The Cu-In (Copper-Indium) System

By P.R. Subramanian* and D.E. Laughlin
Carnegie-Mellon University

Equilibrium Diagram

The assessed Cu-In phase diagram is shown in Fig. 1. The equilibrium phases reported are: (1) the liquid, L; (2) the fcc terminal solid solution, (Cu) or liquid, L; (Cu) or α, with a maximum solid solubility of 10.9 at.% In; (3) the tetragonal solid solution, (In), with very little or no solubility of Cu in (In); (4) $A2$-type β, with a homogeneity range of 18.05 to 24.5 at.% In; (5) γ brass-type γ, with a homogeneity range of 27.7 to 31.3 at.% In; (6) triclinic δ, with a homogeneity range of 28.9 to 30.6 at.% In; (7) several intermediate phases in the composition range between ~34 and ~38 at.% In; (8) ψ, of unknown structure, occurring at ~40.6 at.% In and having a very narrow homogeneity range, and (9) monoclinic $Cu_{11}In_9$, occurring at ~45 at.% In.

The assessed phase diagram is somewhat similar to that reported by [Hansen], which was based on the investigations of [34Wei], [40Hum1], and [51Rey]. The present assessment, however, includes minor revisions in the reported invariant compositions and temperatures. [34Wei] had proposed the existence of a high-temperature phase ϵ in the range 30 to 32 at.% In. However, this phase is not shown in Fig. 1, in view of the high-temperature X-ray work of [47Hei], which showed that γ and ϵ are isostructural, and the metallographic investigation of [51Rey], which gave no evidence for the presence of this phase. The phase diagram in the region 34 to 38 at.% In is proposed on the basis of the work of [72Jai] and may need further revisions. All the data are plotted in Fig. 2, 3, and 4. The composite Cu-In phase diagram is shown in Fig. 1, where the melting points of Cu and In are accepted from [Melt] as 1084.87 and 156.634 °C, respectively.

Table 1 lists the various invariant reactions for the Cu-In system.

Liquidus

[34Wei] determined the liquidus curve across the entire composition field from the results of thermal analysis of 71 alloys. Subsequently, [51Rey] redetermined the liquidus from cooling curves of alloys in the range 26.3 to 34.8 at.% In. The liquidus data of [34Wei] and [51Rey] are listed in Table 2. [34Wei] observed a maximum at 29.1 at.% In and 685 °C, corresponding to the congruent melting of γ. On the other hand, [51Rey] reported the maximum to occur at 29.56 at.% In and 682.3 °C. The heat capacity data of [81Wal] placed the $\delta \leftrightarrow$ L transition temperature for a Cu-30 at.% In alloy at 687 °C. The assessed liquidus in Fig. 1 is based on the data of [34Wei], with the exception of the region between 25.5 and 35.4 at.% In, which is drawn from a combination of the data of [34Wei] and [51Rey]. The resulting maximum is located at ~29.35 at.% In and 684 °C.

(Cu) Terminal Solid Solution or α

From X-ray analysis, [34Wei] determined the maximum solid solubility of α to be ~11.63 at.% In at the eutectoid temperature of 574 °C. At the peritectic temperature, reported by [34Wei] to be 715 °C, the solubility was found to be ~9.5 at.% In. From metallographic investigations, [40Hum1] determined the $\alpha/\alpha + \beta$ phase boundary and reported the maximum solid solubility at 574 °C as 10.9 at.% In. Subsequent solubility determinations by [49Owe] and [53Jon] by the X-ray method revealed the maximum solid

* Present address: Universal Energy Systems, Inc., 4401 Dayton-Xenia Road, Dayton, Ohio 45432

Fig. 1 Assessed Cu-In Phase Diagram

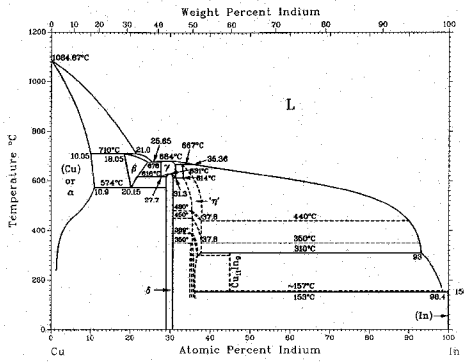

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Fig. 2 Cu-In (Cu) and β Phase Regions with Selected Data

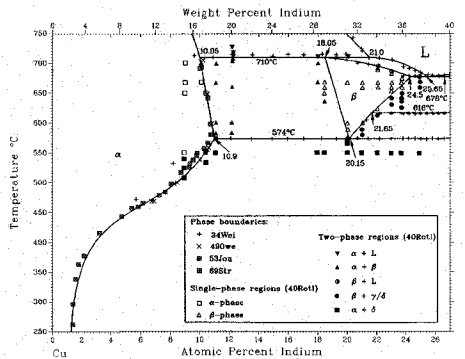

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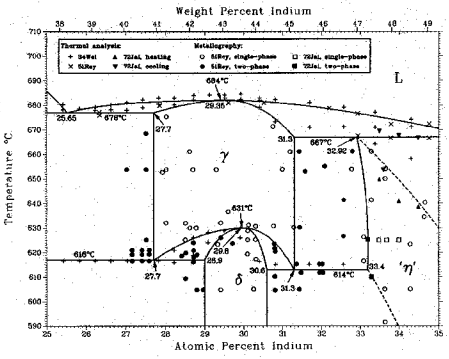
Fig. 3 Cu-In γ and δ Phase Fields with Selected Data



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solubility to occur at 10.85 at.% In and 575 °C. Moreover, the investigations of [53Jon] extended the $\alpha/\alpha + \delta$ boundary down to ~262 °C. More recent lattice parameter measurements by [69Str] gave the solubility of In in (Cu) as 10.4 at.% In at 650 °C, in good agreement with the earlier investigations.

Figure 2 shows the various data reported for the α phase boundary. As seen in Fig. 2, the $\alpha/\alpha + \delta$ phase boundaries of [49Owe] and [53Jon] are in essential agreement with one another, but show higher solubility than those of [34Wei] and [40Hum1]. Moreover, the data of [53Jon] show a change of slope in the α phase boundary at 470 °C. More recent differential scanning calorimetry (DSC) measurements in a two-phase $\alpha + \delta$ alloy of eutectoid composition by [78Kir] showed a discontinuity at 447 °C. This could be related to the change of slope observed in the α solubility curve, although there is a temperature difference of 23 °C between the two reported temperatures. Similarly, heat capacity measurements by [81Wal] for an $\alpha + \delta$ alloy with 20 at.% In showed a steep increase in heat capacity above 427 °C. The data of [53Jon], [78Kir], and [81Wal] therefore seem to suggest that there is a solid-state transformation in the temperature range between 427 and 470 °C. However, [88Cla] maintain that above and below 470 °C, the intermetallic in equilibrium with (Cu) was always the $\delta(Cu_7In_3)$ phase. These authors did not observe any other compound in the $\alpha + \delta$ two-phase field below 574 °C. Table 3 lists the assessed solid solubility of In in (Cu). The maximum solid solubility is accepted as 10.9 at.% In at the eutectoid temperature of 574 °C, and the solubility at the peritectic temperature of 710 °C is accepted as 10.05 at.% In.

