

The Cd-Cu (Cadmium-Copper) System

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Equilibrium Diagram

The assessed Cu-Cd equilibrium diagram (Fig. 1) includes the following phases: (1) the liquid, L; (2) the fcc A1 terminal solid solution, (Cu), with retrograde solubility of Cd and a maximum solubility of 2.56 at.% Cd at 650 °C; (3) C36, MgNi₂-type hexagonal β or Cu₂Cd, with negligible homogeneity range, which forms peritectically at 549 °C; (4) complex cubic γ or Cu₄Cd₉, which forms peritectically at 547 °C, with a maximum homogeneity range of ~5 at.% Cd; (5) complex cubic δ or Cu₅Cd₈, which forms congruently from the liquid at 563 °C, with a maximum homogeneity range between 52.2 and 66 at.% Cd; (6) D8₁₁, Al₅Co₂-type ϵ or Cu₃Cd₁₀, which forms peritectically at 397 °C, with a maximum homogeneity range of ~1.3 at.% Cd; and (7) the cph A3 terminal solid solution, (Cd), with a solubility of ~0.12 at.% Cu at 300 °C.

Figure 1 is based primarily on the experimental work of [24Jen] and closely follows the assessment of [Hansen]. However, modifications were made in the (Cu) boundary and in the ϵ phase field to bring the phase diagram into accord with more recent experimental studies. The various invariant temperatures and compositions are listed in Table 1. The designations adopted in Fig. 1 and Table 1 for the various intermediate phases may not agree with those reported in the literature; the present evaluation follows the nomenclature accepted in [Metals]. A short version of the Cu-Cd evaluation was published in [80BAP]. This evaluation supersedes the earlier work.

Liquidus

The Cu-Cd liquidus was investigated first by [1892Hey], who reported data for the Cd-rich region from 97.9 to 100 at.% Cd. Subsequently, [06Sah] and [24Jen] investigated the liquidus across the entire composition field, but there have been no other confirmatory measurements of the liquidus. Because Cd has a fairly low boiling point (767 °C) and a high vapor pres-

sure, the loss of Cd becomes appreciable, especially in Cd-rich alloys, giving rise to erroneous alloy compositions. According to [24Jen], precautions were taken to restrict the Cd losses to a minimum. Although the liquidus data of [06Sah] and [24Jen] are in good agreement, [06Sah] did not observe the existence of the γ and ϵ .

With regard to γ , [24Jen] reported that this phase does not separate from the liquid even under moderate rates of cooling. At ordinary rates of cooling, such as those normally used for determining cooling curves, the peritectic temperature for the formation of β is depressed below the equilibrium temperature for the formation of γ to ~544 °C. As a result, the formation of γ is suppressed, and β continues to precipitate from the liquid at ~540 °C, and a metastable eutectic of β and δ is formed (see Fig. 2). [67Sam] confirmed the occurrence of this metastable β/δ eutectic. The equilibrium γ/δ eutectic occurs at 47.3 at.% Cd and 544 °C. [1892Hey], [06Sah], and [24Jen] are in excellent agreement with regard to the composition and temperature of the Cd-rich eutectic (97.9 at.% Cd and 314 °C).

A more recent study by [84Kha] showed that under slow heating conditions, the eutectic temperature is 314 °C, in good agreement with earlier reports. With pulse heating, however, melting occurs at 305 °C; [84Kha] attributed this difference in melting temperatures to the evolution of heat accompanying the exothermic formation of the adjacent intermediate phase. Table 2 lists the liquidus data from the various investigations. The melting points of elemental Cu and Cd are accepted from [Melt] as 1084.87 and 321.108 °C, respectively.

