 0.02**,	[77Pot]	105	···	103.5 ± 1.5	**103.5** **± 0.5**	105 [41Bue] 100.3 [60Kul1]	104 [67Rau] 110 [58Dju, 51Hir]
	···, 33.44 ± 0.03 ⟨2.000 ± 0.002⟩	[66Ros]						
	···, 33.44 ± 0.03, ···							
Eutectoid βCh ⇌ αCh + Dj	**33.44 ± 0.06**, **33.41 ± 0.02**, **33.78 ± 0.02**	[77Pot]	···	91 ± 1	93	**90 ± 2**	89.5(e) [60Kul1]	···
	33.47 ± 0.02, 33.41 ± 0.02, ···	[66Ros]						
Peritectoid (Cu) + Dg ⇌ βCh	0, **33.344**, **33.340**	[72Coo]	···	**435**	**435**	435 ± 8	435 ± 10 [73Bar]	470 [58Dju, 51Hir, 49Ued]
	···, 33.34, ···	(c)	**435**(c)					
Eutectoid Dg ⇌ Dj + An	**35.65 ± 0.03**, **34.08 ± 0.02**, **36.36 ± 0.04**	[77Pot]	···	···	···	**72 ± 3**	···	···
	⟨1.805 ± 0.002⟩, ⟨1.934 ± 0.002⟩, ⟨1.750 ± 0.003⟩	[77Pot]						
Peritectoid βCh + Dg ⇌ Dj	**33.47 ± 0.05**, **35.29 ± 0.03**, **33.99 ± 0.02**	[77Pot]	···	91 ± 1	**93 ± 2**	**93 ± 2**	90[72Luq]	···
Peritectoid Dg + Cv ⇌ An	**36.17 ± 0.02**, **50.00 ± 0.02**, **36.36 ± 0.04**	[77Pot]	···	···	···	**75 ± 3**	70 ± 3 [70Mor]	···
	⟨1.765 ± 0.002⟩, ⟨1.000 ± 0.001⟩, ⟨1.750 ± 0.003⟩	[77Pot]						
Peritectic Dg + L ⇌ Cv	**36.60 ± 0.07**, ···, **50.00 ± 0.02**	[77Pot], ···, [77Pot]	···	507	507 ± 3 [66Ros, 58Kul]	**507 ± 2** [77Pot, 65Kul]	508 [67Rau]	···
	⟨1.732 ± 0.005⟩, ···, ⟨2.000 ± 0.001⟩	[77Pot] ···						
	36.59, ···, 50	[66Ros, 67Rau]						
	36.73, ···, ···	[72Coo]						
	36.46, **99.98**, ···	(c)	**507**(c)					
Eutectic/Peritectic L ⇌ Cv + (S)/ Cv + L ⇌ (S)	···, 50, ~100		~**115.22** [81BAP]	···	···	···	···	···

Note: Accepted values shown in boldface type.

(a) References separated by comma pertain to respective compositions in previous column. (b) Temperature datum relates to reference shown on top of that column unless otherwise noted. (c) Calculated values from thermodynamic modeling by [80Sha]. (d) From extrapolation of liquidus data at higher temperatures down to 813 °C. (e) At 33.48 at.% S.

The boundary of the Cu-rich higher temperature miscibility gap, between the liquids L_1 and L_2, has been studied extensively [06Hey, 13Bor, 13Fri, 38Smi, 51Sch, 52Smi, 54Kri, 60Joh, 74Bur, 76Bal, 79Jud]. The results from figures and tables of different works, presented in Fig. 3, indicate fair agreement with one another and de-

Fig. 3 Liquid Miscibility Gap Boundaries Between L_1 and L_2

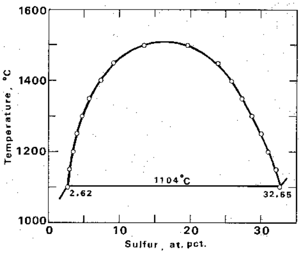


Data from different works.
D.J. Chakrabarti and D.E. Laughlin, 1983.

pict gap boundaries that are nearly vertical up to the highest measured temperature (~1350 °C). In contrast, the gap boundaries reported by [79Mou], presented in Fig. 4, slope rapidly inward with increasing temperature, reaching the critical point at about 1510 °C.

The reason for the difference in the gap shape between [79Mou] and the other works is not clear. Material purity does not appear to be very critical in view of the fair agreement between data from diverse sources, as shown in Fig. 3. The purity of material used by [79Mou] was 99.9996% Cu and 99.5% Cu sulfide. [79Mou] used specimen sampling from the liquid and chemical analysis of the entire solidified mass. The same technique was also adopted by [79Jud] and [13Fri] in Fig. 3, whereas the alternative approach of rapid freezing of the equilibrated layers of liquid alloy, followed by specimen sampling from the solid and chemical analysis, was tried by Johannsen and Vollmer [60Joh] and several others. The latter technique can lead to erroneous results, unless care is taken in specimen sampling to avoid the effect of segregation during solidification. However, good agreement between the results of [60Joh] and [79Jud] and of several others on either side of the gap boundary (see Fig. 3) preclude the experimental techniques being responsible for the difference in the results shown in Fig. 3 and 4.

Fig. 4 Liquid Miscibility Gap Boundary Between L_1 and L_2



According to [79Mou].
D.J. Chakrabarti and D.E. Laughlin, 1983.

The boundary of the same miscibility gap was calculated by Sharma and Chang [80Sha], based on the associated solution model for the thermodynamic behavior of the liquid and optimization of the parameters with the known phase diagram data and thermodynamic values of other phases in the system. The results from the calculated boundary, shown for selected temperatures in Fig. 3, are consistent with those of [79Jud] and others, within the limits of experimental error, but they do not agree with the results in Fig. 4. The internal consistency in the model for the liquid (as also for other phases) adopted by [80Sha] is evident by their ability to predict other invariant temperatures and phase equilibria that are in good agreement with the experimental ones. In another calculation, by [79Lar], the same miscibility gap was shown not to close, even at 1927 °C. Because of the fair-to-good agreement between the various experimental determinations and the calculations, the miscibility gap given in Fig. 3 is considered more reliable, and it is accepted as representative for this evaluation.

The eutectic temperature is accepted to be 1067 °C, and the monotectic temperature, 1105 °C, based on the precise determinations by [06Hey, 13Bor, 60Joh] and [47Jen, 80Joh], respectively. The eutectic composition of the liquid is taken at 1.48 at.% S, following the results of [60Joh, 06Hey], and that of Dg at $Cu_{2.00025}S$, based on the precise determination by [72Coo]; see Fig. 5. The accepted compositions of the phases in equilibrium at the monotectic temperature are: $Cu_{2.002}S$ for Dg, according to [72Coo]; 32.9 at.% S for liquid, L, according to precise thermal analysis by [47Jen, 60Joh], and 1.96 at.% S for the liquid, L, according to [60Joh]. The latter value, though somewhat lower than that of [13Fri] and [76Bal], is more consistent with other data at higher temperatures.

The congruent melting point of Cu_2S occurs at the off-stoichiometric Cu-deficient composition, $Cu_{1.990 \pm 0.004}S$, at

1130 ± 1 °C, according to [15Pos], and $Cu_{1.989}S$ at 1129 °C, according to the precise DTA by [47Jen]. The DTA studies by [72Coo] confirmed these results and gave the value 1130 ± 2 °C, corresponding to the composition on the higher Cu side of the range, $Cu_{1.994}S$ to $Cu_{1.986}S$ (33.40 to 33.49 at.% S). The DTA results of [60Joh] indicated the maximum melting point at 1129 °C to occur at Cu_2S composition and were not supported by the above studies. The accepted congruent temperature and composition are taken at 1130 ± 2 °C and at ~33.40 at.% S from Cook [72Coo].

Part of the boundary of the Dg plus L two-phase field was investigated by several authors [13Fri, 15Pos, 47Jen, 29Jou, 69Joh, 67Rau, 72Coo, 74Rau]. The results showed considerable scatter. The measurements were not continued to low enough temperature to ascertain the composition of the liquid at the monotectic temperature, 813 °C. No determination of the miscibility gap boundaries between L_2 and L_3, or of the composition of the liquid at different invariant reactions at further lower temperatures, is available. The accepted monotectic temperature is taken at 813 °C and the corresponding Dg composition at 36.4 at.% S, according to [60Kul1, 60Kul2, 74Rau] and [67Rau, 74Rau, 72Coo], respectively. The compositions of L_2 and L_3 at 813 °C are taken tentatively to be 40.1 and 99.83 at.% S, respectively, and of L at the peritectic invariant at 507 °C to be 99.98 at.% S, based on the calculations of [80Sha]. The composition of Dg at 507 °C is accepted from [77Pot] to be 36.60 at.% S. At approximately 115 °C, the liquid undergoes a eutectic/peritectic transformation, with Cv of 50 at.% S and the terminal solid solution, (S), containing undetermined but negligible Cu.

Terminal Solid Solubility

The terminal solid solution fields are extremely narrow. The solid solubility of S in Cu determined by electrical conductivity measurements [46Sma] and of S in Cu of two different purities by the radioactive tracer method [59Oud] are presented in Table 2. The solubility of S decreases with increasing purity of Cu.

In the absence of experimental data, the calculated maximum solubility of S in Cu at the eutectic temperature, 1067 °C, according to [80Sha] is accepted to be 0.023 at.%. No data regarding solubility of Cu in S are available.

Intermediate Phases

Of the several intermediate phases discussed previously, all except the βCh and Dg occur as minerals in nature.

Chalcocite (Cu_2S) is a well-known compound that has been recognized for a long time to exist in two polymorphic forms, with the transformation temperature at 100 ± 3 °C (Ref 15 of [Hansen]).

Low-Chalcocite (αCh). The solubility figures from different authors, presented in Table 3 show that the Cu:S ratio at maximum extension of the phase field on the S-rich side varies from 1.991 to 1.995 (33.43 to 33.39 at.% S), with the exception of the data of [72Coo] and [60Kul1]. On the Cu-rich side, there is no reported deviation from stoichiometry. The polymorphic transformation temperature of low-chalcocite (αCh) depends on composition and occurs over the temperature range of 90 to 103.5 °C (see Table 1 and Fig. 2). The transformation on the Cu-rich side occurs via a peritectoid reaction to form βCh and (Cu) (terminal solid solution of S in Cu) at 103.5 ± 0.5 °C [77Pot]. For transformation of the Cu-deficient αCh, confusion persists regarding the invariant temperature and the transformed products, due to the proximity of the temperature to that for the decomposition of Dj. The unresolved temperature for the two reactions was cited at 93 ± 2 °C by [66Ros]. On the basis of the careful studies by [77Pot], the transformation temperature in this evaluation is accepted at 90 ± 2 °C, corresponding to the eutectoid phase equilibrium involving αCh at 33.41 ± 0.02 at.% S, βCh at 33.44 ± 0.06 at.% S, and Dj at 33.78 ± 0.02 at.% S. The $\alpha \rightarrow \beta$ transformation temperature was reported to be 91 °C by [15Pos]. Apparently, this work was performed on the Cu-deficient composition. The $\alpha \rightarrow \beta$ transition temperature at Cu_2S composition increases with pressure, with an initial slope of 0.5 °C/kbar [70Cla].