β Phase

The $\beta/\beta + L$ solidus was determined by [34Wei] from thermal analysis of alloys between 18 and 25 at.% In. However, the $\alpha + \beta/\beta, \beta/\beta + \gamma$, and $\beta/\beta + \delta$ phase boundaries of [34Wei] were not determined precisely. From detailed metallographic investigations, [40Hum1] established the β phase boundaries. On the Cu-rich side, the limiting composition of β was determined by [40Hum1] to be 18.05 at.% In at the peritectic temperature of ~710 °C, in contrast to a value of 18.2 at.% In reported by [34Wei] at 715 °C. Both [34Wei] and [40Hum1] agree with regard to the eutectoid temperature of 574 °C. However, [34Wei] indicated the eutectoid composition to be stoichiometric at 20 at.% In, so that this phase was given the formula Cu_4In. On the other hand, [40Hum1] regarded β to be slightly off-stoichiometric toward the In-rich side. They determined the eutectoid composition to be 20.15 at.% In, on the basis of metallographic examination of alloys with 19.98 at.% In and 20.99 at.% In. On the In-rich side, [40Hum1] placed the limiting composition at 24.5 at.% In at the eutectic temperature of 676 °C whereas the measurements of [34Wei] indicated this composition to be 23.8 at.% In at 679 °C. Moreover, [40Hum1] pointed out that the composition of β on the In-rich side does not extend to 25 at.% In, which is the stoichiometric composition for the formula Cu_3In. On this basis,

Table 1 Reported Temperature-Invariant Reactions in the Cu-In System

Reaction	Compositions of the respective phases, at.% In			Temperature °C	Reaction type	Reference
L ⇔ (Cu)		0.0		1084.87	Melting point	[Melt]
L + (Cu) ⇔ β	20.8	9.5	18.3	715	Peritectic	[34Wei]
	~20.9	10.05	18.05	710	Peritectic	[40Hum1]
	21.0	10.05	18.05	710	Peritectic	Assessed
β ⇔ (Cu) + δ	20.0	11.63	28.7	574	Eutectoid	[34Wei]
	20.15	10.90	...	574	Eutectoid	[40Hum1]
	...	10.90	...	575	Eutectoid	[490we]
	...	10.85	...	575	Eutectoid	[53Jon]
	20.15	10.9	29.05	574	Eutectoid	Assessed
L ⇔ β + γ	25.8	23.8	27.2	679	Eutectic	[34Wei]
	...	24.5	...	676	Eutectic	[40Hum1]
	25.5	...	27.7	677	Eutectic	[51Rey]
	25.65	24.5	27.7	678	Eutectic	Assessed
L ⇔ γ		29.1		685	Congruent	[34Wei]
		29.56		682.3	Congruent	[51Rey]
		29.35		684	Congruent	Assessed
γ ⇔ δ		29.5		631	Congruent	[34Wei]
		30.15		630	Congruent	[51Rey]
		29.8		631	Congruent	Assessed
γ ⇔ β + δ	27.9	22.1	28.2	616	Eutectoid	[34Wei]
	27.7	21.8	28.9	617	Eutectoid	[51Rey]
	27.7	21.85	28.9	616	Eutectoid	Assessed
γ ⇔ δ + "η"	30.8	30.5	32.7	615	Eutectoid	[34Wei]
	31.3	30.6	33.1	613	Eutectoid	[51Rey]
	...	...	33.4	614	Eutectoid	[72Jai]
	31.3	30.6	33.4	614	Eutectoid	Assessed
L + γ ⇔ "η"	35.2	31.2	32.7	671	Peritectic	[34Wei]
	...	31.3	32.9	667	Peritectic	[51Rey]
	35.4	...	33.0	667	Peritectic	[72Jai]
	35.36	31.3	32.92	667	Peritectic	Assessed
L + "η" ⇔ ψ	93.0	38.7	40.6	310	Peritectic	[34Wei]
	...	37.8	...	310	Peritectic	[72Jai]
L + "η" ⇔ $Cu_{11}In_9$	93.0	37.8	45.0	310	Peritectic	Assessed
$Cu_{11}In_9$ ⇔ "η" + L	45.0	36.7	~98.3	~157	Eutectoid	Assessed
L ⇔ η + (In)	98.4	~36.7	~100	153	Eutectic	[34Wei], Assessed
L ⇔ (In)		100		156.634	Melting point	[Melt]

[40Hum2] indicated that β is based on a true 3:2 electron compound, wherein the phase boundaries are displaced from 25 at.% In toward the Cu-rich side because of size factor considerations. The accepted β phase boundaries are shown in Fig. 2.

γ Phase

[34Wei] showed γ to melt congruently at 29.1 at.% and 685 °C, whereas differential thermal analysis (DTA) studies of [51Rey] indicated the congruent melting point to lie at 682.3 °C and 29.56 at.% In. Both reports, however, indicated a very flat maximum. The liquidus and the solidus for γ (Fig. 3) are based on the data of [34Wei] and [51Rey]. Metallographic examinations of alloys in the γ phase field by [51Rey] revealed the limiting composition to be 27.7 at.% In on the Cu-rich side and 31.3 at.% In on the In-rich side. γ is a high-temperature phase, and at lower temperatures, it decomposes eutectoidally into β and δ at the Cu-rich end and into δ and "η'"* at the In-rich end. The eutectoid decomposition temperature on the Cu-rich side is accepted from [34Wei] as 616 °C. On the In-rich side, the eutectoid decomposition temperature was selected from [72Jai] as 614 °C, which is in good agreement with [34Wei] and [51Rey].

Both the β + γ/γ and γ/γ + η' boundaries were determined microscopically by [51Rey] to be composition dependent. Moreover, the γ/γ + η boundary of [51Rey] coincides with the ε/ε + η' boundary of [34Wei], which should really be the γ/γ + η boundary, because ε has been shown to be identical to γ [51Rey]. [51Rey] were

*[72Jai] showed that the phase field of η is comprised of at least 5 different phases. Until this region is fully resolved by further investigations, we prefer to label the phase field in quotes, i.e., "η".

Table 2 Experimental Cu-In Liquidus Data

Composition, at.% In	Temperature, °C	Composition, at.% In	Temperature, °C
[34Wei]		[34Wei], cont.	
0	1083	34.3	674
1.1	1066	35.2	672
2.0	1054	37.1	669
3.1	1041	38.0	662
4.6	1024	40.0	657
5.7	1008	41.4	654
7.0	991	42.5	647
8.2	972	45.0	643
9.5	950	47.0	634
10.8	928	50.0	627
12.1	895	53.0	619
13.5	873	56.0	611
14.9	845	59.0	602
15.9	823	62.0	595
17.0	801	65.0	588
18.2	778	68.0	580
19.2	758	72.0	564
19.9	739	75.0	556
20.7	719	77.0	545
21.4	711	80.0	532
22.2	706	82.0	520
23.0	700	84.0	509
23.8	694	86.0	488
24.2	692	88.0	473
24.6	689	90.0	447
25.0	686	92.0	375
25.4	682	94.0	295
25.8	679	96.0	253
26.2	680	98.0	182
26.6	681	100	155.4
27.0	682	[51Rey]	
27.4	683	26.32	678.0
27.8	684	27.84	681.0
28.2	685	29.56	682.3
28.7	685	30.52	682.0
29.1	685	32.21	679.0
29.5	685	32.94	676.8
29.9	685	33.80	672.7
30.4	684	34.75	671.3
30.8	683	[Melt]	
31.7	682	0	1084.87
32.6	679	100	156.634
33.4	677		

Note: Data are presented as published and not corrected to the 1968 temperature scale (IPTS-68).

