Amsterdam, 1-161 (1986). (Equi Diagram, Crys Structure; Compilation)

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

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The Cu-Yb (Copper-Ytterbium) System

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Equilibrium Diagram

[71Ian] determined the phase relations in the Cu-Yb system and reported the existence of five intermediate phases: Cu_5Yb, Cu_9Yb_2, Cu_7Yb_2, Cu_2Yb, and CuYb. The Yb used in their investigation was reported to be 99.9% pure, whereas the Cu used had a purity of 99.999%. The phase diagram reported by [71Ian] was based on differential thermal analysis (DTA), metallography, and X-ray diffraction. Thermal analysis was carried out using two or more thermal cycles with heating and cooling rates of 10, 5, and occasionally 2 °C/min to ensure reproducibility. [Moffatt] reproduced the Cu-Yb phase diagram from the data of [71Ian], as well as from an earlier report by the same authors [70Ian], and incorporated minor changes of 1 to 3 °C in the various invariant temperatures. The assessed phase diagram for the Cu-Yb system, shown in Fig. 1, is based on the data of [71Ian] with minor adjustments in the elemental melting points, as well as in the βYb ↔ γYb transformation temperature. The phase diagram of the Cu-Yb system is different from those of Cu with the other heavy lanthanides because Cu_2Yb and CuYb melt peritectically. In contrast, in the other lanthanide systems, the 2-to-1 as well as the 1-to-1 phases melt congruently. These deviations from systematics of alloys of Cu with the heavy lanthanides can be attributed to the divalent nature of Yb in its standard state, as compared to the other heavy lanthanides like Gd, Tb, and Dy that are usually trivalent in their standard state.

Table 1 Cu-Yb Experimental Liquidus Data

Composition, at.% Yb	Temperature, °C	Composition, at.% Yb	Temperature, °C
5.0	988	40.0	738
10.0	859	45.0	694
12.5	887	50.0	627
15.0	916	55.0	623
17.5	932	60.0	608
18.2	937	65.0	569
20.0	926	70.0	523
21.3	919	75.0	485
22.5	912	80.0	558
23.8	904	85.0	635
25.0	883	90.0	699
30.0	825	95.0	757
35.0	769		

From [71Ian].

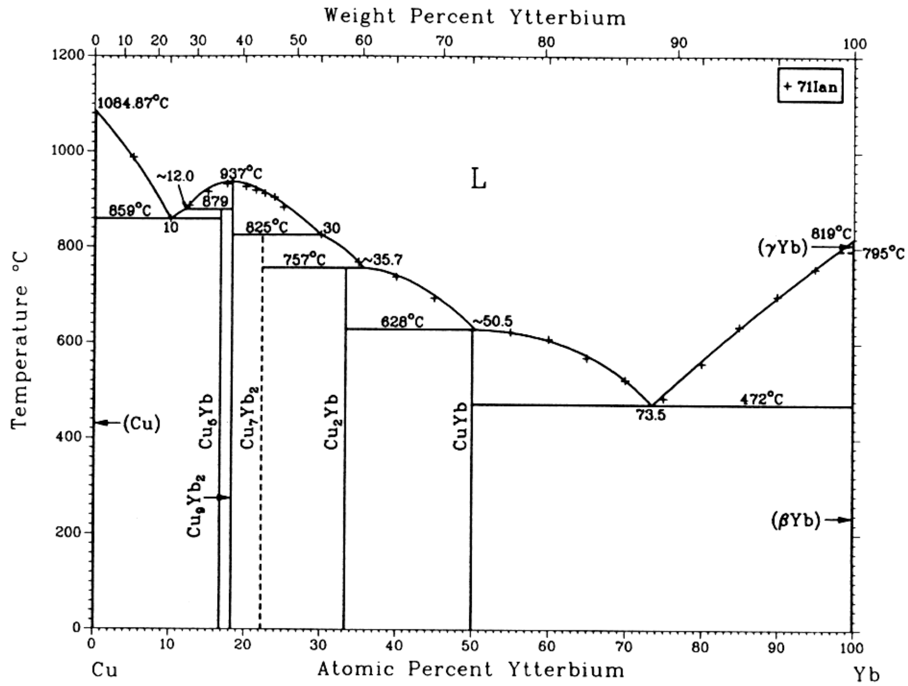
Terminal Solid Solubility

On the basis of lattice parameter measurements, [71Ian] determined that there is no appreciable terminal solid solubility in the Cu-Yb system. [79Dri] reported that the maximum solid solubility of Yb in Cu is ~0.07 wt.% (~0.03 at.%) at the eutectic temperature.