According to [13Bor], Cu raises the boiling point of pure Cd to about 801 °C at 29 at.% Cu and to ~820 °C

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Table 1 Temperature-Invariant Reactions in the Assessed Cu-Cd Phase Diagram

Reaction	Compositions of the respective phases, at.% Cd		Temperature, °C	Reaction type
L \leftrightarrow (Cu)		0.0	1084.87	Melting point
L + (Cu) \leftrightarrow β	44.4	2.07	549	Peritectic
L + β \leftrightarrow γ	44.8	33.33	547	Peritectic
L \leftrightarrow γ + δ	47.3	42.9	544	Eutectic
L \leftrightarrow δ		61.54	563	Congruent
L + δ \leftrightarrow ϵ	92.7	66.0	397	Peritectic
L \leftrightarrow ϵ + (Cd)	97.9	76.8	314	Eutectic
L \leftrightarrow (Cd)		100	321.108	Melting point

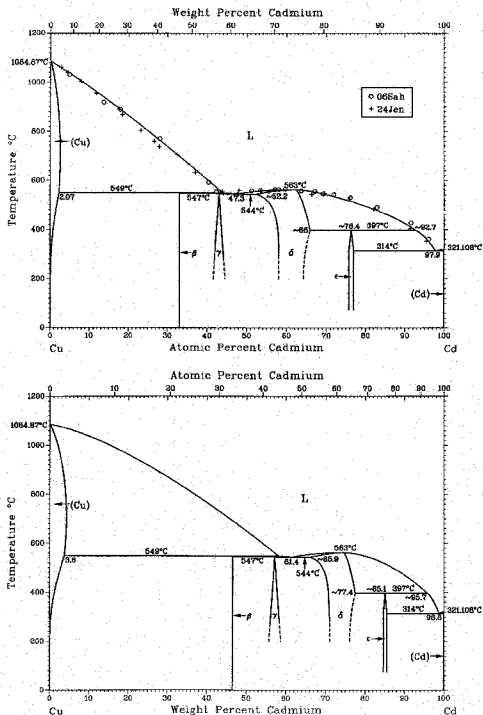
at 45 at. % Cu. There are no data to establish the boiling point trend for Cd at higher Cu contents.

Cu Terminal Solid Solution, (Cu)

The (Cu) solidus and solvus boundaries were determined by X-ray measurements [33Owe, 47Rau, 62Sul], metallography [35Pog, 47Rau], and microhardness measurements [81Gla], covering the temperature

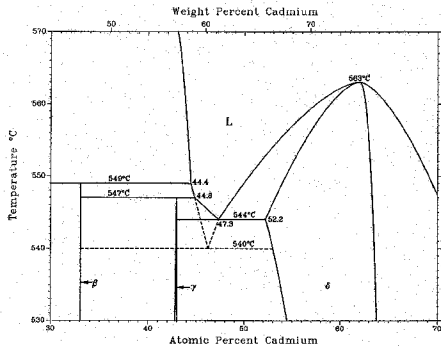
range 250 to 1055 °C (Table 3). The results from these investigations are plotted in Fig. 3. The retrograde shape of the (Cu) solidus was established clearly by [47Rau], [62Sul], and [81Gla], although the actual position of the solidus shows some variations among these investigations. The data of [35Pog] do not show the retrograde nature of the (Cu) solidus. Moreover,

Fig. 1 Assessed Cu-Cd Phase Diagram



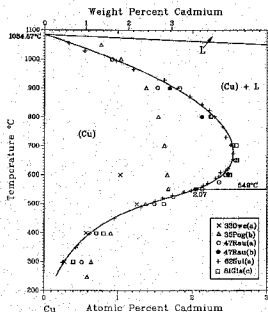
PR. Subramanian and D.E. Laughlin, 1990.

Fig. 2 Assessed Cu-Cd Phase Diagram in the Range 30 to 70 at.% Cd



Dashed lines show the metastable eutectic reaction between β and δ at 540 °C. PR. Subramanian and D.E. Laughlin, 1990.

Fig. 3 Cu-Rich Region of the Cu-Cd Phase Diagram



(a) From X-ray measurements. (b) From metallography.
(c) From microhardness measurements.