Table 3 Assessed Solid Solubility of In in (Cu)

Temperature, °C	Solubility limit(a), at.% In	Temperature, °C	Solubility limit(a), at.% In
262	1.15	700	10.13
300	1.20	710	10.05
350	1.57	750	9.10
400	2.45	800	7.80
450	4.90	850	6.60
500	8.0	900	5.20
550	10.0	950	3.90
574	10.90	1000	2.50
600	10.76	1050	1.0
650	10.46		

(a) Numerical values of the solubility limits are from Fig. 1 and 2.

unable to retain the structure of γ by quenching, and this was confirmed by the more recent observations of [80Kim]. According to [51Hum], γ belongs to the family of electron compounds having the electron concentration 21:13, wherein the ideal composition is Cu_9In_4, but size factor considerations displace the composition of γ toward the Cu-rich direction.

δ Phase

The $\gamma \leftrightarrow \delta$ transformation temperature goes through a maximum at ~29.8 at.% In and 631 °C. On the Cu-rich side, the assessed phase boundaries are in good accord with those of [34Wei] and [51Rey]. However, on the In-rich side, the assessed phase boundaries are derived from the metallographic investigation of [51Rey], and the data of [34Wei] indicated lower transformation temperatures. Heat capacity measurements by [81Wal] indicated the $\delta \leftrightarrow \gamma$ transformation temperature for a 30 at.% In alloy to be 637 °C, which is slightly higher than that observed by [34Wei] and [51Rey]. Metallographic studies of [51Rey] showed that the boundaries of δ are composition independent below ~500 °C. The assessed δ phase stability region is shown in Fig. 3. According to [34Wei], δ is an electron compound with electron concentration 21:13 and with the ideal formula Cu_9In_4. However, more recent publications by [80Vro] and [80Kos] maintained that δ could best be described by the formula Cu_7In_3. The reason cited was that the composition corresponding to Cu_7In_3 lies well within the δ phase field and is close to the maximum in the $\delta \leftrightarrow \gamma$ transition temperature, whereas the formula of Cu_9In_4 assigned by earlier investigators lies outside the In-rich boundary of δ.

"η" Phase

The phase diagram of [34Wei] showed "η" to exist up to 389 °C and in the composition range between 33 and 39 at.% In, with vertical phase boundaries on either side. [34Wei] suggested a possible stoichiometry of Cu_2In. Above 389 °C, η was shown by [34Wei] to transform to the "η'" phase. On the Cu-rich side, the limiting composition of this phase was placed at ~32.7 at.% In at the peritectic temperature of 671 °C, whereas [51Rey] determined the limiting composition to be ~32.9 at.% In at 667 °C. [51Rey] observed that the η phase boundary on the Cu-rich side is vertical up to ~500 °C. However, [51Rey] did not study the "η" $\leftrightarrow$ "η'" transition. On the In-rich side, the "η'"/"η'" + L boundary was determined only partially by [34Wei] and [51Rey].

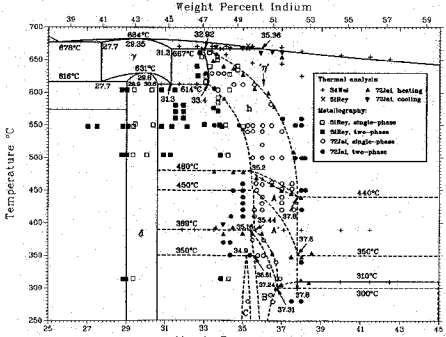
The more recently published data of [72Jai] drastically revised the phase relationships in the "η" phase field for temperatures below ~480 °C. According to [72Jai], the region ~33 to 38 at.% In comprises five different phases, which the authors labelled as "C," "B," "A'," "A," and "h," where the "h," "A," and "A'," phases occupy the "η'" region proposed by [34Wei]. According to [72Jai], the "h" (or $Cu_{2-\delta}In$) is stable between 440 and 660 °C. Between 350 and 480 °C and in the composition range 35.5 to 37.8 at.% In, "A" (or Cu_7In_4) is stable, and between 300 and 450 °C in alloys between 35.4 and 37.8 at.% In, "A'" exists. At temperatures below 389 °C, "B" was reported to exist in the composition range 35.6 to 37.2 at.% In. Finally, "C" was shown to form peritectoidally below 350 °C and in the composition range between 34.1 and 35.2 at.% In, although its formation was not observed by thermal analysis. Moreover, the equilibrium between "B" and "C" was not established clearly in metallographic studies. The limiting composition of "h" corresponds to ~33 at.% In at the peritectic temperature of 667 °C. Figure 4 shows the homogeneity ranges determined for the various phases by [72Jai] from DTA and metallographic investigations. Furthermore, results of X-ray investigations by [72Jai] are consistent with the homogeneity regions shown in Fig. 4.

Table 4 Cu-In Crystal Structure Data

Phase	Composition, at.% In	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(Cu) or α	0 to 10.9	*cF*4	$Fm\bar{3}m$	*A*1	Cu	[King1]
β	18.05 to 24.5	*cI*2	$Im\bar{3}m$	*A*2	W	[Pearson1]
γ	27.7 to 31.3	*cP*52	$P\bar{4}3m$	...	$InMn_3$?	[80Kim](a)
δ	29.05 to 30.6	*aP*40	P1	...	Cu_7In_3	(b)
"η"	32.92 to 37.8	*hP*4	$P6_3/mmc$	$B8_1$	NiAs	[42Lav, 43Mak, 72Jai]
		*hP*6	$P6_3/mmc$	$B8_2$	Ni_2In	[Pearson2]
	35.2 to 37.8	*o***	...	...	...	[72Jai]
$Cu_{11}In_9$	~44	*mC*20	*C*2/*m*	...	AlCu	[81Raj]
(In)	~100	*tI*2	*I*4/*mmm*	*A*6	In	[Massalski]

(a) Prototype proposed by [80Kim] (see text). **(b)** [68Gau, 80Vro, 80Kos, 80Kim]; also see [Pearson3].

Fig. 4 Cu-In Phase Diagram from 25 to 43 at. % In with Selected Data



Note: The phase field labeled "η" was shown by [72Jai] to be comprised of five different phases - h, A, A', B, and C.