Liquidus and Solidus

Experimental data for the Cu-Yb liquidus boundaries are listed in Table 1. The melting points of (Cu) and (Yb) are accepted as 1084.87 °C [Melt] and 819 °C [78Bea, 86Gsc], respectively. The (βYb) → (γYb) transformation temperature is accepted from [78Bea] as 795 °C. The melting point quoted for Yb by [71Ian]

Fig. 1 Assessed Cu-Yb Phase Diagram



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is in good agreement with the accepted value. However, their β → γ transition temperature is 30 °C below the accepted value, and this could be due to the influence of impurities in Yb.

The various invariant reactions occurring in the Cu-Yb system are summarized in Table 2.

Intermediate Phases

[71Ian] reported that Cu_5Yb is the most Cu-rich intermediate phase in the Cu-Yb system. On the other hand, [72Hor] concluded from X-ray diffraction and metallography that the phase richest in Cu has a stoichiometry of $Cu_{6.5}Yb$ and occurs at about 13.3 at.% Cu. Their alloys were prepared by reacting appropriate amounts of Cu and Yb in a sealed Mo container under purified argon at 1100 °C for 10 min, followed by annealing for 3 weeks at 650 °C. Arc melting was not used to prepare the samples because of unmeasurable losses in Yb during the melting process. [72Hor] have not reported the temperature range of stability of $Cu_{6.5}Yb$, and moreover, observed that this phase forms instead of Cu_5Yb. This is in direct contradiction to the reports of the existence of Cu_5Yb by [67Pal] and [71Ian]. Phases with the stoichiometry $Cu_{6.5}Yb$ have not been reported for any of the other lanthanides. Phases with the stoichiometry Cu_7RE have been observed for the heavy trivalent lanthanides Gd, Dy, and Tb, although these phases are stable only at elevated temperatures and decompose on annealing at low temperatures into elemental Cu and a phase richer in the lanthanide component. On the other hand, phases with the stoichiometry Cu_6RE exist for the trivalent lanthanides from La to Gd, and these phases are stable down to room temperature. The stoichiometries, Cu_7RE and Cu_6RE, are not observed in Cu-Yb, and $Cu_{6.5}Yb$, reported by [72Hor], falls in between these two stoichiometries. There is a strong possibility, therefore, that $Cu_{6.5}Yb$ exists as a stable phase only at elevated temperatures, and that it forms either peritectically from the liquid and Cu_5Yb, or peritectoidally from Cu_5Yb and elemental Cu. Because [71Ian] failed to observe $Cu_{6.5}Yb$ in their phase diagram investigation, it can be inferred that this phase forms at a temperature very close to that of the eutectic at the Cu-rich end. Both $Cu_{6.5}Yb$ and Cu_5Yb are reported to form with a hexagonal structure, and their lattice parameters are in very close accord (see "Crystal Structures and Lattice Parameters"). Because there is a large composition difference between $Cu_{6.5}Yb$ and Cu_5Yb (~3.4 at.%), it is unlikely that $Cu_{6.5}Yb$ is part of an off-stoichiometric extension of Cu_5Yb toward higher Cu content, and therefore, the agreement in the lattice parameters of $Cu_{6.5}Yb$ with those of Cu_5Yb may be simply a coincidence.

Of the five intermediate phases reported by [71Ian], Cu_9Yb_2 melts congruently at 937 °C, whereas Cu_5Yb, Cu_7Yb_2, Cu_2Yb, and CuYb form incongruently at 879, 825, 757, and 628 °C, respectively. The stoichiometries for Cu_9Yb_2 and Cu_7Yb_2 have been assigned by [71Ian]

Table 2 Special Points of the Assessed Cu-Yb Phase Diagram

Reaction	Compositions of the respective phases, at.% Yb			Temperature, °C	Reaction Type	Reference
(Cu) ↔ L		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu_5Yb	10	~0	16.7	859	Eutectic	[71Ian]
L + Cu_9Yb_2 ↔ Cu_5Yb	~12	18.2	16.7	879	Peritectic	[71Ian](a)
L ↔ Cu_9Yb_2		18.2		937	Congruent	[71Ian]
L + Cu_9Yb_2 ↔ Cu_7Yb_2	30	18.2	22.2	825	Peritectic	[71Ian]
L + Cu_7Yb_2 ↔ Cu_2Yb	~35.7	22.2	33.3	757	Peritectic	[71Ian](a)
L + Cu_2Yb ↔ CuYb	~50.5	33.3	50	628	Peritectic	[71Ian](a)
L ↔ CuYb + (βYb)	73.5	50	~100	472	Eutectic	[71Ian]
(βYb) ↔ (γYb)		~100		795	Allotropic	[78Bea, 86Gsc]
(γYb) ↔ L		100		819	Melting point	[78Bea, 86Gsc]

(a) Liquidus composition was obtained by interpolation of experimental data in Fig. 1.