Table 2 Solid Solubility of S in Cu

Temperature, °C	Composition, at.% S in Cu [59Oud](a) 99.999% Cu	OFHC Cu(b)	[46Sma](c)
1000	0.0140	0.0170	...
900	0.0052	0.0092	...
800	0.0018	0.0046	0.004
700	0.0006	0.0022	0.002
600	0.0002	0.0008	0.0004

(a) Radioactive tracer measurement. (b) Oxygen-free high conductivity Cu. (c) Electrical conductivity measurement.

Table 3 Homogeneity Ranges of α Chalcocite

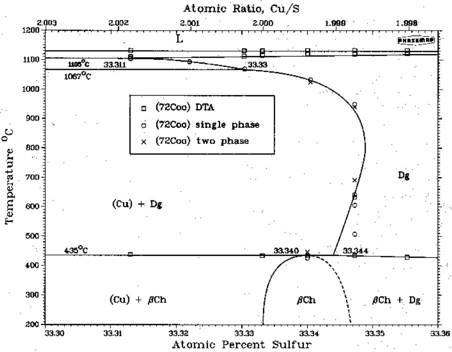
Cu/S ratio	Temperature, °C	Reference
Cu-deficient limit		
1.993 ± 0.002(a)	**90 ± 2**	[77Pot]
1.993 ± 0.002	93	[66Ros]
>1.999	25	[66Ros]
1.991	93	[74Dum]
1.992 to 1.994	$T_{\beta\rightarrow\alpha}$	[72Mat, 72Luq]
1.997	...	[72Coo]
1.987	89.5	[60Kul1]
Cu-rich limit		
2.000 ± 0.002(b)	All	[77Pot]

Note: Accepted values shown in boldface type.

(a) 33.41 ± 0.03 at.% S. (b) 33.33 ± 0.03 at.% S.

High-Chalcocite (βCh). The Cu-rich boundary of this phase lies at Cu_2S stoichiometry up to at least 300 °C, above which it grows deficient in Cu reaching the value Cu:S = 1.9994 (33.340 at.% S) at 435 °C [72Coo] (see Fig. 5). On the Cu-deficient side, the narrow phase field reaches 33.47 at.% S at 93 °C [77Pot, 66Ros] (see Fig. 2). With further increase in temperature, the phase field shrinks to Cu_2S composition between 180 °C [66Ros] and ~200 °C [74Dum]. According to [72Coo], the Cu-deficient boundary of βCh lies between Cu:S ratio of 1.9988 and 1.9994 (33.347 and 33.340 at.% S, respectively) at temperatures between 200 and 435 °C. A further extension of the boundary at still high temperatures to 33.67 at.% S at about 315 °C was reported by [74Dum] based on solid-electrolyte galvanic cell and electrical conductivity measurements (see Fig. 6). No other studies corroborating these observations are available, so the result must be

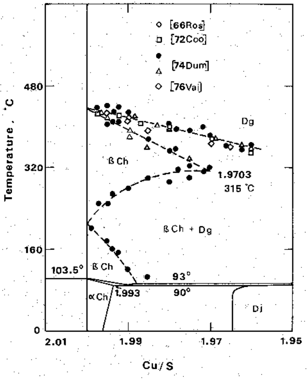
Fig. 5 Enlarged View of Cu-Saturated Boundary of Digenite



After Cook [72Coo].

D. J. Chakrabarti and D. E. Laughlin, 1983.

Fig. 6 S-Saturated Boundaries of β Chalcocite



After [74Dum]; ● = electrical conductivity data [74Dum], △ = emf data [74Dum].

D. J. Chakrabarti and D. E. Laughlin, 1983.

Table 4 Homogeneity Ranges of β Chalcocite

Cu/S ratio	Temperature, °C	Reference
Cu-deficient limit		
1.990 ± 0.005(a)	**90 ± 2**	[77Pot]
1.988 ± 0.005(b)	**93 ± 2**	[77Pot]
1.988 ± 0.002	~93	[66Ros, 74Dum]
1.990 ± 0.003 to 2.000	~105	[66Ros]
2.000	>180	[66Ros]
2.000	~220	[74Dum]
1.9703	315	[74Dum]
Cu-rich limit		
2.000	<300	[72Coo, 74Dum]
1.9994(c)	435	[72Coo]
1.99925	435	[74Dum]
1.9996 ± 0.0002	400	[57Wag]

Note: Accepted values shown in boldface type.

(a) 33.44 ± 0.06 at.% S, eutectoid. (b) 33.47 ± 0.06 at.% S, peritectoid. (c) 33.340 at.% S, peritectoid.

considered tentative. The βCh phase-field determinations according to several authors are presented in Table 4. The data for the Cu-rich and Cu-deficient boundaries are accepted from the works of Cook [72Coo] and Potter [77Pot], respectively.

The transformation of βCh to Dg is sluggish, as it involves the structural change from a hexagonal to a cubic close-packing of S atoms. Presence of oxygen further promotes the sluggishness [66Ros]. Accurate measurements by [72Coo], free from oxygen contamination effects, indicated βCh to undergo a peritectoid decomposition at 435 °C, at composition 33.34 at.% S, to form (Cu) and Dg of 33.344 at.% S.

Because the $\alpha \rightarrow \beta$ transformation of Ch does not alter the hexagonal close-packing of S atoms, the transformation is very rapid. However, the βCh could be metastably cooled 18 to 20 °C below this transformation temperature [73Mul, 77Pot].

Digenite ($Cu_{2-\delta}S$). This phase, synthesized at the composition Cu_9S_5 [36Rah] and identified with the mineral digenite [41Bue1, 42Bue2], was studied extensively and was believed to exist in two polymorphic forms. They were the high-digenite (Dg), which is the high-temperature polymorph, and its ordered modification at low temperatures, the so-called low-digenite (αDg). The X-ray superstructure reflections of αDg were noted to correspond to lattice multiplicities 5.0 to 6.0 of the Dg subcell [52Ruh, 58Dju, 58Don, 63Mor, 70Mor]. The $\alpha\text{Dg} \rightarrow \text{Dg}$ transition temperature was quoted between 73 and 83 °C depending on composition [63Moh, 63Mor], and the stability range of αDg at room temperature was quoted between $Cu_{1.79}S$ and $Cu_{1.765}S$ [66Ros, 77Pot]. However, subsequent works confirmed that αDg is not an equilibrium phase [69Mor], and that, at room temperature, a two-phase field of An and Dj exists at the supposed αDg composition [69Mor, 70Mor, 71Mor, 73Bar, 77Pot].

The homogeneity range of Dg was studied extensively by various methods at different temperature intervals extending over the entire phase field. Some of the methods used on the Cu-deficient boundary were: coulometric titration [60Weh], X-ray [57Ruh, 66Ros], specimen quenching [66Ros], vapor pressure [67Rau, 74Rau], emf [77Pot], and DTA [15Pos, 47Jen, 60Joh, 71Van, 72Coo]. On the Cu-rich side, in addition to the above techniques [57Ruh, 60Weh, 66Ros, 67Rau, 72Luq, 72Coo, 77Pot], the very sensitive technique involving metal whiskers was used [72Coo]. This enabled the delineation of the phase boundary between 435 and 1130 °C with extreme precision and consistency. Based on these works, an enlarged view of the Dg phase field is presented in Fig. 7. The Cu-rich boundary, based on [72Coo], is shown in Fig. 5. Selected data from different works are presented in Table 5.

Dg is stable over an extensive composition field between 33.31 at.% S (Cu:S = 2.002) at 1105 °C [72Coo] and 36.60 at.% S (Cu:S = 1.732) at 507 °C [66Ros, 77Pot]. It is stable from 1130 ± 2 °C, where it is formed by congruent reaction from the melt [15Pos, 47Jen, 72Coo] to 72 ± 3 °C, where it eutectoidally decomposes into Dj and An [77Pot]. The composition of the Cu-deficient boundary is nearly constant up to about 200 °C [57Ruh, 66Ros], whereas the Cu-rich boundary rapidly approaches the Cu_2S stoichiometry. The latter at still higher temperatures deviates from stoichiometry, first becoming Cu deficient and then, above ~1060 °C, enriched in Cu, approaching 33.31 at.% S at 1105 °C [72Coo]. Works of [74Rau] and [80Sha] agree qualitatively with the unusual shape of the boundary determined by [72Coo]. The congruent melting composition of Dg deviates from stoichiometry to Cu:S ratio of 1.994 (33.40 at.% S) [72Coo] (see Fig. 8).

Table 5 Selected Values for Solid Solution Limits of Digenite

Composition Cu/S ratio	at.% S	Temperature, °C	Reference
S-enriched limit			
1.94	34.0	1102	[72Coo]
1.884	34.67	1067	[72Coo]
1.869	34.86	1050	[72Coo]
1.798	35.74	951	[72Coo]
1.747	**36.40**	813	Selected
1.754	36.31	812	[72Coo]
1.748	36.39	721	[72Coo]
1.756	36.28	690	[66Ros]
1.743	36.46	640	[66Ros]
1.745	36.43	600	[66Ros]
1.73	36.63	507 ± 3	[66Ros]
1.718	36.79	507	[72Coo]
1.732	**36.60**	507 ± 2	[77Pot, 67Rau]
1.751	36.35	407	[66Ros]
1.760	36.23	305	[57Ruh]
1.766	36.15	200	[66Ros]
1.764	36.18	200	[77Pot]
1.764	36.18	150	[77Pot]
1.765	36.17	105	[77Pot]
1.765	**36.17**	75 ± 3	[77Pot]
Cu-enriched limit			
1.994	**33.40**	1130	[72Coo]
1.99875	33.3472	1120	[72Coo]
2.002	**33.31**	1104	[72Coo]
2.00025	**33.3306**	1067	[72Coo]
1.99935	33.3406	1028	[72Coo]
1.99875	33.3472	948	[72Coo]
1.99875	33.3472	640	[72Coo]
1.999	33.34	435	[72Coo]
1.944	33.97	300	[72Coo]
1.901	34.47	200	[66Ros]
1.902	34.46	200	[77Pot]
1.877	34.76	150	[77Pot]
1.874	34.79	150	[66Ros]
1.835	35.27	100	[77Pot]
1.833	**35.30**	93 ± 2	Selected
1.805	**35.65**	72 ± 3	[77Pot]

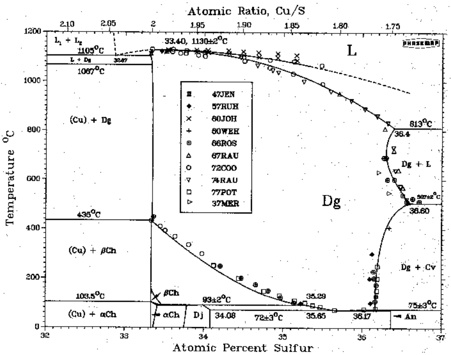
Note: Accepted compositions at invariant points shown in boldface type.

Djurleite ($Cu_{1.960 \pm 0.015}S$). This phase was first observed by Djurle [58Dju] in synthetic samples near the composition $Cu_{1.96}S$, but it also occurs in mineral deposits [62Mor, 62Ros]. Its X-ray pattern was confused with that of αCh, which led to the earlier erroneous conclusion that the αCh phase field extended from Cu_2S to $\sim Cu_{1.96}S$ at room temperature [41Bue, 52Ruh]. Single-phase Dj was synthesized by [66Ros] at the composition $Cu_{1.969 \pm 0.004}S$. Careful studies by [77Pot], however, revealed that Dj is not a line compound, but a solid solution with Cu:S ratio between 1.965 and 1.934 (33.73 to 34.08 at.% S).