PR. Subramanian and D.E. Laughlin, 1990.

their data show a marked disagreement with those reported later and are therefore not considered in the assessment of the solidus boundary. The solidus data of [62Sul] and [81Gla] are in fair agreement, whereas the discrepancy in the solvus data is somewhat larger. Isopeitic measurements by [57Ray] confirmed the solubility to lie between 1.3 and 1.4 at.% Cd at 500 °C. The accepted (Cu) solvus is from [62Sul], who determined the boundary from lattice parameter measurements on alloys annealed between 300 and 1055 °C for periods ranging from 4707 h at the lowest temperature to 0.2 h at 1055 °C. The assessed retrograde maximum of 2.56 at.% Cd at 650 °C is in close accord with [47Rau], [62Sul], and [81Gla]. The (Cu) solubility is accepted as 2.07 at.% Cd at the peritectic temperature of 549 °C.

β Phase

The (Cu) + L \rightarrow β peritectic reaction was reported by [06Sab] to occur between 545 and 552 °C from differential thermal analysis (DTA) measurements. Subsequently, thermal [24Jen], lattice parameter [62Sul], and microhardness measurements [81Gla] confirmed the peritectic temperature to lie at 549 °C. β is stoichiometric at the Cu_2Cd composition, with almost no homogeneity range.

γ Phase

The formation of γ is suppressed under normal rates of cooling [24Jen], probably because of the complexity of the γ unit cell. This gives rise to the metastable β/δ

eutectic at $\sim 540^\circ\text{C}$. [24Jen] identified the existence of this phase from metallographic investigation of alloys containing 36.1 to 51.2 at.% Cd, following annealing at 450°C for extended periods. [67Sam] confirmed this by noting the gradual conversion of the metastable β/δ eutectic into γ from X-ray analysis of powder samples taken after various stages of annealing. γ forms at 547°C through the peritectic reaction $L + \beta \rightleftharpoons \gamma$, with a homogeneity range reported as ~ 2 at.% Cd at 300°C [24Jen]. A recent transmission electron microscopy (TEM) investigation by [87Ben] suggested that equilibrium γ forms by the solid state decomposition of a metastable tetragonal phase that initially forms from the melt.

Table 2 Experimental Cu-Cd Liquidus Data

Composition, at.% Cd	Temperature, $^\circ\text{C}$	Composition, at.% Cd	Temperature, $^\circ\text{C}$
From [1892Hey]			
97.88	312.86	97.97	315
98.29	314.1	98.97	318
98.84	315.95	100	321.7
98.97	316.56	From [24Jen]	
99.23	317.13	0	1083
99.45	318.25	1.8	1060
99.61	319.12	3.7	1038
99.75	319.35	7.1	1002
99.86	319.8	11.0	957
99.89	320.14	16.9	893
99.94	320.18	17.9	868
100	320.19	22.6	808
From [06Sah]			
0	1084	26.1	760
4	1032	27.5	737 (739)
13	919	31.9	708
17.1	891	36.4	635
27.5	772	43.6	553
32	708	43.8	541
40	591	46.9	538
42	552	48.0	560
45.4	541	53.4	558
51	556	55.3	556
53.2	561	60.1	562
56.9	564	66.2	543
57.7	564	69.3	546 (548)
59.4	564	75.9	523 (527)
63.4	561	82.1	484 (495)
67	557	91.5	406
69	547	95.7	354
72	542	98.6	317.5
76	528	99.2	320
83	491	100	321
91.5	429	From [Melt]	
96.2	362	0	1084.87
		100	321.108

Note: Liquidus temperatures correspond to data from cooling curves. Temperatures on heating are given in parentheses.