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Table 5 Cu-In Lattice Parameter Data

Phase	Composition, at.% In	Lattice parameters, nm a	b	c	Comment	Reference
Cu	0	0.36146	...	...	At 25 °C	[King4]
β	20.50	0.30140	...	...	Quoted from 650 °C	[34Wei]
	18.64(a)	0.30461	...	...	At 672 °C	[41And]
γ	29.6	0.92503	...	...	At 650 °C	[51Rey]
δ	...	1.815	...	...	γ brass type	[39Wei]
	...	0.899	...	0.916	c/a = 1.02,(b)	[51Rey]
	...	1.007	0.911	0.672	α = 90°, β = 83°, γ = 107°,(c)	[68Gau]
	29.6	3.595	...	3.663	(d)	[72Fou]
	30.0	1.0071	0.9131	0.6726	α = 90.2°, β = 82.84°, γ = 106.82°	[80Vro]
	...	1.0071	0.9126	0.6724	α = 90.22°, β = 82.84°, γ = 106.81°	[80Kos]
	29.6(e)	1.000	0.910	0.672	α = 89.9°, β = 82.6°, γ = 106.9°	[80Kim]
"η"	35.6	0.4278	...	0.5249	c/a = 1.227	[42Lav]
	36.0	0.4289	...	0.5263	Quenched from 500 °C, c/a = 1.227	[43Mak]
	41.3(f)	0.4266	...	0.5282	c/a = 1.229	[43Mak]
	36.0	0.4280	...	0.5249	At 580 °C	[72Jai]
	37.0(g)	2.1375	0.7405	0.5218	At 440 °C	[72Jai]
	...	3.4194	0.7395	0.5262	At 350 °C	[72Jai]
$Cu_{11}In_9$	44.0	1.2814	0.4354	0.7353	At 280 °C, Monoclinic, β = 54.49°	[81Raj]
In	100	0.3253	...	0.4947	At 25 °C, c/a = 1.521	[Massalski]

(a) Cu-rich boundary. **(b)** Tetragonally deformed γ brass structure. **(c)** As reported in [80Vro]. **(d)** Superlattice structure based on a tetragonal cell. **(e)** Annealed at 575 °C and quenched to room temperature. **(f)** Appears to be in the (ψ) + (In) phase field. **(g)** Values for the orthorhombic structure reported by [72Jai].

From experimental emf vs temperature measurements for alloys between 32.0 and 36.5 at.% In, [76Vin] deduced that on the Cu-rich side, the boundary of "η" is 32.5 at.% In at 450 °C, whereas that of "η'" is ~35.8 at.% In at 500 °C. Although the boundary of the former phase is in good agreement with that of [72Jai], the boundary of the latter phase is richer in In by about 0.8 at.%. Also, [76Vin] observed a transition in the emf vs temperature data at ~460 °C, which they attributed (within limits of experimental error) to the "η" ⇔ "η'" transition, or according to the nomenclature of [72Jai], to the "A" ⇔ "h" transition. Phase boundaries reported by "η" by [78Gur] from diffusion measurements suggested a homogeneity range of ~5 to 6 at.% In, which is inconsistent with the other investigations. Heat capacity vs temperature measurements by [83Wal] on a Cu-35 at.% In alloy showed endotherms at 402 and 467 °C, which they associated with the "B" ⇔ "A'" transition and the combined effect of the "A'" ⇔ "A" and "A" ⇔ "h" transitions, respectively, of [72Jai]. They did not observe any thermal effect corresponding to the "C" ⇔ "B" transition.

Similarly, measurements on a 37.5 at.% In alloy showed peaks at 157, 317, and 362 °C. (The cause of the peak at 157 °C will be discussed below.) According to [81Wal], the peaks at 317 and 362 °C correspond to the transitions "B" ⇔ "A'" and "A'" ⇔ "A," respectively. However, no thermal effect was observed by [81Wal] corresponding to the "A" ⇔ "h" transition. From the results of [72Jai] and [81Wal], it can be concluded that the phase relationships in the "η" phase field are very complex and need further investigation. The recent compilation of [Pearson3] designated the composition of "η" as $Cu_{16}In_9$.

ψ Phase

[34Wei] proposed the peritectic formation of ψ from "η" and (In) at 310 °C and 40.6 at.% In. This phase was depicted to have a very narrow range of homogeneity. The occurrence of ψ has not been confirmed by subsequent investigations. Recent heat capacity vs temperature measurements on a Cu-37.5 at.% In alloy by [81Wal] indicated the presence of a thermal effect at 157 °C, which the authors attributed to the presence of free In in the alloy. From a comparison of the heat effect for the endotherm at 157 °C with the enthalpy of fusion of pure In, [81Wal] derived the amount of free In in the 37.5 at.% In alloy, from which the composition of the adjacent $Cu_{2-x}In$ ("B") was estimated to be 36.7 at.% In. This is in good agreement with the results of [72Jai], if one assumes that the boundary of "B" in the In-rich side is almost vertical below 200 °C. From these observations, [81Wal] concluded that ψ does not exist. As such, this phase is not shown in the assessed phase diagram. [81Raj] examined alloys in the vicinity of 44

Table 6 (Cu) Lattice Parameter Data

Composition, at.% In	Lattice parameter, nm	Comment	Composition, at.% In	Lattice parameter, nm	Comment
[34Wel]			**[Massalski], cont.**		
0	0.36153	(a)	5.2	0.36650	(a)
2.0	0.36330	(a)	8.2	0.36900	(a)
3.1	0.36450	(a)	10.8	0.37100	(a)
4.6	0.36580	(a)			
[47Owe]					
0	0.36147	(a)	10.9	0.37158	(a)
1.0	0.36241	(a)			
[52Owe]					
1.38	0.36274	At 18 °C, (b)	5.83	0.36694	At 18 °C, (b)
2.55	0.36383	At 18 °C, (b)	9.12	0.36997	At 18 °C, (b)
3.78	0.36501	At 18 °C, (b)	10.84	0.37147	At 18 °C, (b)
5.08	0.36624	At 18 °C, (b)			
[53Jon]					
0	0.36147	At 18 °C, (c)	8.49	0.36949	At 18 °C, (c)
2.0	0.36343	At 18 °C, (c)	9.0	0.36988	At 18 °C, (c)
4.01	0.36529	At 18 °C, (c)	9.82	0.37067	At 18 °C, (c)
5.87	0.36698	At 18 °C, (c)	10.50	0.37121	At 18 °C, (c)
7.61	0.36860	At 18 °C, (c)			
[56Stl]					
6.0	0.36701	At 18 °C	10.0	0.37077	At 18 °C
8.0	0.36876	At 18 °C			
[69Str]					
0	0.36149	25 °C	1.683	0.36297	Quenched from 650 °C
0.138	0.36160	Quenched from 650 °C	2.250	0.36359	Quenched from 650 °C
0.277	0.36169	Quenched from 650 °C	4.587	0.36575	Quenched from 650 °C
0.556	0.36203	Quenched from 650 °C	7.030	0.36800	Quenched from 650 °C
1.117	0.36251	Quenched from 650 °C	10.05	0.37072	Quenched from 650 °C
[69De]					
1.67	0.36306	At 30 °C	5.16	0.36762	At 236 °C
1.67	0.36338	At 80 °C	5.16	0.36825	At 324 °C
1.67	0.36378	At 144 °C	5.16	0.36888	At 416 °C
1.67	0.36436	At 236 °C	5.16	0.36950	At 505 °C
1.67	0.36492	At 324 °C	6.19	0.36727	At 30 °C
1.67	0.36552	At 416 °C	6.19	0.36763	At 80 °C
1.67	0.36611	At 505 °C	6.19	0.36809	At 144 °C
5.16	0.36626	At 30 °C	6.19	0.36860	At 212 °C
5.16	0.36658	At 80 °C	6.19	0.36924	At 300 °C
5.16	0.36700	At 144 °C	6.19	0.36963	At 350 °C
[75Cha]					
4.0	0.36525	(a)	7.0	0.36800	(a)
[Massalski]					
10	0.37080	(a)	0	0.36146	At 25 °C

(a) Annealing temperature, 650 °C. **(b)** Annealing temperature, 600 to 700 °C. **(c)** Annealing temperature, 500 to 600 °C.

at.% In after annealing at 1100 °C, followed by quenching and reannealing at 280 °C. The results showed the presence of a homogeneous single-phase region, and [81Raj] assigned the stoichiometry $Cu_{11}In_9$ to this phase. From the heat capacity measurements of [81Wal], it is evident that $Cu_{11}In_9$ should be a high-temperature phase and that its lower limit of existence should lie at temperatures greater than 157 °C.