The decomposition temperature of Dj was considered to lie between 90 and 93 ± 2 °C [66Ros, 72Coo, 72Luq], but the precise details of the equilibrium were not known until the definitive study of Potter [77Pot]. The results are shown in Fig. 9 and Tables 1 and 6.

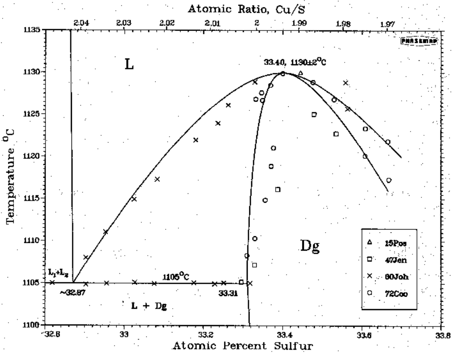
Anilite ($Cu_{1.75}S$). Although An was discovered first as a natural mineral by Morimoto *et al.* [69Mor], it also was synthesized in the laboratory [69Mor, 77Pot]. Thus, the doubts raised regarding the stability of this phase by [72Coo, 72Ric] are unwarranted. The formation temperature and composition of An obtained by [77Pot] on synthetic samples are 75 ± 3 °C and Cu/S = 1.750 ± 0.003 (36.36 at.% S), respectively. The solid solution field of An, if it exists, is very narrow and could be contained within the compositional uncertainty stated by [77Pot]. Other determinations of the compositional limits of An correspond to 1.75 by [70Mor], 1.75 ± 0.06 for the natural An by [73Gob] and 1.75 ± 0.05 by [71Cla2], in agreement with the accepted results of [77Pot].

Fig. 7 Homogeneity Range of Digenite



D. J. Chakrabarti and D. E. Laughlin, 1983.

Fig. 8 Enlarged View of Digenite Field near Congruent Point

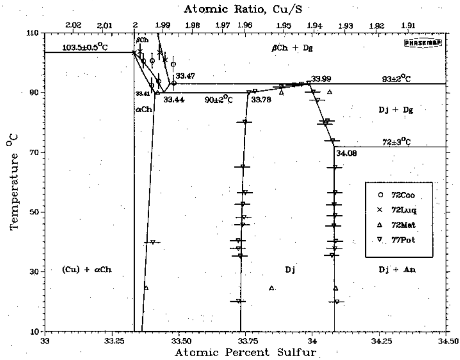


D. J. Chakrabarti and D. E. Laughlin, 1983.

αDg was mistaken for An as the room temperature equilibrium phase in the past for two reasons: (1) anilite transforms into αDg on grinding (such as during specimen preparation), and (2) the X-ray reflections from An often coincide with the positions of the supposed superstructure reflections of αDg.

Covellite (CuS) is essentially a stoichiometric compound with a very narrow solid solution field [72Mat]. The Cu:S ratio is determined to lie within ±0.01 [58Kul], ±0.002 [65Kul] of stoichiometry, based on lattice parameters, and ±0.001 [77Pot] on emf measurements, respectively. The peritectic decomposition temperature of Cv is at

Fig. 9 Enlarged View of Djurleite Field in Equilibrium with α and β Chalcocites



D. J. Chakrabarti and D. E. Laughlin, 1983.

Table 6 Composition and Upper Temperature Limits of Stability of Djurleite

Composition Cu/S ratio	at.% S	Temperature, °C	Reference	Method
1.965-1.934	33.73-34.08	93 ± 2	[77Pot]	a
1.96	33.8	≥75	[58Dju]	b
1.973-1.962	33.64-33.76	93 ± 2	[66Ros]	b
1.953-1.914	33.86-34.32	90	[72Luq]	c
1.955-1.935	33.84-34.07	···	[72Mat]	d
1.96	33.8	···	[69Cav]	a
1.93 ± 0.015	34.1 ± 0.17	91 ± 1	[72Coo]	e
1.97	33.7	···	[67Tak]	b

Note: From Potter [77Pot], with values reported by [72Luq] and [66Ros] modified by him.

(a) emf by aqueous electrolyte electrochemical cell. (b) High-temperature X-ray. (c) Differential thermal analysis. (d) emf by solid electrolyte electrochemical cell. (e) Disappearing phase in low-temperature equilibrium.

507 ± 2 °C, in good agreement among different measurements (see Table 1) [58Kul, 65Kul, 66Ros, 67Rau, 72Coo, 77Pot]. The cubic form of Cv reported by [70Kaz] has not been confirmed as an equilibrium phase in any other study.

Metastable Phases

A number of metastable phases occur in the Cu-S system because of the slow kinetics of those transformations that require structural alterations in the stacking sequence of the close-packed planes. The αCh, βCh, Dj, and Cv have structures with hexagonal close-packing of S atoms [32Oft, 63Bue, 63Wue, 67Tak, 71Eva], whereas Dg [63Mor] and An [69Mor, 70Mor] exhibit cubic close-packing of S atoms. Thus, transformations between phases with different stacking sequences are sluggish, often leading to the occurrence of metastable phases. Figure 10 maps the regions in which the various metastable phases have been observed experimentally.

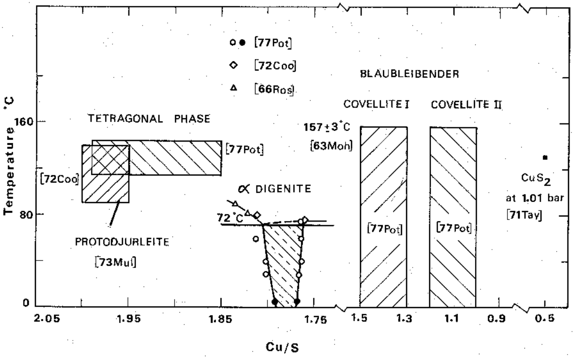
Low-Digenite (αDg). Digenite phase is not stable in the Cu-S binary system below 72 °C, where it occurs as a metastable phase. This phase is designated as αDg. However, αDg is stabilized at room temperature in the presence of Fe in the range of 0.4 to 1.6 at.%, together with 36.15 to 36.55 at.% S and the remainder Cu [71Mor].

Dg samples (of unspecified composition) brought down to 0 °C by rapid cooling (10 °C/min) were found to transform within a few hours, first to αDg and, in turn, to stable An [77Pot]. The degree of metastability of αDg varied with the composition in αDg and increased with the Cu content. For a $Cu_{1.80}S$ sample, the transformation of αDg to An in a rapidly cooled Dg sample occurred on prolonged holding (several months) at room temperature whereas, for the $Cu_{1.75}S$ sample, transformation required slight heating [70Mor].

αDg was found to be metastable with respect to An plus Dj by a free energy difference of 670 J/mol at 25 °C, and its limits at 25 °C were estimated to be between the Cu:S ratio of 1.790 and ~1.766 (35.84 to ~36.15 at.% S) by [77Pot], in reasonable agreement for the latter with [66Ros].

Tetragonal Phase. The tetragonal phase was recognized as a metastable polymorph of Dg by [58Dju]. Both [72Coo] and [72Luq], however, incorrectly identified the phase to be stable and indicated the homogeneity range to extend from $Cu_{1.96}S$ to $Cu_{2.00}S$ at 91 to 140 ± 5 °C [72Coo] and from $Cu_{1.89}S$ to $Cu_{2.00}$ at up to 175 °C [72Luq]. The presence

Fig. 10 Map of Metastable Regions in the Cu-S System



D. J. Chakrabarti and D. E. Laughlin, 1983.

of a tetragonal phase in natural deposits was reported by [71Cla1].

The tetragonal phase was recognized to be metastable at ambient pressure by [77Ros] and was confirmed to be formed at room temperature only under pressure (amounting to a few kilobars) by [70Ski]. The relatively small transformation pressure required explains the formation of this phase on grinding Ch [64Jan] and its observation in X-ray powder diffraction or metallographic studies. [77Pot] observed the formation of this phase in electrodes of electrochemical cells at Cu:S ratio of 1.85 to 1.99 and between 115 and 145 °C, but the resultant assemblage was always measured to have higher free energy than that for the stable phases βCh plus Dg. The rate of transformation to the stable phases is variable and is dependent on composition and temperature [66Ros].

Protodjurleite. A phase similar to Dj but at a higher Cu level, which varied between a Cu:S ratio of 1.961 at 93 °C and 1.970 at 75 °C, was observed to form when samples of composition (Cu/S) between 1.960 and 1.990 were cooled from above 100 °C [73Mul]. This phase was termed protodjurleite by [73Mul] and was considered to be a metastable Cu-rich form of Dj. This was confirmed by [77Pot] by emf measurements, showing that protodjurleite had a free energy approximately 250 J/mol of $Cu_{\sim 1.965}S$ greater than that of the equilibrium two-phase mixture of Dj plus αCh.

Blaubleibender Covellite (Bl-Cv). Blaubleibender or "blue remaining" covellite phase has somewhat different X-ray pattern and optical properties from Cv and contains 2 to 8 at.% more Cu than does Cv (Cu:S = 1.1 to 1.4). It is formed as a product of oxidation synthesis of Dg and Ch at room temperature [59Fre, 61Fre], or by heating Dg and Ch in excess S [63Moh]. The phase is metastable below 157 ± 3 °C with a narrow homogeneity range of 47.7 to 48.8 at.% Cu (Cu:S = 1.1 to 1.05) at 50 °C, according to [63Moh]. The phase is also present in abundance in natural minerals that were subjected to atmospheric oxidation and progressive degeneration to lower Cu-bearing sulfides [69Sil]. Two distinct types of Bl-Cv were recognized [63Gob] and, on the basis of X-ray and optical properties, their compositions in terms of Cu:S ratio are given as 1.1 ± 0.1 and 1.4 ± 0.1 by [77Pot] and as 1.1 to 1.2 and 1.1 to 1.4, respectively, by [71Moh].

Bl-Cv is absent in equilibrium structures [71Moh] and was confirmed by both the emf [77Pot] and E-pH measurements (i.e., measurements of the type shown in "Pourbaix" diagrams) [72Ric] to be metastable with respect to the equilibrium Cv plus An mixture. The reported similarity in the structures between Cu-rich Bl-Cv (Bl-Cv II) and Dg, and between S-rich Bl-Cv (Bl-Cv I) and Cv [77Pot], explains the preponderance of Bl-Cv in nonequilibrium phases. Because the Dg to Cv transition involves a change from cubic to hexagonal close-packing of S atoms, transitions to Bl-Cv phases (presumably with intermediate structures) are possibly favored kinetically.

CuS_2, synthesized first by [66Mun], is formed under high temperature and pressure. According to [71Tay], the phase is stable at 25 °C above 8 kbar, but can exist metastably for long periods of time, reportedly up to 4 months, at 130 °C and 1 atm.