δ Phase

The liquidus is very flat in the region corresponding to the congruent formation of δ . [06Sah] and [24Jen] assumed its composition to be Cu_2Cd_3 at the congruent maximum. More recent studies showed that δ is the Cu_5Cd_8 prototype; consequently, the congruent point in Fig. 1 and 2 is shown to correspond to the Cu_5Cd_8 composition (61.54 at.% Cd). Metallographic investiga-

Table 3 (Cu) Solvus and Solidus Phase Boundaries

Composition, at.% Cd	Temperature, $^\circ\text{C}$	Composition, at.% Cd	Temperature, $^\circ\text{C}$
From [33Owe](a)		From [62Sul](a), cont.	
0.28	300	0.95	450
0.57	400	1.31	490
1.26	500	1.50	510
1.03	600	1.60	520
From [35Pog](b)		1.74	530
0.59	250	1.88	539
0.65	300	1.89	540
0.91	400	1.99	546
1.38	500	2.07	550
1.68	550	2.13	557
1.67	600	2.15	560
1.63	700	2.21	570
1.60	750	2.32	588
1.55	800	2.36	593
1.50	850	2.38	608
1.38	900	2.45	613
1.26	950	2.48	621
1.04	1000	2.56	652
0.77	1050	2.55	672
From [47Rau](a)		2.52	700
0.52	300	2.46	730
0.71	400	2.41	766
1.49	500	2.30	800
1.75	525	2.23	823
2.14	550	2.13	843
2.37	575	1.97	871
2.46	600	1.81	900
2.58	650	1.62	929
2.56	700	1.21	965
2.26	800	0.97	994
1.52	900	0.55	1028
0.92	1000	0.33	1055
From [47Rau](b)		From [81Gla](c)	
2.06	550	0.40	300
2.49	600	0.80	400
2.53	700	1.62	500
2.14	800	2.50	600
1.70	900	2.60	650
From [62Sul](a)		2.60	700
0.26	300	2.27	800
0.43	350	1.82	900
0.63	400		

(a) From lattice parameter measurements. (b) From metallography. (c) From microhardness measurements.

tion by [24Jen] indicated a wide homogeneity range for this phase, extending from ~52.2 at.% Cd on the Cu-rich side to ~64 at.% Cd on the Cd-rich side. Subsequent metallographic and magnetic susceptibility measurements [50Now] on alloys annealed at 400 °C for 48 h showed the limiting composition to lie at somewhat higher Cd contents—about 66 at.% Cd. [76Wal] studied the δ phase transformation with electrical resistivity and heat capacity measurements on a Cu-59.4 at.% Cd alloy. The heat capacity vs temperature trend showed an anomalous heat effect in the range 133 to 197 °C of 29 J/mol, which the authors speculated to be associated with a short-range ordering effect.

ϵ Phase

The early phase diagram investigation of [06Sah] did not reveal the existence of ϵ . The metallographic investigation of [24Jen] showed that this phase forms at 397 °C through the peritectic reaction $L + \delta \rightarrow \epsilon$, with a composition corresponding to Cu_3Cd_3 and a homogeneity range of ~1 at.% Cd at 300 °C. More recent metallographic and DTA measurements [82Raj] confirmed the peritectic formation of this phase at 397 °C, but with a stoichiometry of $\text{Cu}_3\text{Cd}_{10}$. Metallography showed the maximum homogeneity range to extend from ~75.6 to 76.9 at.% Cd. In alloys containing ~75 to 76 at.% Cd, [82Raj] observed an unexplained DTA effect at ~247 °C.

Table 4 Lattice Parameter Data for the Metastable (Cd) Terminal Solid Solution

Composition, at.% Cu	Lattice parameters, nm	
	<i>a</i>	<i>c</i>
0.....	0.2979	0.5616
0.5.....	0.2980	0.5606
1.0.....	0.2980	0.5595
2.0.....	0.2980	0.5584
2.5.....	0.2978	0.5578
3.0.....	0.2980	0.5578

Note: Measurements taken on rapidly quenched samples. Equilibrium values at 0 at.% Cu are $a = 0.29793$ and $c = 0.56196$ nm at 25 °C [Masalski]. From [76Mas].