Fig. 5 Variation of the Lattice Parameter of (Cu) with Composition

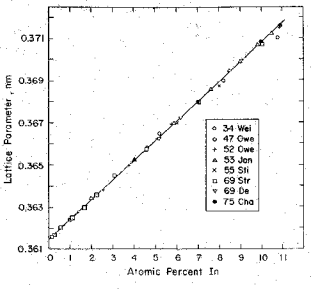

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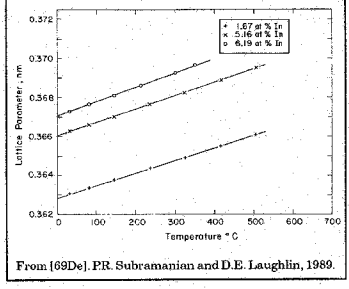
Fig. 6 Temperature Dependence of the Lattice Parameter of (Cu) at Various Compositions



From [69De]. P.R. Subramanian and D.E. Laughlin, 1989.

Crystal Structures and Lattice Parameters

Table 4 summarizes the crystal structures reported for the Cu-In system, and the lattice parameters are listed in Table 5. Table 6 lists lattice parameter data for (Cu) as reported by several investigators.

(Cu) Terminal Solid Solution

Figure 5 shows the composition dependence of the lattice parameters of (Cu), measured by [34Wei], [47Owe], [52Owe], [53Jon], [55Sti], [69Str], [69De], and [75Cha]. The trend shows that the lattice parameters of (Cu) are in accord with Vegard's law. [69Str] described the composition dependence of the lattice parameters of (Cu) (or α) through the following equation:

$$a(\alpha) = 0.36149 + 9.1 \times 10^{-4} X_{In} \text{ nm}$$

where X is the atomic percent of In. In the present evaluation, the data of Fig. 5 were fitted to yield the expression:

$$a(\alpha) = 0.36146 + 9.313 \times 10^{-4} X_{In} \text{ nm}$$

[69De] measured the temperature dependence of the lattice parameters of (Cu) for alloys with 1.67, 5.16, and 6.19 at.% In in the temperature range 30 to 505 °C. The resulting data (Fig. 6) show a linear temperature dependence. Also, the data for 1.67 and 5.16 at.% In were fitted by [69De] to give the following equations:

Cu-1.67 at.% In: $a_T = 0.362888 + 6.068 \times 10^{-6} T + 5.473 \times 10^{-10} T^2 + 1.485 \times 10^{-13} T^3$

and

Table 7 Atomic Positions Reported for Cu-In γ Structure

Atom	Wyckoff notation	x	z
Cu	4(e) xxx	0.096	...
Cu	4(e) xxx	0.600	...
Cu	4(e) xxx	−0.165	...
Cu	4(e) xxx	0.325	...
4Cu+2In	6(f) 00z	...	0.361
4Cu+2In	6(g) xxz	0.5	0.858
Cu	12(i) xxz	0.311	0.036
Cu	12(i) xxz	0.806	0.542

From [80Kim].

Cu-5.16 at.% In: $a_T = 0.366071 + 6.323 \times 10^{-6} T + 12.302 \times 10^{-10} T^2 - 4.219 \times 10^{-13} T^3$

where a_T is the lattice parameter in nm at the temperature T in °C. Thermal expansion coefficients, determined by [69De] from the temperature dependence of the lattice parameters of (Cu), show small increases with increasing temperature and increasing In concentration.

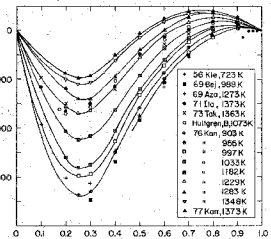
β

High-temperature β belongs to the class of electron compounds with valence electron concentration 3:2 and has the $A2$, W-type bcc structure. Lattice parameters reported for this phase by [34Wei] and [41And] are included in Table 5.

γ

Identified by [47Hel] and [51Rey] to be of the complex cubic γ brass structure, γ was reported by [51Rey] to have a lattice parameter of 0.92503 nm for a 29.6 at.% In γ phase alloy. No other lattice parameter reports were found in the literature. According to [51Hum],

Fig. 7 Enthalpy of Mixing of Liquid Cu-In at Various Compositions and Temperatures



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this phase is based on a distorted modification of the normal γ brass structure. From a reevaluation of previously published X-ray intensity data for γ from [51Rey], [80Kim] concluded that the structure of this phase is in accord with calculations for a model structure with a P cell with space group $P\bar{4}3m$. Moreover, the In and Cu atoms were reported by [80Kim] to follow the $InMn_3$ type of ordering. The various positions of the atoms in this new structure are shown in Table 7 [80Kim].

δ

The structure of δ has been the subject of numerous investigations. Publications by [34Wei] and [39Wei] reported that this phase has the complex cubic γ brass structure. [47Hel] reported δ to be a superstructure based on NiAs-type, hexagonal structure. Subsequently, [51Rey] indicated that the structure of this phase is consistent with a tetragonally deformed γ brass structure. Selected area diffraction studies of [63Cor] confirmed the presence of the superlattice structure reported by [47Hel], as well as a tetragonally deformed unit cell corresponding to the structure proposed by [51Rey]. Based on powder and single-crystal X-ray diffraction data, [68Gau] concluded that δ has a triclinic cell and reported lattice parameters for this phase.

Although X-ray and electron diffraction studies of [72Fou] confirmed the observations of [63Cor], lattice parameters reported for the tetragonal structure are much larger than the values reported by [51Rey]. More recent single-crystal X-ray investigations of [80Vro], [80Kos], and [80Kim] showed that δ has a triclinic structure, confirming the observations of [68Gau]. Moreover, lattice parameters reported for the triclinic cell by these investigators are in excellent agreement with the results of [68Gau]. However, [80Kim] pointed out that the structure of δ closely resembles the tetragonally deformed γ brass structure, as well as the partially filled NiAs-type structure with $c/a = 1.225$ or the Ni_2In structure.