Disputed Phases

Hexagonal-Tetragonal Phase. A "pseudohexagonal" [70Coo] tetragonal phase, with Cu:S ratio between 1.75 and 1.93, was reported by several workers [69Cav, 79Fla,

Table 7 Crystal Structure and Lattice Parameters of Equilibrium Phases

Phase	Approximate composition, at.% S	Pearson symbol	Space group	Prototype	Lattice parameters, nm a	b	c	Comment	Reference
(Cu)	~0	$cF4$	$Fm3m$	Cu	0.36147	···	···	(a)	[Landolt-Börnstein]
α chalcocite (αCu_2S)	~33.33	$mP144$ (?)	$P2_1/c$	···	1.5246 ± 0.0004	1.1884 ± 0.0002	1.3494 ± 0.0003	(b)	[71Eva]
β chalcocite (βCu_2S)	~33.3	$hP6$	$P6_3/mmc$(c)	$InNi_2$	0.395	···	0.675	(d)	[63Wue]
Djurleite ($Cu_{\sim 1.96}S$)	33.7-34.1(e)	$oP380$ (?)	$Pmnm$ $P2_1nm$ (?) $Pmn2_1$	···	2.695 ± 0.005	1.571 ± 0.003	1.356 ± 0.003	(f)	[67Tak]
Digenite ($Cu_{2-\delta}S$)	35.5-36.2(g)	$cF12$	$Fm3m$(h)	CaF_2	0.5567	···	···	(j)	[63Mor]
Anilite ($Cu_{1.75}S$)	36.36 ± 0.04	$oP44$ (?)	$Pnma$	···	0.789 ± 0.016	0.784 ± 0.016	1.101 ± 0.022	(k)	[69Mor, 70Kot]
Covellite (CuS)	50	$hP12$	$P6_3/mmc$(m)	CuS	0.3794 ± 0.0003	···	1.6332 ± 0.001	(n)	[58Dju]
(S)	~100	$oF128$	$Fddd$	αS	1.04646	1.28660	2.44860	(p, q, r)	[61Coo]
		$mP48$	$P2_1/a$	βS	1.092	1.098	1.104	(q, s, t)	[Pearson]
		$hR6$	$R3$	εS	0.646	···	···	(q, u, v)	[55Don]

(a) At 18 °C on Cu metal. (b) $\beta = 116.35 \pm 0.01°$. (c) From [63Bue]. (d) At 125 ± 5 °C on single crystal of natural chalcocite. (e) At 72 °C. (f) On single crystal of mineral from Neudorf, Germany. (g) At 80 °C. (h) From [63Mor]. (j) At 80 ± 3 °C on single crystal of mineral from Butte, MT. (k) On synthetic crystal. (m) From [32Oft]. (n) On synthetic sample. (p) On single crystal at room temperature. (q) On elemental S. (r) Stable form at room temperature and 1 atm. (s) $\beta = 83° 16'$. (t) Formed from melt by recrystallization at 1 atm. (u) $\alpha = 115° 18'$ for rhombohedral unit cell. (v) Recrystallized from cold toluene.

Table 8 Crystal Structure and Lattice Parameters of Metastable Phases

Phase	Approximate composition, at.% S (Cu/S)	Pearson symbol	Space group	Prototype	Lattice parameters, nm a	c	Comment	Reference
Protodjurleite	33.7⟨1.97⟩(75 °C) 33.8⟨1.96⟩(93 °C)	···	···	···	···	···	(a)	[73Mul]
Tetragonal	33.8 ⟨1.96⟩	$tP12$	$P4_32_12$	Ge III(H.P.)	0.39962	1.1287	···	[64Jan]
Hexagonal-tetragonal Cu_xS	34.1 to 36.4 ⟨1.93 to 1.75⟩	···	···	···	1.5475 ± 0.0001	1.3356 ± 0.0001	(b)	[70Coo]
Low Digenite (αDg)	35.84 to 36.15 ⟨1.790 to 1.766⟩ at 25 °C[77Pot]	···	$R\bar{3}m$	···	1.616	···	(c)	[58Don]
Blaubleibender covellite I	41.7 ± 1.7 ⟨1.4 ± 0.1⟩	···	···	···	···	···	(d)	[77Pot]
Blaubleibender covellite II	47.7 ± 2.3 ⟨1.1 ± 0.1⟩	···	···	···	···	···	(e)	[77Pot]
CuS_2	66.67 ⟨0.5⟩	···	$Pa3$ (?)(f)	···	0.57897 ± 0.00002	···	At 22 °C(g)	[71Tay]

(a) A Cu-rich form of djurleite. (b) Hexagonal or tetragonal; structure stabilized in presence of oxygen. (c) Rhombohedral, $\alpha = 13°56'$; on synthetic Cu_9S_5. (d) X-ray diffraction pattern similar to digenite [77Pot]. (e) X-ray diffraction pattern similar to covellite [77Pot]. (f) From [Landolt-Börnstein]. (g) Pseudocubic pyrite-like structure.

72Cla, 73Fla]. However, the phase could be formed by oxidation synthesis of Ch or Dg [72Coo] or by reacting An and Dg in the presence of oxygen at 60 °C [77Pot]. Thus, the phase is apparently stable in the Cu-S-O ternary system, although its occurrence as a metastable phase in the Cu-S binary system has not been confirmed [72Coo, 77Pot].

$Cu_{\sim 1.9}S$. The existence of a phase below 25 °C with a hexagonal structure and with a narrow homogeneity range near $Cu_{1.9}S$ was reported by [72Mat], based on electrochemical measurements, and by [64Eli], based on X-ray measurements. Both [72Coo] and [76Vai] failed to observe the phase, however. Also, the data by [72Mat] do not support the claimed existence of the phase $Cu_{1.9}S$ [77Pot], and the X-ray data by [64Eli] could be identified as a mixture of An and Dj [76Pot], the stable phases at room temperature. Apparently, the $Cu_{\sim 1.9}S$ phase does not exist in the Cu-S system.

Crystal Structures and Lattice Parameters

The crystal structure and accepted lattice parameters of equilibrium phases and component elements are presented in Table 7, and those for the metastable phases are presented in Table 8. For structural notation, the Pearson symbol [Pearson; 81Hub] is used and, in its absence, the corresponding crystal/Bravais lattice type is indicated.

β Chalcocite. Based on the studies at 112 °C on single crystals of natural chalcocite, the crystal structure of βCh is represented by hexagonal close-packing of S atoms having two formula units (Cu_2S) per unit cell [42Bue1, 42Bue2]. The four Cu atoms are distributed in the approximate ratios of 1.24 : 1.63 : 1.13 over the sites 2*b*, 4*f*, and 6*g* in the interstices between the S atoms, corresponding to three-fold, four-fold, and two-fold coordinations, respectively [63Bue]. The Cu atoms are in a highly mobile fluid-like state in the lattice, presumably because of their ability to assume tetrahedral, trigonal, or linear coordination [63Bue, 65Sad].

The lattice parameters of synthetic βCh [58Dju] and of the mineral chalcocite [42Bue1, 63Wue] are presented in Table 9. The results of [63Wue], based on the pure, single crystal of natural chalcocite, are accepted for Table 7.

α Chalcocite. The rapidity of transformation between αCh and βCh and the close similarity in their X-ray patterns led [42Bue1, 44Bue] to conclude the existence of a simple lattice periodicity relation between them and a small structural displacement on phase inversion. The αCh was considered to form a superstructure based on the basic structure of βCh, having the cph symmetry of S atoms, with the unit cell *A*-centered orthorhombic of 96 formula units (Cu_2S) and of space group $Ab2m$. According to [63Bue], the Cu atoms occupied the trigonal and tetrahedral sites and were less mobile than in the βCh because of the lower available thermal energy.

According to [71Eva], however, X-ray data from the above studies showed deviations from orthorhombic symmetry and, besides, αCh was often contaminated with orthorhombic Dj phase. Careful X-ray studies by these authors on a natural crystal fragment of αCh free of Dj indicated a monoclinic symmetry with 48 Cu_2S/cell and the space group $P2_1/c$, having the lattice parameters as indicated in Table 7. The present structure also displays hexagonal close-packing of S atoms, with the exception that the Cu atoms are in triangular coordination with respect to them.

Lattice parameter results from different works are presented in Table 10.

Table 9 Lattice Parameters of β Chalcocite (βCu_2S)

Reference	Lattice parameters, nm *a*	 *c*	Temperature, °C
[63Wuc](a) ..	0.395	0.675	125 ± 5
[42Bue1]	0.389 ± 0.004	0.668 ± 0.007	112
[58Dju](b) ...	0.3961 ± 0.0004	0.6722 ± 0.0007	152
	0.3981 ± 0.0004	0.6761 ± 0.0007	300
	0.4005 ± 0.0004	0.6806 ± 0.0007	460
[75Gor]	0.396	0.672	300 and 400

(a) On single crystal of natural chalcocite. (b) On powdered synthetic sample.

Digenite. The X-ray powder patterns of a synthetic Cu_9S_5 sample were indexed by [36Rah], based on the model of fcc close-packing of S atoms. The positions of the Cu atoms, however, could not be ascertained.

Investigation of single crystals of both synthetic and natural digenite samples by [63Mor] confirmed the fcc close-packing of S atoms and suggested the statistical distribution of 9/10 of the Cu atoms over 24 equivalent sites in each of the S tetrahedra. This amounts to 192 sites in a unit cell. The coordinates given were: $x = 0.310$, $y = 0.300$, $z = 0.290$ for 7.2 Cu and $x = y = z = 0$ for 4 S atoms. The unit cell of Dg contains 4 $Cu_{1.8}S$ [58Dju].

The lattice parameter versus composition and temperature values for Dg from different works are presented in Table 11. The accepted values in Table 7 are taken from [63Mor].

Djurleite. Because single-phase Dj is hard to find in nature or to form synthetically, most samples of Dj studied were mixed with other phases that produced complex X-ray patterns. A complex structure with low symmetry was proposed by [58Dju]. However, studies by [67Tak] on single-phase, synthetic Dj and on untwinned single crystals from massive natural Dj indicated the structure to be orthorhombic or "pseudoorthorhombic". The lattice parameters are presented in Table 7, as are the space groups compatible with the structure. The S atoms are in cph

Table 11 Lattice Parameter of Digenite ($Cu_{2-\delta}S$)

Deviation from stoichiometric composition, δ	Temperature, °C	Lattice parameter, nm *a*	Reference
0.20	80	0.5567(a)	[63Mor](b)
0	465	0.5725 ± 0.001	[58Dju](c)
	500	0.5735 ± 0.001	[58Dju](c)
	500, 700	0.573	[75Gor]
0.04	500	0.5707 ± 0.0006	[58Dju](d)
0.10	500	0.5681 ± 0.0006	[58Dju]
0.18	80	0.5577 ± 0.0006	[58Dju]
	152	0.5593 ± 0.0006	[58Dju]
	300	0.5610 ± 0.0006	[58Dju]
	500	0.5639 ± 0.0006	[58Dju]
0.20	170	0.5575 ± 0.0016	[36Rah]
0.158	100	0.55961	[66Ros](e)
0.232	100	0.55646	[66Ros](e)
0.102	200	0.56383	[66Ros](e)
0.232	200	0.55776	[66Ros](e)
0.043	350	0.56872	[66Ros](e)
0	450	0.57260	[66Ros](e)

(a) Av. 0.5570 ± 0.0005. (b) On single crystal of natural digenite from Butte, MT. (c) Reported for Cu_2S having fcc structure. (d) Reported for $Cu_{1.96}S$ having fcc structure. (e) Composition at digenite phase boundary based on synthetic and natural samples.