Table 5 Cu-Cd Crystal Structure Data

Phase	Composition, at.% Cd	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(Cu).....	0 to 20.6	<i>cF4</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	A1	Cu	[King1]
β	33.3	<i>hP24</i>	<i>P6</i> $\bar{3}$ <i>mmc</i>	C36	MgNi ₂	[62Sul]
γ	41.8 to 44.1(a)	<i>cF1124</i>	<i>F</i> $\bar{4}$ <i>3m</i>	...	Cu ₄ Cd ₃	[67Sam]
δ	52.2 to 66	<i>cI52</i>	<i>I</i> $\bar{4}$ <i>3m</i>	...	Cu ₃ Cd ₄	[74Bra]
ϵ	75.6 to 76.9	<i>hP28</i>	<i>P6</i> $\bar{3}$ <i>mmc</i>	D8 ₁₁	Al ₃ Co ₂	[82Raj]
(Cd).....	~99.8 to 100	<i>hP2</i>	<i>P6</i> $\bar{3}$ <i>mmc</i>	A3	Mg	[King1]

(a) At 300 °C.

Cd Terminal Solution, (Cd)

The solid solubility of Cu in (Cd) was reported to be 0.12 at.% Cu at 300 °C by [24Jen] and between 0.09 and 0.17 at.% Cu at 270 °C by [28Tam]. [76Mas] reported that the equilibrium solid solubility of Cu in (Cd) is about 0.2 at.% Cu.

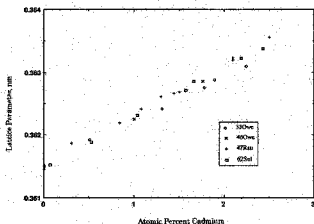
Metastable Phases

Extensive studies have been reported on the structure of Cu-Cd alloys obtained by electrodeposition on various cathodes [66Ahu, 74Lon, 78Boj1, 78Boj2, 78Boj3, 80Lag, 81Lag1, 81Lag2, 81Lag3]. From these reports, it is evident that the solubility of Cd in (Cu) can be dramatically extended from the equilibrium value of ~2.1 at.% Cd to a maximum value of ~27 at.% Cd, with solid solubility increasing with increasing deposition potential. Moreover, the metastable solid solubility of Cd in (Cu) was found to depend on the surface orientation of the single-crystal cathode. In electrodeposited alloys in the composition range between ~13 and 98 at.% Cd, [66Ahu] observed the formation of β , δ , ϵ , and (Cd) phases, depending on composition. According to these authors, γ is not formed as a primary product of electrolysis, but occurs only after annealing; this is analogous to the behavior reported for γ in melt-formed alloys [24Jen].

From the variation of the lattice parameters of (Cd) terminal solid solution in rapidly quenched samples (see Table 4), [76Mas] concluded that the solubility limit of Cu in (Cd) is extended metastably to a value of ~2.5 at.% Cu. [76Mas] observed no difference between the lattice parameters of a splat-cooled ϵ phase and those of the equilibrium ϵ phase.

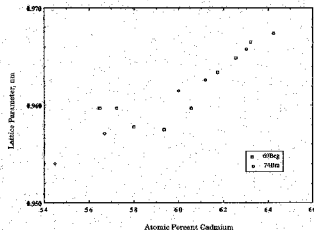
[87Ben] examined rapidly solidified Cu-Cd alloys in the composition region 37.2 to 60.5 at.% Cd by TEM. The presence of an icosahedral phase with point group $m\bar{3}5$ was detected in the 60.5 at.% Cd alloy. In alloys with 44.8 and 50.7 at.% Cd, [87Ben] observed a tetragonal phase with $c = 0.99$ nm, a cubic phase with $a = 2.587$ nm, and another cubic phase with a large unit cell of $a = 3.25$ nm and composition close to Cu_3Cd_4 . The alloy with 37.2 at.% Cd was glassy.