Table 3 Cu-Yb Experimental Lattice Parameters

Phase	Crystal structure	Lattice parameters, nm *a*	*b*	*c*	Reference
$Cu_{6.5}Yb$	Hexagonal	0.5004	...	0.4118	[72Hor](a)
Cu_5Yb	Hexagonal	0.4992	...	0.4126	[67Pal]
		0.4994	...	0.4126	[71Ian]
Cu_9Yb_2	Tetragonal	0.496	...	1.384	[71Ian](b)
$Cu_{23}Yb_6$	Cubic	1.203	...	...	[84Tsv](c)
Cu_2Yb	Orthorhombic	0.428	0.676	0.740	[63Sto]
		0.4286	0.6894	0.7382	[68Ian]
		0.4291	0.6899	0.7386	[71Ian]
CuYb	Orthorhombic	0.7568	0.4260	0.5771	[71Ian]
		0.7568	0.4257	0.5776	[76Deb]

(a) [72Hor] determined that this phase is the most Cu-rich intermediate phase and that it forms instead of Cu_5Yb. (b) Structure based on a tetragonal cell. (c) Formed only at high pressures (7.7GPa).

Table 4 Cu-Yb Crystal Strucuture Data

Phase	Composition, at.% Yb	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Cu_5Yb	~16.67	*hP*6	*P*6/*mmm*	$D2_d$	$CaCu_5$
Cu_2Yb	~33.3	*oI*12	*Imma*	...	$CeCu_2$
CuYb	~50	*oP*8	*Pnma*	*B*27	FeB
(γYb)	100	*cI*2	$Im\bar{3}m$	*A*2	W
(βYb)	~99.97 to 100	*cF*4	$Fm\bar{3}m$	*A*1	Cu
(αYb)	100	*hP*2	$P6_3/mmc$	*A*3	Mg

on the basis of thermal, X-ray, and metallographic data from as-cast as well as annealed alloys.

[69Gsc] indicated that Yb is in the divalent state in Cu_5Yb. Subsequent magnetic susceptibility measurements by [71Ian] show that Yb is divalent in Cu_5Yb, Cu_2Yb, and CuYb. Accordingly, it is observed that the melting temperatures of Cu_5Yb, Cu_2Yb, and CuYb are anomalous, because they fall well below the values obtained by interpolation of melting data for the corresponding trivalent lanthanide phases (see "The Copper-Rare Earth Systems," in this issue). Their respective lattice parameters also indicate that the valence of Yb in these three phases is less than three. However, [71Ian] determined that Yb is trivalent in both Cu_9Yb_2 and Cu_7Yb_2. For Cu_9Yb_2, the trivalency of Yb is not apparent from the melting temperature, which shows a deviation similar to that observed for the other Cu-Yb phases, i.e., towards lower temperatures with respect to the normal trend exhibited by the corresponding alloys of the trivalent lanthanides. According to [69Gsc], Yb is trivalent in many of its alloys, even though in the standard state Yb is divalent, and this is because the energy required to promote Yb from the divalent to the trivalent state is fairly low (~38 kJ/mol).