Table 10 Lattice Parameters of α Chalcocite (αCu_2S)

Reference	Lattice parameters, nm *a*	 *b*	 *c*
[71Eva](a)	1.5246 ± 0.0004	1.1884 ± 0.0002	1.3494 ± 0.0003
[36Rah]	1.18	2.69	1.34
[42Bue1]	1.190	2.728	1.341
[58Dju](b)	1.1881 ± 0.0004	2.7323 ± 0.0008	1.3491 ± 0.0004
[63Wil](c)	1.182(= 3*a*′)	2.700(= 4*b*′)	1.340(= 2 *c*′)
[70Coo]	1.1848 ± 0.0002	2.7330 ± 0.0005	1.3497 ± 0.0003

(a) Based on monoclinic symmetry; $\beta = 116.35° \pm 0.01$. (b) On powdered synthetic sample at room temperature. (c) *a*′, *b*′, *c*′ are subcell dimensions determined by electron diffraction on surface film.

Table 12 Lattice Parameters of Covellite (CuS)

Reference	Lattice parameters, nm a	c
[58Dju]	0.3794 ± 0.0003	1.6332 ± 0.001
[32Oft]	0.375	1.623
[54Ber]	0.3796	1.636
[76Pot, 76Eva]	0.37938	1.6341

Table 13 Subcell Edge Dimension of α Digenite

Cu/S ratio	Subcell edge dimension (a'), nm	Lattice multiplicity factor, N	Reference
1.75	0.5558	5.0	[70Mor]
1.76	0.5542	5.0	[58Don]
1.768	0.55575	5.0	[66Ros]
1.78	0.5564	5.0	[58Dju]
1.789	0.55684	5.0	[66Ros]
1.79	0.556	5.0	[63Mor]
1.75	0.55577	5.21	[71Mor]

arrangement and the unit cell content is $Cu_{252}S_{128}$, representing 128 formula units.

Anilite. The crystal structure is orthorhombic with the space group *Pnma*, in which the S atoms approximate the fcc arrangement and the Cu atoms are ordered in the interstices in tetrahedral and triangular coordination [69Mor, 70Kot]. The lattice parameters measured on synthetic crystals by the Weissenberg method by the above authors are presented in Table 7.

Covellite. The crystal structure of CuS, according to [32Oft], is hexagonal, with 6 CuS/cell and the atoms in the following positions:

2Cu in (*d*) at $\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$; 4 Cu in (*f*) at $\frac{1}{3}$, $\frac{2}{3}$, 0.107

2 S in (*c*) at $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$; 4 S in (*e*) at 0, 0, 0.0625

Studies on the single crystals of CuS from Leonard Mine, Montana by [54Ber] confirmed the above structure, except for the slight modification in the 4 S atom site (*e*) to 0, 0, 0.064. Lattice parameter results are presented in Table 12. Those given by [58Dju] were based on synthetic samples of defined composition and are accepted as representative in Table 7.

Metastable Phases

Low-Digenite (αDg). The crystal structure of αDg was thought to be a supercell of cubic symmetry, with the cell edge five times that of Dg [58Don, 70Mor]. The subcell edge dimension (a) varied with composition, from 0.5542 to 0.5568 nm, as shown in Table 13. The lattice multiplicity factor (N) varied with composition, from 5.0 at $Cu_{1.75}S$ to 6.0 at $Cu_{1.80}S$; see Table 14. All αDg in equilibrium with Cv were found to be the 5.2a type, and with Dg the 5.7a type [70Mor].

[58Don] ascribed the apparent cubic symmetry in αDg to the complex effects of twinning. He deduced the true symmetry from his X-ray data to be rhombohedral, with one Cu_9S_5 per unit cell. The lattice parameter results are presented in Table 8.

Tetragonal Phase. A tetragonal metastable modification of Dg having the lattice parameters, a = 0.4008 ± 0.002 nm and c = 1.1268 ± 0.0006 nm, at room temperature and the cell content of $4Cu_{1.96}S$ was reported by [58Dju]. The detailed results from the careful studies by [64Jan] are presented in Table 8. The structure consists of S atoms in a slightly deformed close-packed arrangement.

Table 14 Variation of N with Composition in α Digenite

Cu/S ratio	Lattice multiplicity factor, N
1.75	5.0
1.765	5.2
1.79	5.7
1.80	6.0

Note: According to Morimoto and Koto [70Mor].

Table 15 Lattice Parameter of CuS_2

Reference	Lattice parameter, nm a	Comment
[69Hin]	0.564	At 25 °C and 64 kbar
[66Mun]	0.5796	...
[71Tay]	0.57897 ± 0.00002	At 22 °C

Protodjurleite. No structure or lattice parameter data are available.

Blaubleibender Covellite. No lattice parameter data are available. According to [77Pot], the X-ray diffraction pattern of Bl-Cv I is similar to that of Cv, and of Bl-Cv II to that of Dg.

CuS_2. The lattice parameter determined by [66Mun] based on a cubic pyrite-type structure, space group $Pa3$, is in fair agreement with other reported results, as shown in Table 15. However, the presence of strong anisotropy in optical properties is indicative, according to [71Tay], of a "pseudocubic structure" having lower symmetry than that of pyrite. The accepted lattice parameter value (in Table 8) is taken from [71Tay], in view of their use of high-purity materials (99.99+ purity Cu and S) and of precise measurements.

Thermodynamics

Expressions for the standard Gibbs energy of formation of the Cu-S intermediate phases, derived from the emf measurements from 0 to 250 °C and from the Cu:S ratio 0.95 to 2.10 by Potter [77Pot], are presented in Tables 16 and 17 for the equilibrium and metastable phases, respectively. The values of standard Gibbs energy, enthalpy, and entropy of formation of αCh from calorimetric and other thermochemical measurements, and from third law evaluations of equilibrium data, are presented in Table 18. Also included in Table 18 are the selected values of ΔH^0 and ΔS^0 at 298 K from [74Mil] and [61Kel], respectively. The standard Gibbs energies of formation of βCh at two temperatures, of Dg at Cu-saturated composition and of Cv, together with the enthalpy of formation at 298.15 K, are presented in Tables 19, 20, and 21, respectively. The values of ΔH^0_{298} for Cv, estimated from Gibbs-Duhem integration of data by [60Weh], and from dissociation pressure data by the third law method [74Mil] are somewhat higher (55.64 and 57.32 kJ/mol of CuS, respectively) and are not included in Table 21. The results by [77Pot] for the differ-

Table 16 Standard Gibbs Energy and Enthalpy of Formation of Cu-S Intermediate Phases

Phase	Formula	Gibbs energy of formation (ΔG^0), J/mol	Gibbs energy of formation ($-\Delta G^0_{298.15}$), kJ/mol	Enthalpy of formation ($-\Delta H^0_{298.15}$), kJ/mol	Temperature range of ΔG^0, K
α Chalcocite	$Cu_{2.00}S$	$-80\,442 - 17.2\,T \pm 502$	85.57 ± 0.50	80.71 ± 0.50	273.15 to 376.65
β Chalcocite	$Cu_{2.00}S$	$-76\,927 - 25.15\,T - 0.004\,T^2 \pm 1255$	84.78	...	376.65 to 708.15
Djurleite	$Cu_{1.934}S$	$-79\,760 - 13.72\,T \pm 418$	83.85 ± 0.42	79.75 ± 0.42	273.15 to 345.15
Djurleite	$Cu_{1.965}S$	$-80\,241 - 14.77\,T \pm 418$	84.64 ± 0.42	80.25 ± 0.42	273.15 to 363.15
Anilite	$Cu_{1.75\pm0.003}S$	$-76\,019 - 8.45\,T \pm 293$	78.53 ± 0.4	76.02 ± 0.4	273.15 to 348.15
Covellite	CuS	$-53\,246 - 2.26\,T \pm 209$	53.93 ± 0.21	53.26 ± 0.21	273.15 to 388.36
Covellite	CuS	$-56\,684 + 6.64\,T \pm 209$	...	...	388.36 to 717.75

Note: From Potter [77Pot]. The elementary entity for "mol" used in this table is the corresponding formula unit of the respective compound.

Table 17 Standard Gibbs Energy and Enthalpy of Formation of Metastable Cu-S Compounds

Phase	Formula	Gibbs energy of formation (ΔG^0), J/mol	Gibbs energy of formation ($-\Delta G^0_{298.15}$), kJ/mol	Enthalpy of formation ($-\Delta H^0_{298.15}$), kJ/mol	Temperature range of ΔG^0, K
α Digenite	$Cu_{1.765\pm0.002}S$	$-76\,843 - 4.90\,T \pm 418$	78.32 ± 0.42	76.84	273.15 to 348.15
Blaubleibender covellite I	$Cu_{1.1\pm0.1}S$	$-56\,329 - 1.88\,T \pm 418$	56.90 ± 0.42	...	273.15 to 423.15
Blaubleibender covellite II	$Cu_{1.4\pm0.1}S$	$-61\,400 - 9.87\,T \pm 418$	64.35 ± 0.42	...	273.15 to 423.15

Note: From Potter [77Pot]. The elementary entity for "mol" used in this table is the corresponding formula unit of the respective compound.

Table 18 Standard Gibbs Energy and Enthalpy of Formation of α Chalcocite at 298.15 K

Standard Gibbs energy of formation ($-\Delta G^0$), kJ/mol	Enthalpy of formation ($-\Delta H^0$), kJ/mol	Entropy of formation (S^0), J/mol·K	Reference
85.56 ± 0.50	80.71 ± 0.50	...	[77Pot](a)
88.70 ± 2.1	83.55 ± 2.1	17.20	[53Bro](b)
84.10 ± 2.1	78.66 ± 2.1	...	[55Ric](b)
86.61 ± 2.1	80.12 ± 2.1	...	[68Rob]
86.19 ± 2.1	79.50 ± 2.1	...	[69Wag]
86.61 ± 2.1	80.75 ± 2.1	...	[71Eri]
87.28 ± 2.1	81.17 ± 1.3	...	[73Kin]
89.08	83.43	...	[50Sud1, 50Sud2](b)
86.19	79.5	...	[52NBS](b)
85.19	80.48	...	[50Tan]
90.37	75.73	...	[68Arn](b)
	82.01	...	[58Kub](c)
	79.71	...	[57Wag](a)
85.77 ± 1.3	79.50 ± 1.3	120.9 ± 2.1	[74Mil]
		120.9 ± 2.1	[61Kel]

Note: The term "mol" in this table stands for g-mole of Cu_2S.

(a) Electromotive force. (b) Vapor pressure for the reaction $2Cu(s) + H_2S \rightleftharpoons Cu_2S(s) + H_2$. (c) In the revised compilation [79Kub], the authors give the ΔH^0 and ΔS^0 values that were taken from [74Mil].

ent phases correspond closely to literature values and are of relatively higher precision.

The variation of heat capacity (C_p) with temperature for αCh, βCh, and Dg of Cu_2S composition, according to [60Kel], [69Kel], and [74Mil] and the corresponding free energy function, $(G^0 - H_{298})/T$, standard entropy, S^0, heat increments, $(H_T - H_{298})$, and equilibrium constant, log K, data for the reaction, $2\,Cu(s) + H_2S \rightleftharpoons Cu_2S(s) + H_2$, after Kellog [69Kel] are presented in Table 22. Heats of transition and heats of fusion for αCh and Dg phases are presented in Table 23. Variations of C_p with temperature for αCh, βCh, Dg, and Cv are presented in Table 24, after Mills [74Mil].