Fig. 4 Lattice Parameter of the (Cu) Solid Solution as a Function of Composition



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Fig. 5 Variation of Lattice Parameters with Composition in δ



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Crystal Structures and Lattice Parameters

Crystal structure data for the equilibrium Cu-Cd phases are summarized in Table 5, and lattice parameters are listed in Tables 6 and 7. Pertinent features of the phases are summarized below.

(Cu) Terminal Solid Solution

Lattice parameter data for the fcc (Cu) terminal solid solution are plotted in Fig. 4. In general, the trends show good agreement. At higher Cd concentrations, the lattice parameters reported by [33Owe] are somewhat lower.

β Phase

From powder X-ray data, [52Kri] reported that β has the hexagonal C14, MgZn₂-type structure, with four formula units of Cu₂Cd in the unit cell. Subsequently, [61Bor] suggested that this phase is isotypic with MgNi₂, rather than MgZn₂, with a c parameter double that of [52Kri]. [61Bor] observed that long annealing periods are required to obtain equilibrium β . Conse-

Table 6 Lattice Parameter Data for the (Cu) Terminal Solid Solution

Reference	Composition, at.% Cd	Lattice parameter, nm	Comment
[33Owe](a)	0	0.36151	Annealed at 500 °C
	0.51	0.36192	Annealed at 500 °C
	1.31	0.36241	Annealed at 500 °C
	1.78	0.36275	Annealed at 500 °C
	1.89	0.36288	Annealed at 500 °C
[46Owe]	2.24	0.36309	Annealed at 500 °C
	0	0.36147	Annealed at 500 °C
	1.0	0.36225	Annealed at 500 °C
[47Rau](a)	1.76	0.36285	At 549 °C
	0	0.36150	(b)
	0.31	0.36187	(b)
	0.84	0.36219	(b)
	1.08	0.36241	(b)
	1.30	0.36261	(b)
	1.44	0.36266	(b)
	1.50	0.36268	(b)
	2.09	0.36319	(b)
	2.09	0.36323	(b)
2.5	0.36356	(b)	
[62Sul]	0.07	0.36152	Annealed at 650 °C
	0.53	0.36188	Annealed at 650 °C
	1.04	0.36231	Annealed at 650 °C
	1.57	0.36271	Annealed at 650 °C
	1.66	0.36285	(c)
	2.19	0.36322	Annealed at 650 °C
[75Cha]	2.43	0.36337	Annealed at 650 °C
	1	0.36225	At 550 °C
	2	0.36230	At 650 °C
[Massalski]	1	0.36310	At 550 °C
	2	0.36310	At 650 °C
	0	0.36146	At 25 °C

(a) From graph. (b) Annealed for periods ranging from 2 h at 1000 °C to 500 h at 300 °C. (c) Composition of alloy may not be accurate.

quently, the discrepancy in the data of [52Kri] could be attributed to incomplete equilibrium, because the alloy of [52Kri] was annealed for only 24 h at 500 °C. The C36, MgNi₂-type (space group *P6₃/mmc*, Pearson symbol *hP24*) structure of β was confirmed subsequently by [62Sul] and [67Sam].

γ Phase

[38Lav] reported that γ is isomorphous with the Al-Mg β phase of approximate composition Al₃Mg₂, whose structure subsequently was determined by [44Per] to be complex cubic, with ~1166 atoms/cell. Preliminary investigations by [62Sam] and [65Sam] on single crystals of γ with Cu₄Cd₃ composition showed that it is complex cubic, with ~1116 atoms/cell. However, the diffraction pattern was observed to be quite different from that of β Al₃Mg₂, in contradiction to the report of [38Lav]. Powder diffraction data of [65Dey] showed that γ is tetragonal, with possible space group *P4₃/nnc*.