According to [80Kim], the triclinic distortion of δ might be due to the largely disparate atomic radius ratio ($R_{In}/R_{Cu} = 1.30$), resulting in a lower symmetry to improve the packing efficiency. However, increasing the temperature would cause δ to revert to the cubic symmetry γ, due to larger thermal vibrations. [80Kos] and [80Vro] observed that the presence of pseudosymmetry in δ make its structure determination very difficult, and that the diffraction pattern for this phase could also be indexed on the basis of a pseudocubic cell with a lattice parameter of 0.9058 nm [80Vro] or 0.887 nm [80Kos]. Orientation relationships between (Cu) and the pseudocubic δ were determined by [80Vro] to obey the classical Kudjumov-Sachs relationship. Additionally, [80Vro] found that δ is twinned, resulting in the following crystallographic relationship between (Cu) and the twinned δ_1, and δ_2 phases:

$$(\bar{1}51)_{\delta_1} \,||\, (110)_{\alpha'}\ (10\bar{4})_{\delta_1} \,||\, (111)_{\alpha}$$

and

$$(\bar{1}51)_{\delta_2} \,||\, (110)_{\alpha'}\ (104)_{\delta_2} \,||\, (111)_{\alpha}$$

Structure analysis by [80Kos] showed δ to consist of In and some Cu atoms arranged in layers parallel to the $(1\bar{3}0)$ direction and with planes of Cu atoms between these mixed layers. The resulting space group was reported by [80Kos] to be $P\bar{1}$. The Pearson symbol for this structure if $aP40$ [Pearson3].

"η"

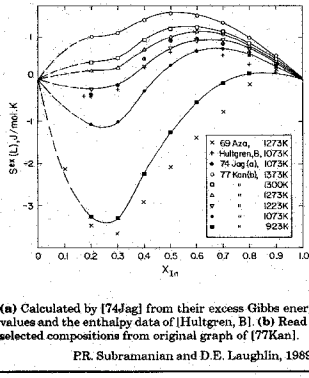
Early reports by [42Lav] and [43Mak] indicated that "η" is isotypic with the $B8_17$NiAs-type structure. Subsequently, the compilation by [Pearson2] reported that "η" has a partially filled $B8_{23}Ni_2In$-type structure. The more recent crystallographic investigation of [72Jai] revealed that the $Cu_{2-x}In$ phase with NiAs-type structure is stable only between 440 and 660 °C. In alloys between 35.5 and 37.8 at.% In and in the temperature range between 350 and 480 °C, [72Jai] reported the existence of the phase $Cu_{2-x}In$ ("A") or Cu_7In_4 with orthorhombic symmetry. However, the X-ray pattern of a 36 at.% In alloy that had been annealed at 580 °C in the "A" phase region revealed a hexagonal structure with lattice parameters in good agreement with the report of [34Wei]. In alloys between 35.4 and 37.8 at.% In and in the temperature range 300 to 450 °C, the phase $Cu_{2-x}In$ ("A") was reported to be present. Domain structures were observed in metallographs of alloys in the "A" and "A'" phase field. Although the X-ray patterns of "A" and "A'" were observed to be similar, [72Jai] reported visible differences in the location of the superstructure lines. [72Jai] did not determine the crystal structures of the $Cu_{2-x}In$ (C) and $Cu_{2-x}In$ (B) phases. However,

the authors indicated that "B" is completely ordered, whereas "A" and "A'" show some disorder. Further investigations are required to clarify the crystallographic features of the various phases in the "η" phase field.

$Cu_{11}In_9$

According to [81Raj], $Cu_{11}In_9$ has a monoclinic end-centered structure, isotypical with AlCu, whose structure was determined by [72Elb]. The resulting structure was reported to have a space group symmetry $C2/m$. [81Raj] showed that the monoclinic structure of $Cu_{11}In_9$ can be derived from the NiAs-type cell, wherein the face diagonal of the NiAs cell forms the a axis of the monoclinic cell, and the c axis of the monoclinic cell is contracted with respect to the original NiAs cell as a result of vacancies.

Fig. 8 Excess Entropy of Mixing of Liquid Cu-In at Various Compositions and Temperatures



(a) Calculated by [74Jag] from their excess Gibbs energy values and the enthalpy data of [Hultgren, B]. **(b)** Read at selected compositions from original graph of [77Kan].

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Thermodynamics

Liquid

Thermodynamic properties of liquid Cu-In alloys were determined by calorimetry [56Kle, 69Bej, 71Ita, 73Tak, 75Ita, 76Kan], emf measurements [69Aza, 74Jag, 77Kan], chemical equilibrium study [73Jac], and theory [73Tak].

[Hultgren,B] assessed the various thermodynamic properties of liquid Cu-In alloys from experimental data up to 1969. Figure 7 shows data for the enthalpy of mixing ($\Delta_{mix}H$) from [56Kle], [69Bej], [69Aza], [71Ita], [73Tak], and [77Kan], along with the selected values of [Hultgren,B]. [71Ita] fitted their experimental enthalpy data to the following equations:

10.4 to 50.6 at.% In: $H(L) = X(1-X)$
$[-31\,920 + 55\,700\,X]$

and

50.6 to 90.6 at.% In: $H(L) = X(1-X)$
$[-21\,030 + 42\,910\,X$
$- 17\,280\,X^2]$

where X is the atomic fraction of In.

The more recent work [75Ita] by the same authors showed enthalpy values that are in good accord with their earlier report [71Ita]. Theoretical calculations of the enthalpy of mixing of liquid Cu-In by [73Tak] are in excellent agreement with their experimental data at 1363 K. [76Kan] determined the enthalpy of formation of liquid Cu-In alloys in the temperature range 900 to 1350 K. Their enthalpy data show a strong temperature dependence, as seen in Fig. 7. Moreover, the values

Table 8 Coefficients to Determine Temperature Dependence of the Enthalpies (H(L)) and Excess Entropies (S^{ex}(L)) of Mixing of Liquid Cu-In Alloys at Various Compositions

Composition, at.% In	For $H(L) = A + BT$(a) Coefficients		For $S^{ex}(L) = C + DT$(b) Coefficients	
	$-A$	B	$-C$	$D \times 10^3$
0.20	16 490	10.80	11.25	9.00
0.25	17 440	11.31	...	...
0.30	17 030	11.05	11.51	9.28
0.40	13 760	9.22	8.93	7.60
0.50	10 000	7.16	6.39	5.85
0.60	6 640	5.17	4.20	4.20
0.70	4 124	3.60	2.63	2.91
0.80	2 120	2.15	1.41	1.76
0.90	654	0.866	0.60	0.82

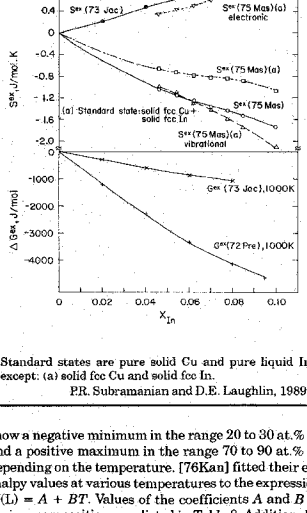
Note: Resulting values in J/mol, J/mol·K.
(a) Reported by [76Kan]. **(b)** Determined in the present evaluation from the numerical data of [77Kan].