Table 19 Standard Gibbs Energy of Formation of β Chalcocite

Gibbs energy of formation ($-\Delta G$), kJ/mol of Cu_2S	Temperature, K	Reference
92.633 ± 1.3	573.15	[77Pot](a)
94.56 ± 4.2	573.15	[57Wag](b)
95.19 ± 4.2	573.15	[73Bar]
98.32 ± 4.2	708.15	[73Bar]
96.69 ± 1.3	708.15	[77Pot](a)

(a) Electromotive force with aqueous electrolyte. (b) Electromotive force with solid electrolyte.

Table 20 Standard Gibbs Energy of Formation of Digenite at Cu-Saturated Composition(a)

Gibbs energy of formation ($\Delta G^0_{Cu_2S}$), J/mol of Cu_2S	Temperature, K	Reference
$-128\,072 + 28.45\,T$	973 to 1273	[76Nag]
$-125\,194 + 25.83\,T$	800 to 1300	[68Arn]
$-128\,449 + 26.99\,T$	960 to 1180	[68Sod]
$-131\,461 + 30.75\,T$	800 to 1313	[55Ric]

(a) From reaction equilibrium for: $2\,Cu(s) + \frac{1}{2}S_2(g) \rightleftharpoons Cu_2S(s)$.

Table 21 Standard Gibbs Energy and Enthalpy of Formation of Covellite at 298.15 K

Gibbs energy of formation ($-\Delta G^0_{CuS}$), kJ/mol of CuS	Enthalpy of formation ($-\Delta H^0_{CuS}$), kJ/mol of CuS	Reference
49.20 ± 4.2	48.53 ± 4.2	[68Rob]
53.81 ± 2.1	53.14 ± 2.1	[69Wag]
52.97 ± 4.2	52.3 ± 4.2	[74Mil]
53.39 ± 2.1	52.7 ± 2.1	[73Kin]
53.94 ± 0.21	53.26 ± 0.21	[77Pot]
48.03	...	[72Mat]

For data on activity of S in Cu-S melts, refer to [79Lar, 80Sha] and the references therein, and to [74Mil] for other partial molar quantities.

Table 22 Thermodynamic Properties of Allotropes of Cu_2S

Temperature, K	Phase	Heat capacity(a) (C_p^0), J/mol · K	Entropy (S^0), J/mol · K	Free energy function ($(G^0-H_{298})/T$), J/mol · K	Heat increments ($H_T - H_{298}$), J/mol	Equilibrium constant(b), log K
298.15	αCh	76.3	118.38	118.38	0	15.627
376	αCh	79.6 (82.5)	...	...	...	...
376	βCh	90.0 (100.5)	...	...	...	...
400	βCh	90.0 (99.7)	152.26	122.06	12075	11.948
500	βCh	90.0 (96.7)	172.33	130.19	21071	9.837
600	βCh	90.0 (93.6)	188.73	138.62	30066	8.429
700	βCh	90.0 (90.5)	202.60	146.79	39062	7.418
708	βCh	90.0	...	...	...	...
708	Dg	84.9 (85.0)	...	...	...	...
800	Dg	84.9	215.17	154.63	48434	7.019
900	Dg	84.9	225.18	161.93	56928	6.048
1000	Dg	84.9	234.13	168.71	65421	5.277
1100	Dg	84.9	242.22	175.03	73915	4.649
1200	Dg	84.9	249.61	180.94	82408	4.131
1300	Dg	84.9	256.41	186.49	90902	3.694
1400	Dg	84.9 (85.0)	262.71	191.71	99395	3.322

Note: From Kellog [69Kel]. The elementary entity for "mol" used in this table is the corresponding formula unit of the respective phase. Reference state for Cu_2S: αCh at 298 K, βCh at 400 to 700 K, Dg at 800 to 1400 K. Reference state for Cu: crystal at all temperatures. Reference state for S: rhombohedral crystal at 298 K; liquid, 400 to 700 K; $S_2(g)$, 800 to 1400 K.

(a) C_p values in parentheses from [74Mil]. (b) Equilibrium constant for reaction: $2Cu(s) + H_2S \rightleftharpoons Cu_2S(s) + H_2$.

The thermodynamic properties of the Cu-S liquid were analyzed by Kellog [76Kel] and by Larrain *et al.* [79Lar] using an associated solution model that postulated the species Cu_2S and CuS in equilibrium in the liquid and a regular solution behavior. The model accounted for the boundaries of the metal-rich miscibility gap consistent with the phase diagram data, but the application was restricted to limited composition ranges. Sharma and Chang [80Sha] also applied the associated solution model, but assumed the existence of only Cu_2S in addition to Cu and S in the liquid. Based on the above model for the liquid, a statistical thermodynamic model for the digenite phase after [79Sha], and appropriate thermodynamic equations for other phases, the calculated phase boundaries were in good accord with known phase diagram data and thermodynamic properties of other phases (see Table 1). Several critical compositions not determined experimentally are accepted provisionally from the calculations of [80Sha] and are indicated within parentheses in Fig. 1.

Cited References

06Hey: E. Heyn and O. Bauer, "Copper and Sulfur", *Metallurgie, 3*, 73-82 (1906) in German. (Equi Diagram; Experimental)

13Bor: K. Bornemann and K. Wagenmann, "Electroconductivity of Metallic Alloys in Liquid State", *Ferrum, 11*, 276-282 (1913); *11*, 293-294 (1914), quoted in [Hansen]. (Equi Diagram; Experimental)

13Fri: K. Friedrich and M. Waehlert, "Investigation on Systems with Layer Formation. II. Copper-Copper Sulfide", *Metall. u. Erz., 10*, 976-979 (1913) in German. (Equi Diagram; Experimental)

15Pos: E. Posnjak, E. T. Allen, and H. E. Merwin, *Econ. Geol., 10*, 491-535 (1915); *Z. Anorg. Allg. Chem., 94*, 95-138 (1916) in German. (Equi Diagram; Experimental)

29Jou: J. G. Joukoff, "On the Solubility of Cu-Sulfides in Cu-S at High Temperatures", *Metall. u. Erz., 26*, 137-141 (1929) in German. (Equi Diagram; Experimental)

32Oft: I. Oftedal, "Crystal Structure of Covellite, CuS", *Z. Krist., 83*, 9-25 (1932) in German. (Crys Structure; Experimental)

***36Rah:** P. Rahlfs, "Cubic High Temperature Modifications of Sulfides, Selenides and Tellurides of Ag and of Univalent Cu", *Z. Phys. Chem., B31*, 157-194 (1936) in German. (Crys Structure; Experimental)

37Mer: H. E. Merwin and R. H. Lombard, "The System Cu-Fe-S", *Econ. Geol., 32*(2), 203-284 (1937). (Equi Diagram; Experimental)

38Smi: C. S. Smith, "Cu Alloys Containing S, Se and Te", *Trans. AIME, 128*, 325-336 (1938). (Equi Diagram; Experimental)

41Bue: N. W. Buerger, "The Chalcocite Problem", *Econ. Geol., 36*, 19-44 (1941). (Crys Structure; Experimental)

42Bue1: M. J. Buerger and N. W. Buerger, "Structural Relations Between High and Low Chalcocite", *Am. Miner., 27*, 216-217 (1942). (Crys Structure; Experimental)

42Bue2: N. W. Buerger, "X-ray Evidence of Existence of Mineral Digenite Cu_9S_5", *Am. Miner., 27*, 712-716 (1942). (Crys Structure; Experimental)

***44Bue:** M. J. Buerger and N. W. Buerger, "Low Chalcocite and High Chalcocite", *Am. Miner., 29*, 55-65 (1944). (Crys Structure; Experimental)

46Sma: J. S. Smart and A. A. Smith, "Effect of P, As, S and Se on Some Properties of High Purity Cu", *Trans. AIME, 166*, 144-155 (1946). (Equi Diagram; Experimental)

***47Jen:** E. Jensen, "Melting Relations of Chalcocite", *Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat.-Naturw. Kl., 6*, 1-14 (1947). (Equi Diagram; Experimental; #)

49Ued: R. Ueda, "X-ray and Thermal Studies of Phase Transformations of Cuprous Sulfide", *J. Phys. Soc. Jpn., 4*, 287-292 (1949). (Equi Diagram; Experimental)

50Sud1: K. Sudo, "The Equilibrium in Reduction of Solid Cuprous Sulfide by Hydrogen Gas", *Sci. Rep. Res. Inst., Tohoku Univ., A2*, 513-518 (1950). (Thermo; Experimental)

Table 23 Heats of Transition and Fusion for Allotropes of Cu_2S

Transition mode	Temperature, K	Enthalpy of transition ($-\Delta H_{Tr}$), J/mol	Entropy of transition ($-\Delta S_{Tr}$), J/mol · K	Enthalpy of fusion ($-\Delta H_{Fusion}$), J/mol	Reference
βCh + (Cu) → αCh	376	3849	10.25	···	[74Mil]
	376	3849			[60Kel]
(Cu) + Dg → βCh	717	1201	1.67	···	[74Mil]
	623	837			[60Kel]
	708	837			[69Kel]
L → Dg(s)	1402	···	···	9623 ± 2092	[74Mil]
				9623 ± 837	[55Ric]

Note: The term "mol" in this table stands for the g-mole of Cu_2S.

Table 24 Heat Capacity Variation with Temperature for Cu-S Intermediate Phases

Temperature, K	Phase	Heat capacity (C_p), J/mol·K
298 to 376	αCh	$52.84 + 78.74 \times 10^{-3}\ T$
376 to 717	βCh	$112.05 - 30.75 \times 10^{-3}\ T$
717 to 1400	Dg	85.02
298 to 1000	Cv	$44.35 + 11.05 \times 10^{-3}\ T$

Note: From [74Mil]. The term "mol" in this table stands for g-mole of the formula units of the respective phases.