Finally, [67Sam] (same author as [62Sam] and [65Sam]) conducted a detailed structural investigation of γ . Alloy samples prepared from elements of 99.9%

purity were annealed for 1680 h at temperatures ranging from ~520 °C to slightly above the melting point (547 °C) to obtain single crystals of Cu₄Cd_{2.89} composition. Density measurements were observed to be in accord with the data of [65Dey]. According to [67Sam], however, comparison of their powder data with those of [65Dey] showed that although there is qualitative agreement between the two patterns, 16 lines from the pattern of [65Dey] could not be explained on the basis of any established Cu-Cd phases. [67Sam] attributed these lines to the presence of oxides; moreover, there were missing reflections in the pattern of [65Dey]. From Laue, rotation, and Weissenberg data, [67Sam] determined that γ is complex cubic, with a lattice parameter of 2.5871 nm and space group *F43m*. The unit cell was shown to contain 1124 atoms distributed among 29 crystallographically different positions. The structure is of considerable complexity and is made up of 568 icosahedra of ligancy 12, 288 centered pentagonal prisms, 144 centered polyhedra of ligancy 15, and 124 Friedel polyhedra of ligancy 16. The atomic positional parameters are listed in [67Sam].

Table 7 Lattice Parameter Data for the Cu-Cd Intermediate Phases

Phase	Composition, at.% Cd	Lattice parameters, nm			Comment	Reference
		a	b	c		
β	33.3	0.496	...	0.799(a)	c/a = 1.61	[52Kri]
		0.500	...	1.617	c/a = 3.23	[61Bor]
	33.2	0.50115	...	1.6210	c/a = 3.23, (b)	[62Sul]
γ	42.9	2.583	[62Sam]
		2.587	[65Sam]
		1.3701	...	0.9444(c)	Annealed at 470 °C, (d)	[65Dey]
	42.0	2.5871	Annealed between 520 and 547 °C	[67Sam]
	49.0	0.99(c)	Metastable	[87Ben]
	60.5	0.9655	Annealed between 250 and 300 °C	[31Bra]
	60.3	0.9615	Annealed at 300 °C	[33Owe]
	61.54	0.955	[67Sam]
		0.95888	Annealed at 530 °C	[68Hei]
	56.46	0.9597	[69Beg]
56.51	0.9597	[69Beg]	
57.23	0.9597	[69Beg]	
58.01	0.9578	[69Beg]	
59.36	0.9575	[69Beg]	
60.55	0.9597	[69Beg]	
61.74	0.9634	[69Beg]	
62.53	0.9649	[69Beg]	
63.21	0.9665	[69Beg]	
64.24	0.9674	[69Beg]	
60	0.9615	[74Bra]	
54.5(d)	0.9540	Single crystal; at 23 °C	[74Bra]	
56.7(d)	0.9571	Quenched from 538 °C	[74Bra]	
61.2(d)	0.9626	Quenched from 451 °C	[74Bra]	
63.0(d)	0.9658	Quenched from 538 °C	[74Bra]	
				Quenched from 451 °C	[74Bra]	
ϵ	75.0	0.811	...	0.876	...	[61Bor]
		0.810	...	0.876	Annealed at 250 °C	[63Dey]
		0.8124	...	0.8755	...	[76Mas]
	76.5	0.8118	...	0.8751	(e)	[82Raj]

(a) Not accepted; incomplete equilibrium due to short annealing periods. (b) Annealed at 525 °C. (c) Reported to be tetragonal. (d) Composition of the γ phase in alloys quenched from the two-phase field, obtained from the phase boundary data of [Hansen]. (e) Powder data from alloys annealed at 365 °C and water quenched; single-crystal data from alloys annealed at 375 °C and cooled to room temperature over a period of 3 days.

Convergent beam electron diffraction investigations [87Ben] of melt-spun Cu-44.8 and -50.7 at.% Cd alloys indicated the presence of a tetragonal phase with $c = 0.99$ nm, similar to that reported by [65Dey], in addition to the complex cubic phase reported by [67Sam]. Although the authors stated that the tetragonal phase can be formed directly from the melt without the need for prolonged annealing, they subsequently suggested that this phase is metastable and most likely leads to the precipitation of the equilibrium cubic phase. It seems that the stability of this tetragonal phase reported by [65Dey] and [87Ben] is at best marginal.