Table 9 Partial Molar Quantities of In and Cu in Solid (Cu)

Composition, atomic fraction In	Partial excess Gibbs energy, J/mol In	Partial excess Gibbs energy, J/mol Cu	Composition, atomic fraction In	Partial excess Gibbs energy, J/mol In	Partial excess Gibbs energy, J/mol Cu	Composition, atomic fraction In	Partial excess Gibbs energy, J/mol, In	Partial excess enthalpy, J/mol, In
[72Pre], 1000 K			[73Jac], 900 K			[74Bha], 1000 K		
0.020	58 116	42	0.01	...	29	0.0459	−472	13 933
0.040	54 601	126	0.02	7740	109	0.0541	184	21 171
0.060	46 986	544	0.04	6904	297	0.0621	786	21 338
0.080	39 581	1088	0.06	5858	485	0.0700	987	19 916
0.095	28 033	2218	0.08	4435	682	0.0774	859	9 665
			0.10	...	870	0.0847	480	11 381
						0.0996	−1018	42 509

Note: The partial quantities are referred to pure solid Cu and pure liquid In as standard states.

Fig. 9 Integral Molar Excess Gibbs Energies and Excess Entropies of (Cu)



Standard states are pure solid Cu and pure liquid In, except: (a) solid fcc Cu and solid fcc In.

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show a negative minimum in the range 20 to 30 at.% In and a positive maximum in the range 70 to 90 at.% In depending on the temperature. [76Kan] fitted their enthalpy values at various temperatures to the expression $H(L) = A + BT$. Values of the coefficients A and B at various compositions are listed in Table 8. Additionally, [76Kan] combined their enthalpy of mixing data to yield the following numerical expression:

$$H(L) = X(1-X)[(-152\,670 + 98.58\,T) + (296\,450 - 188.94\,T)X - (150\,180 - 101.9\,T)X^2]$$

for a three-coefficient fit and

$$H(L) = X(1-X)[(-99\,680 + 72.87\,T) - (278\,650 - 99.92\,T)X + (1\,825\,900 - 923.2\,T)X^2 - (2\,683\,000 - 1434.5\,T)X^3 + 1\,252\,000 - 688.7\,T)X^4]$$

for a five-coefficient fit, where X is the atomic fraction of In and T is the absolute temperature in K.

Excess entropies of mixing (S^{ex}) reported in [69Aza], [74Jag], [77Kan], and in the compilation of [Hultgren,B] are shown in Fig. 8. The excess entropy values are positive at all compositions for temperatures above 1273 K. Additionally, the excess entropies reach a minimum at compositions between 20 and 30 at.% In. [74Jag] pointed out that this minimum corresponds more or less to the composition of β, and they attributed the minimum to the presence of partial order in the liquid state. This is also reflected in the composition dependence of the enthalpy of mixing (Fig. 7). [77Kan] determined the temperature dependence of S^{ex} at various compositions. Their numerical data were used in this evaluation to determine the coefficients of the expression: $S^{ex}(L) = C + DT$ (Table 8). The enthalpy and entropy data of [76Kan] and [77Kan], respectively, are by far the most comprehensive, and moreover, indicate a temperature dependence which has not been measured by other investigators. As such, their data are accepted in the present evaluation, and are shown in solid lines in Fig. 7 and 8.

Solid

Thermodynamic properties of the α or (Cu) phase have been measured by calorimetry [56Kle], emf [72Pre], chemical equilibrium [73Jac], and atomic absorption spectroscopy [74Bha]. Partial molar quantities from these investigations are summarized in Table 9. The partial Gibbs energy data are too disparate to derive any average values. Based on the calorimetric measurements of [56Kle], [Hultgren,B] concluded that the

Table 10 Integral Excess Molar Quantities of β, γ, δ, η, and ψ

Phase	Composition, at.% In	Temperature, K	Gibbs energy, J/mol	Enthalpy, J/mol	Entropy, J/mol·K	Reference
β	20.86	903	...	431	...	[76Kan]
		941	...	464	...	[76Kan]
	21.94	903	...	2423	...	[76Kan]
γ	29.95	903	...	5230	...	[76Kan]
		941	...	3310	...	[76Kan]
	30.87	941	...	3874	...	[76Kan]
	31.16	903	...	6100	...	[76Kan]
		941	...	6088	...	[76Kan]
δ	29.4	723	...	8636	...	[56Kle]
	30.3	723	...	8406	...	[56Kle]
	29.4	723	5595	...	4.16	[75Vin]
	30.6	723	5748	8745	4.16	[75Vin]
	29.0	723	5586	...	4.19	[76Vin]
		773	5404	...	4.19	[76Vin]
	30.6	723	5748	8745	4.11	[76Vin]
		773	5572	8662	4.07	[76Vin]
	30.0	298	7714	...	...	[83Kut]
"η"(a)	33.8	723	...	8011	...	[56Kle]
	37.5	723	...	7660	...	[56Kle]
	36.5	723	5712	7757	2.82	[75Vin]
	39.0	723	5601	7382	2.42	[75Vin]
	35.2	773	5608	7548	2.50	[76Vin]
	35.8	723	5738	7780	2.84	[76Vin]
		773	5624	7445	2.42	[76Vin]
	36.5	723	5712	7673	2.69	[76Vin]
		773	5600	7422	2.32	[76Vin]
	37.5	773	5584	7264	2.16	[76Vin]
	37.7	723	5656	7466	2.43	[76Vin]
	34.31	903	...	6636	...	[76Kan]
	34.76	903	...	6402	...	[76Kan]
	34.0	298	7778(b)	...	...	[83Kut]
	36.0	298	7907(b)	...	...	[83Kut]
ψ(c)	40.0	298	8125	...	...	[83Kut]

Note: Standard states refer to pure solid Cu and pure solid In.
(a) Alloys in the η phase field are not differentiated on the basis of the phase diagram of [72Jai], but are generally referred to as "η." **(b)** Average value. **(c)** This phase has not been accepted in the present review.

enthalpy of mixing is zero for an α alloy with 5 at.% In. Similarly, [73Jac] reported that the partial molar enthalpy relative to solid In is zero at all compositions within the α phase field. In contrast, the data of [74Bha] showed large negative values for the partial molar enthalpy of In (ΔH_{In}). However, [74Bha] indicated that these values may not be very precise. [74Bha] could not explain the minimum observed in their excess partial molar Gibbs energy curve at ~7 at.% In, although in a subsequent publication by the same authors [75Mas], they associated the minimum with an inflection in the concentration dependence of the integral excess entropy of α.

Because [73Jac] reported zero values for ΔH_{In}, S^{ex} values were extracted from their excess Gibbs energy (G^{ex}) values at 900 K. The G^{ex} data of [73Jac] were then extrapolated from 900 to 1000 K using these S^{ex} values. The resulting G^{ex} at 1000 K, compared with the G^{ex} data of [72Pre] in Fig. 9, show a large discrepancy. [75Mas] used the data of [74Bha] to derive S^{ex} values for α. Additionally, these investigators calculated the vibrational and electronic contribution to the excess entropy. These S^{ex} values are also shown in Fig. 9, along with the S^{ex} values from [73Jac]. The data of [73Jac] show positive values, whereas the S^{ex} data of [74Bha] indicate negative values. However, the S^{ex} data of [73Jac] are subject to large uncertainties, because they were derived with the assumption that the enthalpy of mixing relative to solid Cu and liquid In is zero for α.