50Sud2: K. Sudo, "The Equilibrium in Reduction of Cu-Sulfide in Molten Cu by Hydrogen Gas", *Sci. Rep. Res. Inst., Tohoku Univ., A2*, 519-530 (1950). (Thermo; Experimental)

50Tan: T. Tanaka, K. Watanabe, and J. Kurihara, "Physical Chemistry of Cu Metallurgy. II. Reduction Equilibria of Cuprous Sulfide and Hydrogen", *Mem. Fac. Eng., Hokkaido Univ., 8*(1), 14-22 (1950), quoted in [68Arn]. (Thermo; Experimental)

51Hir: E.J. Hirahara, "Physical Properties of Cuprous Sulfide Semiconductors", *J. Phys. Soc. Jpn., 6*, 422-427 (1951); *2*, 211-213 (1947). (Equi Diagram; Experimental)

51Sch: R. Schumann and O.W. Moles, "S Activities in Liquid Cu-Sulfide", *Trans. AIME, 191*, 235-241 (1951). (Equi Diagram, Thermo; Experimental)

52NBS: Results from Nat. Bur. Std., Washington, DC (1952), quoted in [53Bro]. (Thermo; Compilation)

52Ruh: W. Ruhl, Diplomarbeit, Univ. of Erlangen (Germany) (1952), quoted by [58Dju]. (Crys Structure; Experimental)

52Smi: D. Smith, Ph. D. thesis, M.I.T., MA, U.S.A. (1952), quoted in [60Joh]. (Equi Diagram; Experimental)

53Bro: A. A. Brooks, "Thermodynamic Study of the Equilibrium $2Cu(s) + H_2S(g) = Cu_2S(\gamma) + H_2(g)$", *Am. Chem. Soc. J., 75*, 2464-2467 (1953). (Thermo; Experimental)

54Ber: L.G. Berry, "Crystal Structure of Covellite, CuS, and Klockmannite, CuSe", *Am. Miner., 39*, 504-509 (1954). (Crys Structure; Experimental)

54Kri: W.A. Krivsky, Ph.D. thesis, M.I.T., MA, U.S.A. (1954), quoted in [60Joh]. (Equi Diagram; Experimental)

55Don: J.D.H. Donnay, "Lattice of Rhombohedral S", *Acta Cryst., 8*, 245 (1955). (Crys Structure; Experimental)

55Ric: F.D. Richardson and J.E. Antill, "Thermodynamic Properties of Cuprous Sulfide and Its Mixtures with Na-Sulfide", *Trans., Farad. Soc., 51*, 22-33 (1955). (Thermo; Experimental)

***57Ruh:** W. Ruhl and E. Saur, "X-ray Study and Phase Diagram of Cupric Sulfide–Cuprous Sulfide System", *Ber. Oberhess, Ges. Naturw. Heilk. Giessen, Naturw. Abt., 28*, 35-47 (1957) in German. (Equi Diagram, Crys Structure; Experimental; #)

57Wag: J.B. Wagner and C.J. Wagner, "Investigations on Cuprous Sulfide", *J. Chem. Phys., 26*, 1602-1606 (1957); *J. Electrochem. Soc., 104*, 509-511 (1957). (Thermo; Experimental)

***58Dju:** S. Djurle, "X-ray Study of Cu-S System", *Acta Chem. Scand., 12*, 1415-1426 (1958). (Crys Structure, Meta Phases; Experimental)

58Don: G. Donnay, J.H.D. Donnay, and G. Kullerud, "Crystal and Twin Structure of Digenite, Cu_9S_5", *Am. Miner., 43*, 228-242 (1958). (Crys Structure; Experimental)

58Kub: O. Kubaschewski and E.L. Evans, *Metallurgical Thermochemistry*, 3rd ed., Pergamon Press, New York (1958). (Thermo; Compilation)

58Kul: G. Kullerud, "The Cu-S System", *Carnegie Inst. Yearbook, 57*, 215-218 (1958); *56*, 195-197 (1957). (Equi Diagram; Experimental)

59Fre: G. Frenzel, "Idaite, a New Mineral, Natural Cu_5FeS_6", *Neues Jahrb. Miner. Abh., 93*, 87-132 (1959) in German. (Meta Phases; Experimental)

***59Oud:** J. Oudar, "Solubility of S in Cu at 600-1000°", *Compt. Rend., 249*, 259-261 (1959) in French. (Equi Diagram; Experimental)

***60Joh:** F. Johannsen and H. Vollmer, "Study of Copper-Copper Sulfide System", *Z. Erzbergbau. Metallhuettenwes., 13*, 313-322 (1960) in German. (Equi Diagram; Experimental; #)

60Kel: K.K. Kelly, "Data on Theoretical Metallurgy. XIII. High Temperature Heat Capacity and Entropy Data for Elements and Inorganic Compounds", U.S. Bur. Mines, Bull. 584 (1960). (Thermo; Compilation)

60Kul1: G. Kullerud, "The Cu-S System", *Carnegie Inst. Yearbook, 59*, 110-120 (1960). (Equi Diagram; Compilation)

60Kul2: G. Kullerud and R.A. Yund, "Cu-S System", *Geol. Soc. Am. Bull., 71*, 1911-1912 (1960). (Equi Diagram; Experimental)

60Weh: V. Wehefritz, "The System Cu-S", *Z. Phys. Chem. N.F., 26*, 339-359 (1960) in German. (Equi Diagram; Experimental)

61Coo: A.S. Cooper, W.L. Bond, and S.C. Abrahams, "Lattice and Molecular Constants in Orthorhombic S", *Acta Cryst.*, 14, 1008 (1961). (Crys Structure; Experimental)

61Fre: G. Frenzel, "The Cu Excess of 'Blue-Remaining' Covellite", *Neues Jahrb. Miner. Monatsh., 9*, 199-204 (1961) in German. (Meta Phases; Experimental)

61Kel: K.K. Kelley and E.G. King, "Data on Theoretical Metallurgy. XIV. Entropies of Elements and Inorganic Compounds", U.S. Bur. Mines, Bull. 592, 1-149 (1961). (Thermo; Compilation)

62Mor: N. Morimoto, "Djurleite, a New Cu-Sulfide Mineral", *Miner. J., 3*, 338-344 (1962). (Equi Diagram; Experimental)

62Ros: E.H. Roseboom, "Djurleite, $Cu_{1.96}S$, a New Mineral", *Am. Miner., 47*, 1181-1184 (1962). (Equi Diagram; Experimental)

63Bue: M.J. Buerger and B.J. Wuensch, "Distribution of Atoms in High Chalcocite, Cu_2S", *Science, 141*, 276-277 (1963). (Crys Structure; Experimental)

63Moh: G.H. Moh, "Low Temperature Sulfide Synthesis", *Carnegie Inst. Yearbook, 62*, 214-215 (1963); *63*, 208-209 (1964). (Meta Phases; Experimental)

63Mor: N. Morimoto and G. Kullerud, "Polymorphism in Digenite", *Am. Miner., 48*, 110-213 (1963). (Equi Diagram, Crys Structure; Experimental)

63Wil: H. Wilman, "Electron Diffraction Results on Thermal Transformations and Structures of Phases in Cu-S and Ag-S Systems", *Acta Cryst., 16*(2), A182-A183 (1963). (Crys Structure; Experimental)

63Wue: B.J. Wuensch and M.J. Buerger, "Crystal Structure of Chalcocite, Cu_2S", *Miner. Soc. Am. Spec.*, Paper 1, 164-170 (1963). (Crys Structure; Experimental)

64Eli: E.N. Eliseev, L.E. Rudenko, L.A. Sinev, B.L. Koshurinikov, and N.I. Solovov, "Polymorphism of Cu-Sulfides in System Cu_2S-$Cu_{1.85}S$", *Miner. Sb. L'vovsk, Gos. Univ., 18*(4), 385-400 (1964) in Russian. (Meta Phases; Experimental)

64Gat: G. Gattow and O. Rosenberg, "Copper-Sulfur Compounds of Type $CuS_{>1}$", *Naturwiss., 51*(9), 213 (1964) in German. (Equi Diagram; Experimental)

64Jan: A. Janosi, "Structure of Tetragonal Cuprous Sulfide", *Acta Cryst., 17*(3), 311-312 (1964) in French. (Crys Structure; Experimental)

65Kul: G. Kullerud, "Covellite Stability Relations in Cu-S System", *Freiber. Forschung., C186*, 145-160 (1965). (Equi Diagram; Experimental)

65Sad: R. Sadanaga, M. Ohmasa, and N. Morimoto, "Statistical Distribution of Cu Ions in Structure of β Chalcocite", *Miner. J.* (Tokyo), *4*(4), 275-290 (1965), reported in [71Eva]. (Crys Structure; Experimental)

66Mun: R. A. Munson, "Synthesis of Copper Sulfide", *Inorg. Chem., 5*(7), 1296-1297 (1966). (Meta Phases, Crys Structure, Pressure; Experimental)

***66Ros:** E. H. Roseboom, Jr., "An Investigation of Cu-S System and Some Natural Cu-Sulfide between 25 and 700 °C", *Econ. Geol., 61*, 641-672 (1966). (Equi Diagram, Meta Phases; Experimental; #)

67Rau: H. Rau, "Defect Equilibria in Cubic High Temperature Cu-Sulfide (Digenite)", *J. Phys. Chem. Solids, 28*, 903-916 (1967). (Equi Diagram, Thermo; Experimental; #)

67Tak: H. Takeda, J. D. H. Donnay, E. H. Roseboom, and D. E. Appleman, "Crystallography of Djurleite, $Cu_{1.97}S$", *Z. Krist., 125*, 404-413 (1967). (Crys Structure; Experimental)

68Arn: D. Arndt and E. Kordes, "Anomalies in Equilibrium of Reaction $[Cu_2S] + (H_2) \rightleftarrows 2[Cu] + (H_2S)$", *Z. Anorg. Allg. Chem., 359*, 1-13 (1968). (Thermo; Experimental)

68Rob: R. A. Robie and D. R. Waldbaum, "Thermodynamic Properties of Minerals and Related Substances at 298.15 K and One Atmosphere Pressure and at Higher Temperature", U. S. Geol. Surv. Bull., *1259*, 256 (1968). (Thermo; Compilation)

68Sod: J. Sodi and J. F. Elliott, "Free Energy of Formation of Re-Sulfide", *Trans. AIME, 242*(10), 2143-2145 (1968). (Thermo; Experimental)

69Cav: P. Cavallotti and G. Salvago, "Electrode Behavior of Cu-Sulfides in Aqueous Solutions", *Electrochim. Metall., 4*, 181-210 (1969), quoted in [77Pot]. (Meta Phases; Experimental)

69Hin: E. Hinze and A. Neuhaus, "Reflection Microscopic and X-ray Studies of Cuprous Sulfide, Cu-Selenide and Cu Telluride at Pressures up to 80 Kilobars", *Naturwiss., 56*(3), 136 (1969) in German. (Crys Structure; Experimental)

***69Kel:** H. H. Kellog, "Thermochemical Properties of the System Cu-S at Elevated Temperature", *Can. Met. Quart., 8*(1), 3-23 (1969). (Thermo; Experimental)

***69Mor:** N. Morimoto, K. Koto, and Y. Shimazaki, "Anilite, Cu_7S_4, a New Mineral", *Am. Miner., 54*, 1256-1268 (1969). (Equi Diagram, Crys Structure; Experimental; #)

69Sil: R. H. Sillitoe and A. H. Clark, "Cu and Cu-Fe Sulfides as Initial Products of Supergene Oxidation, Copiapo Mining District, Northern Chile", *Am. Miner., 54*, 1684-1710 (1969). (Meta Phases; Experimental)

69Wag: D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", U. S. Nat. Bur. Stand. Tech. Note 270-4, 141 (1969). (Thermo; Compilation)

70Cla: J. B. Clark and E. Rapoport, "Effect of Pressure on Solid-Solid Transitions in Some Ag and Cuprous Chalcogenides", *J. Phys. Chem. Solids, 31*, 247-254 (1970). (Equi Diagram, Pressure; Experimental)

70Coo: W. R. Cook, Jr., L. Shiozawa, and F. Augustine, "Relationship of Cu-Sulfide and Cd-Sulfide Phases", *J. Appl. Phys., 41*(7), 3058-3063 (1970). (Meta Phases, Crys Structure; Experimental)

70Fla: A. Flamini and O. Grubessi, "...Digenite, $Cu_{1.96}S$, Chalcocite", *Period. Miner.*, Spec. Vol., *39A*, 243-263 (1970) quoted in [77Pot]. (Meta Phases; Experimental)