δ Phase

Structural analysis by [31Bra] showed that the unit cell of δ has atomic positions similar to that of γ brass, with 52 atoms/cell. However, intensity studies indicated that the distribution of atoms in these positions is not the same in Cu-Cd and Cu-Zn. Powder X-ray data of [33Owe] confirmed that this phase is analogous to γ brass, with four formula units of Cu_5Cd_3 in the unit cell. Subsequent refinements of the structure of δ , based on single-crystal X-ray investigations of [68Hei] and [74Bra], confirmed the observations of [31Bra], although there are minor variations in the reported positional parameters of the Cu and Cd atoms (see [Pearson3]).

The atomic distribution data of [31Bra] and [68Hei] showed 20 Cu and 32 Cd atoms distributed in the various sites as follows: 8 Cu atoms each in an inner tetrahedral and outer tetrahedral site, respectively, and the remaining 4 Cu and 32 Cd atoms distributed among an octahedral and a distorted cubo-octahedral position. The results of [74Bra] showed a slightly higher Cu concentration at the octahedral site, suggesting that increasing the Cu contents within the δ phase field leads to preferential occupancy of the additional Cu atoms at the octahedral sites. [69Beg] and [74Bra] studied the variation of the lattice parameter of δ with composition. Their results contradict one another, as seen in Fig. 5. The lattice parameter trend of [69Beg] shows a minimum at ~59 at.% Cd, whereas that of [74Bra] shows a monotonic linear increase with increasing Cd concentration.

ϵ Phase

X-ray studies by [61Bor], [63Dey], and [67Sam] showed that ϵ has hexagonal structure. From density measurements, [63Dey] reported a unit cell with six formula units of Cu_3Cd_3 . From single-crystal and powder X-ray data, [82Raj] concluded that ϵ , with approximate stoichiometry $\text{Cu}_3\text{Cd}_{10}$, is homeotypic with $\text{Mn}_3\text{Al}_{10}$, with space group $P6_3/mmc$. Because an extra atom position, 2(d), with 6m2 symmetry is partly filled, the prototype is not truly $\text{Mn}_3\text{Al}_{10}$, but $D8_{11}$, Al_3Co_2 (as pointed out by [Pearson3]). Lattice parameter data from [61Bor], [63Dey], [76Mas], and [82Raj] are in reasonable agreement, although [70Tro] claimed that the indexing of the diffraction lines for ϵ by [63Dey] was erroneous.

Thermodynamics

Liquid

Thermodynamic data for liquid Cu-Cd alloys were determined by emf [54Ric, 57Nik], vapor pressure [31Je], 42Sch, 68Aza, 80Str], calorimetry [56Kle], and theory [68Bo]. The assessed thermodynamic data in [Hultgren,B] were based on [54Ric], [56Kle], [57Nik], and [68Aza]. Data of [31Je] and [42Sch] were rejected on the grounds that their methods were unreliable.

Solid

Thermodynamic measurements for various Cu-Cd solid phases were conducted by calorimetry [23Bil, 24Sch, 41Kub], emf [66Vec, 67Vec], and vapor pressure [61Bor]; and results are summarized in [Hultgren,B]. Partial molar enthalpy and Gibbs energy values determined by [84Zos] from emf measurements are unusually large.

[81Gl] calculated the interaction parameters for (Cu) and L based on experimental liquidus and solidus boundaries and as thermodynamic data from [Hultgren,B]. The (Cu) solidus calculated from their optimized interaction parameters is in close accord with their own experimental data. No other thermodynamic calculations of phase boundaries have been reported in the literature.

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- *Indicates key paper.
#Indicates presence of a phase diagram.

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