Thermodynamic quantities of alloy formation have been measured for β by calorimetry [56Kle, 77Kan], for γ by calorimetry [76Kan, 81Wal], for δ by calorimetry [56Kle, 81Wal] and emf [75Vin, 76Vin, 83Kut], for "η" by calorimetry [56Kle, 76Kan, 83Kut] and emf [75Vin, 76Vin, 83Kut], and for ψ by emf [83Kut]. The integral enthalpies, entropies, and Gibbs energies of formation of the various phases are summarized in Table 10. The enthalpy and entropy values of Table 10 show a small temperature and composition dependence. Moreover, the data for the various investigators show satisfactory

agreement with one another. [76Kan] reported values of 6790 J/mol and 7.1 J/mol·K for the enthalpy and entropy of fusion, respectively, of γ. In disagreement, [81Wal] reported enthalpy and entropy values of 9300 J/mol and 9.7 J/mol·K, respectively, for the fusion of γ. The enthalpy and entropy of the $\delta \leftrightarrow \gamma$ transition was reported as 2450 J/mol and 2.7 J/mol·K, respectively, by [81Wal]. From DSC measurements, [81Wal] obtained the heat capacity of a δ phase alloy with 30 at.% In as:

$$C_p(\delta) = 23.81 + 0.00568\,T - 64\,200\,T^{-2}\ \text{J/mol·K}$$

in the temperature range 250 to 700 K and the heat capacity of a η phase alloy with 35 at.% In as:

$$C_p(\text{“}\eta\text{”}) = 20.63 + 0.0132\,T + 11\,960\,T^{-2}\ \text{J/mol·K}$$

in the temperature range 250 to 600 K.

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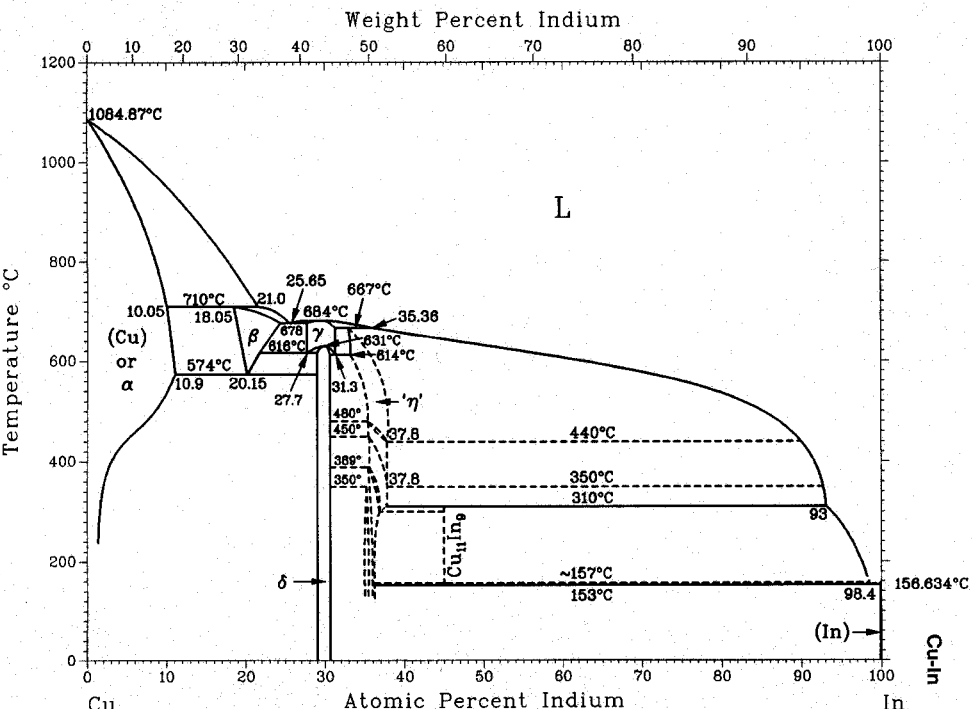
* Indicates key paper.

\# Indicates presence of a phase diagram.

Cu-In evaluation contributed by **P.R. Subramanian,** Universal Energy Systems, Inc., 4401 Dayton-Xenia Road, Dayton, Ohio 45432, and **D.E. Laughlin,** Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213. This work was supported by ASM INTERNATIONAL 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 1986. Part of the bibliographic search was provided by ASM INTERNATIONAL and part through other sources, including the bibliographic information provided by Dr. I. Ansara through his THERMET file, which is gratefully acknowledged. Professor Laughlin is the ASM/NIST Data Program Category Editor for binary copper alloys.


Weight Percent Indium
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Atomic Percent Indium
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In
Cu-In
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10.05
18.05
684°C
β
γ
678
616°C
631°C
614°C
(Cu)
or
α
574°C
10.9
20.15
27.7
31.3
'η'
480°
450°
389°
350°
37.8
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440°C
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δ
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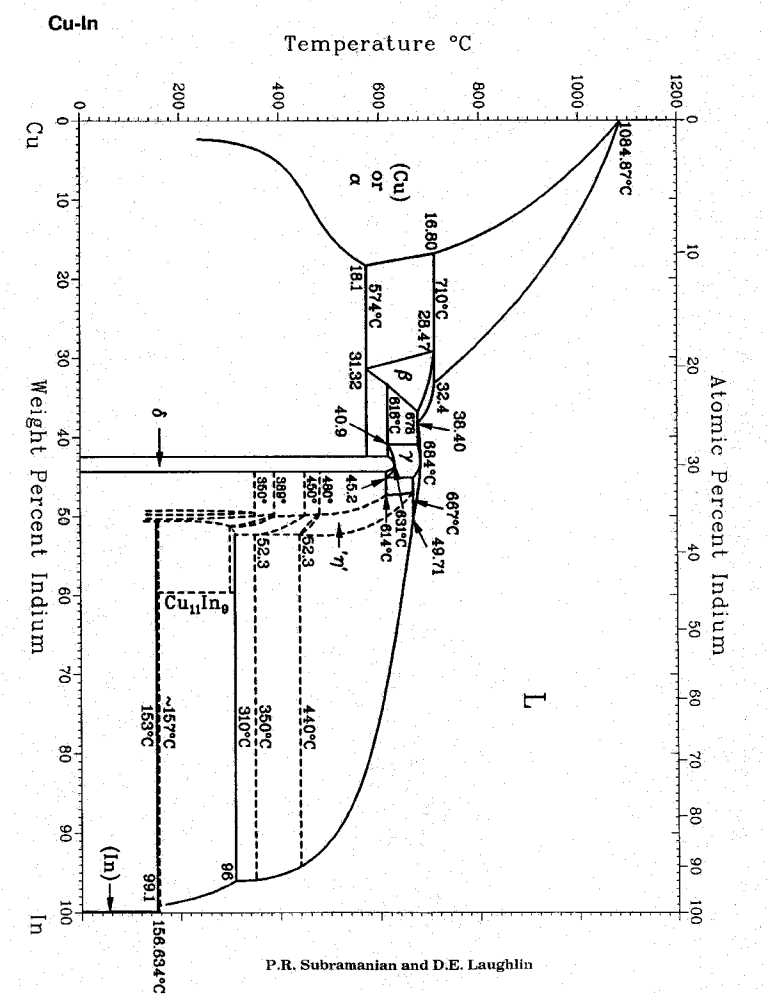
153°C
98.4
156.634°C
(In)



P.R. Subramanian and D.E. Laughlin