70Kaz: M. M. Kazinets, "Structure of Some Phases of a Cu-S System", *Kristallogr., 14*(4), 704-706 (1970) in Russian; TR: *Sov. Phys.—Crystall., 14*(4), 599-600 (1970). (Crys Structure; Experimental)

70Kot: K. Koto and N. Morimoto, "Crystal Structure of Anilite", *Acta Cryst., B26*(7), 915-924 (1970). (Crys Structure; Experimental)

***70Mor:** N. Morimoto and K. Koto, "Phase Relations of Cu-S System at Low Temperatures: Stability of Anilite", *Am. Miner., 55*(1-2), 106-117 (1970). (Equi Diagram, Meta Phases, Crys Structure; Experimental)

70Ski: B. J. Skinner, "Stability of Tetragonal Polymorph of Cu(I) Sulfide", *Econ. Geol., 65*(6), 724-728 (1970). (Meta Phases, Pressure; Experimental)

70Vai: F. C. Vaissiere: thesis, Montpellier, France (1970), quoted in [74Dum]. (Equi Diagram; Experimental)

71Cla1: A. H. Clark and R. H. Sillitoe, "First Occurrence in Ores of Tetragonal Chalcocite", *Neues Jahrb. Miner. Monatsh, 2*, 418-424 (1971). (Meta Phases; Experimental)

71Cla2: A. H. Clark and R. H. Sillitoe, "Supergene Anilite from Mina Estrella (Salado), Atacama, Chile", *Neues Jahrb. Miner. Monatsh, 2*, 515-523 (1971). (Equi Diagram; Experimental)

71Eri: G. Eriksson, "Thermodynamic Studies of High Temperature Equilibrium: II. Calculation of Free Energy Function and Heat Content Function for Solid (Cu, S, O) Substances", *Acta Polytech. Scand., 99*, 19-32 (1971). (Thermo; Experimental)

***71Eva:** H. T. Evans, Jr., "Crystal Structure of Low Chalcocite", *Nat. Phys. Sci., 232*(29), 69-70 (1971). (Crys Structure; Experimental)

71Moh: G. H. Moh, "Blue-Remaining Covellite and Its Relations to Phases in S-rich Portion of Cu-S System at Low Temperatures", Miner. Soc. Jpn. Spec. Paper 1, 226-232 (1971). (Meta Phases; Experimental)

71Mor: N. Morimoto and A. Gyobu, "Composition and Stability of Digenite", *Am. Miner., 56*, 1189-1909 (1971). (Equi Diagram, Meta Phases, Crys Structure; Experimental; #)

71Tay: L. A. Taylor and G. Kullerud, "Pyrite Type Compounds", *Carnegie Inst. Wash. Yearbook, 69*, 322-325 (1971); *Neues Jahrb. Miner. Monatsh, 10*, 458-464 (1972). (Meta Phases, Crys Structure; Experimental)

71Van: A. V. Vanyukov, V. P. Bystrov, and V. A. Snurnikova, "Phase Equilibria in Cu-S System", *Tsvet. Metal., 44*(11), 11-15 (1971) in Russian; TR: *Sov. J. Non-Ferr. Met., 44*(11), 11-14 (1971). (Equi Diagram; Experimental)

72Cla: A. H. Clark, "Natural Occurrence of Hexagonal $Cu_{1.83}S$ in Rancagua, Chile", *Nature, 238*(86), 123-124 (1972). (Meta Phases; Experimental)

***72Coo:** W. R. Cook, Jr., "Phase Changes in Cu_2S as a Function of Temperature", Natl. Bur. Stds. (U.S.A.) Spec. Publ. 364, 703-712 (1972); Ph.D. thesis, Case Western Reserve University, Cleveland, OH; Gould Labs Univ. Microfilm Order No. 72-27 (1971). (Equi Diagram; Experimental; #)

72Luq: H. Luquet, F. Guastavino, J. Bougnot, and J. C. Vaissiere, "Study of Cu-S System between $Cu_{1.78}S$-$Cu_{2.1}S$ by Differential Thermal Analysis", *Mater. Res. Bull., 7*, 955-962 (1972) in French. (Equi Diagram, Meta Phases; Experimental)

72Mat: H. J. Mathieu and H. Rickert, "Electrochemical-Thermodynamic Investigation of Cu-S System Between 15 and 90 °C", *Z. Phys. Chem. N.F., 79*, 315-330 (1972) in German. (Thermo, Equi Diagram; Experimental)

72Ric: D. T. Rickard, "Covellite Formation in Low Temperature Aqueous Solutions", *Miner. Depos., 7*(2), 180-188 (1972); *Tscheermaks Miner. Petrog. Mitt., 19*(1), 60-75 (1973), quoted in [77Pot]. (Equi Diagram, Meta Phases; Experimental)

73Bar: P. B. Barton, Jr., "Solid Solutions in System Cu-Fe-S. Part I: The Cu-S and CuFe-S Joins", *Econ. Geol., 68*, 455-465 (1973). (Equi Diagram; Experimental)

73Fla: A. Flamini, G. Graziani, and O. Grubessi, "A New Synthetic Phase in Cu-S System", *Period. Miner., 42*, 257-265 (1973). (Meta Phases; Experimental)

73Gob: R. J. Goble and D. G. W. Smith, *Can. Miner., 12*, 95-103 (1973). (Equi Diagram, Meta Phases; Experimental)

73Kin: L. G. King, A. D. Mah, and L. B. Pankratz, "Thermodynamic Properties of Cu and Its Inorganic Compounds", *Intl. Copper Res. Assoc., Mon.*, No. 11, 257 (1973). (Thermo; Compilation)

73Mul: B. J. Mulder, "Protodjurleite, a Metastable Form of Cuprous Sulfide", *Krist. Tech., 8*(7), 825-832 (1973). (Meta Phases; Experimental)

74Bur: B.P. Burylev, N.N. Fedorova, and L.Sh. Tsemekhman, "Phase Diagrams of Cu-S, Cu-Se and Cu-Te Systems", *Zh. Neorg. Khim., 19*, 2283-2285 (1974) in Russian; TR: *Russ. J. Inorg. Chem., 19*(8), 1249-1250 (1974). (Equi Diagram; Experimental)

74Dum: A. Dumon, A. Lichanot, and S. Gromb, "Study of Cu-S Phase Diagram in Compositional Area $Cu_{2.000}S$-$Cu_{1.960}S$", *J. Chim. Phys., 71*(3), 407-414 (1974) in French. (Equi Diagram; Experimental; #)

74Mil: K.C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworths, London (1974). (Thermo; Compilation)

***74Rau:** H. Rau, "Homogeneity Range of Cubic High Temperature Cuprous Sulfide (Digenite)", *J. Phys. Chem. Solids, 35*, 1415-1424 (1974). (Equi Diagram, Thermo; Experimental; #)

75Gor: S.S. Gorelik, A.N. Dubrovina, R.Kh. Leksina, T. Turdaliev, and Yu.M. Ukrainskii, "Dilatometric and X-Ray Investigation of Copper Chalcogenides at 20-700 °C", *Izv. Akad. Nauk SSSR, Neorg. Mater., 11*(1), 28-32 (1975) in Russian; TR: *Inorg. Mater., 11*(1), 21-24 (1975). (Crys Structure; Experimental)

76Bal: C.W. Bale and J.M. Toguri, "Thermodynamics of Cu-S, Fe-S and Cu-Fe-S Systems", *Can. Met. Quart., 15*(4), 305-318 (1976). (Equi Diagram, Thermo; Experimental)

76Eva: H.T. Evans, Jr. and J.A. Konnert, "Crystal Structure Refinement of Covellite", *Am. Miner., 61*, 996-1000 (1976). (Crys Structure; Experimental)

***76Kel:** H.H. Kellog, "Thermochemical Modelling of Molten Sulfides", *Physical Chemistry in Metallurgy*, R.M. Fischer, R.A. Oriani, and E.T. Turkdogan, Ed., U.S. Steel Res. Lab., Monroeville, PA, 49 (1976). (Thermo; Experimental)

76Nag: M. Nagamori, "A Thermodynamic Study of Digenite Solid Solution ($Cu_{2-\delta}S$) at 600 to 1000 °C and a Statistical Thermodynamic Critique on General Nonstoichiometry", *Met. Trans., 7B*, 67-80 (1976). (Thermo; Experimental)

76Pot: R.W. Potter, II and H.T. Evans, Jr., "Definitive X-ray Powder Data for Covellite, Anilite, Djurleite and Chalcocite", *U.S. Geol. Survey J. Res., 4*, 205-212 (1976). (Crys Structure; Experimental)

76Vai: J.C. Vaissiere and F.M. Roche, "Contribution to Study of Phase Diagram of Cu_xS ($1.75 \le x \le 2$) Between 10 and 200 °C", *Mater. Res. Bull., 11*(7), 851-856 (1976). (Equi Diagram; Experimental)

***77Pot:** R.W. Potter, II, "An Electrochemical Investigation of the System Cu-S", *Econ. Geol., 72*(8), 1524-1542 (1977). (Equi Diagram, Meta Phases, Thermo; Experimental; #)

79Jud: V.P. Judin and E. Eerola, "Thermodynamics of Metallic Impurities in Cu-Saturated Cu-Sulfide Melts", *Scand. J. Metall., 8*, 128-132 (1979). (Thermo, Equi Diagram; Experimental; #)

79Kub: O. Kubaschewski and E.L. Evans, *Metallurgical Thermochemistry*, 5th ed., Pergamon Press, NY (1979). (Thermo; Compilation)

79Lar: J.M. Larrain, L.L. Sang, and H.H. Kellog, "Thermodynamic Properties of Cu-S Melts", *Can. Met. Quart., 18*, 395-400 (1979). (Thermo, Equi Diagram; Theory)

79Mou: M. Moulki and J. Osterwald, "Miscibility Gap between Liquid Cu and Liquid Cu-Sulfide", *Z. Metallkd., 70*(12), 808-810 (1979) in German. (Equi Diagram; Experimental)

79Sha: R.C. Sharma and Y.A. Chang, "A Thermodynamic Equation of State for Digenite, $Cu_{2-\delta}S$", *Chin. J. Mater. Sci., 11*(1), 58-62 (1979). (Thermo; Theory)

***80Sha:** R.C. Sharma and Y.A. Chang, "A Thermodynamic Analysis of Cu-S System", *Met Trans., 11B*, 575-583 (1980). (Thermo, Equi Diagram; Theory; #)

81BAP: *Bull. Alloy Phase Diagrams*, 2(1), 145-146 (1981), quoting melting points of elements on the 1968 temperature scale. (Equi Diagram; Compilation; #)

81Hub: C.R. Hubbard and D.L. Calvert, "The Pearson Symbol", *Bull. Alloy Phase Diagrams, 2*(2), 153-157 (1981). (Crys Structure; Review)

*Indicates key paper.
#Information from this paper used in drawing evaluated phase diagrams.

Cu-S evaluation contributed by **D.J. Chakrabarti** and **D.E. Laughlin,** Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213, USA. Work was supported by the International Copper Research Association, Inc., (INCRA) and the Department of Energy through the Joint Program on Critical Compilation of Physical and Chemical Data coordinated through the Office of Standard Reference Data (OSRD), National Bureau of Standards. Literature searched through 1980. Professor Laughlin is the ASM/NBS Data Program Category Editor for binary copper alloys.