Fig. 2 Assessed vs Calculated Cu-Yb Phase Diagram

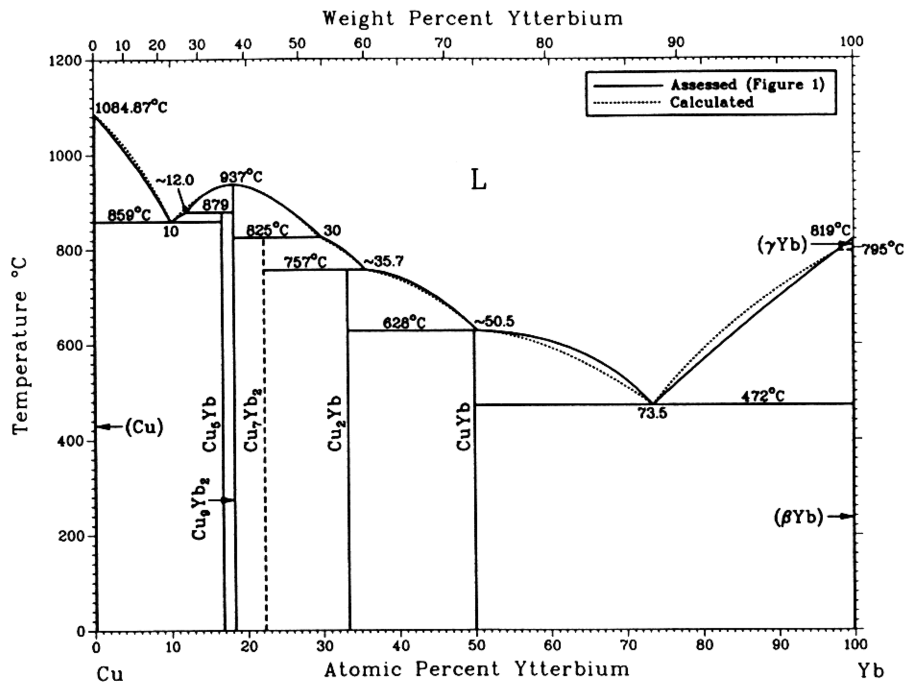

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Table 5 Cu-Yb Lattice Parameter Data

Phase	Composition, at.% Yb	Lattice parameters, nm a	b	c	Comment	Reference
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
Cu_5Yb	~16.67	0.4993	...	0.4126	...	[67Pal, 71Ian]
Cu_2Yb	~33.3	0.4289	0.6897	0.7384	...	[68Ian, 71Ian]
CuYb	~50	0.7568	0.4259	0.5774	...	[71Ian, 76Deb]
(γYb)	100	0.444	...	...	At 763 °C(a)	[78Bea, 86Gsc]
(βYb)	~99.97 to 100	0.54848	...	...	At 25 °C	[78Bea, 86Gsc]
(αYb)	100	0.38799	...	0.63859	At 23 °C(b)	[78Bea, 86Gsc]

(a) The bcc (γYb) phase is stabilized by impurities, and the temperature of measurement is below the transition temperature listed in Table 2. (b) Reported to be stable below −3 °C.

Crystal Structures and Lattice Parameters

Table 3 gives the experimental values for the lattice parameters of the four Cu-Yb intermediate phases. Crystal structure information for the Cu-Yb system is summarized in Tables 4 and 5.

[72Hor] reported that $Cu_{6.5}Yb$ crystallizes with a hexagonal unit cell and with a structure closely related to that of $CaCu_5$. From detailed structural analysis, [72Hor] concluded that the difference in composition between $Cu_{6.5}Yb$ and its prototype $CaCu_5$ is due to the substitution of 18% of the Yb sites by pairs of Cu atoms, resulting in the unit cell $Cu_{5.36}Yb_{0.82}$. The presence of long-range order among the Cu atom pairs was ruled out by the absence of superstructure lines in the X-ray diffraction patterns, leading [72Hor] to conclude that the substitution occurs either at random or with short-range order.

Cu_5Yb has the hexagonal $CaCu_5$ structure, and the lattice parameters reported for this phase by [67Pal] and [71Ian] are in close agreement with one another and also with the data reported by [72Hor] for $Cu_{6.5}Yb$.

[71Ian] encountered difficulties in performing structural analysis of both Cu_9Yb_2 and Cu_7Yb_2, primarily because it was impossible to obtain good single crystals of the alloys. For Cu_9Yb_2, preliminary X-ray analysis indicated the presence of a four-fold axis and a struc-

Table 6 Cu-Yb Thermodynamic Properties

Lattice stability parameters for Cu(a)

$G^0(\text{Cu, L}) = 0$

$G^0(\text{Cu, fcc}) = -13\,054 + 9.613\,T$

Lattice stability parameters for Yb(b)

$G^0(\text{Yb, L}) = 0$

$G^0(\text{Yb, bcc}) = -7660 + 7.014\,T$

$G^0(\text{Yb, fcc}) = -9410 + 8.652\,T$

Integral molar Gibbs energies(c)

$G(\text{L}) = X(1-X)(-81\,745 + 45\,369X) + RT[X \ln X + (1-X)\ln(1-X)]$

$\Delta_f G(Cu_5Yb) = -23\,552 + 7.36\,T$

$\Delta_f G(Cu_9Yb_2) = -28\,219 + 10.42\,T$

$\Delta_f G(Cu_7Yb_2) = -32\,816 + 13.58\,T$

$\Delta_f G(Cu_2Yb) = -33\,645 + 12.95\,T$

$\Delta_f G(CuYb) = -31\,258 + 12.54\,T$

Note: Standard states: pure liquid Cu and pure liquid Yb. Gibbs energies are expressed in J/mol, and temperatures are in K. X is the atomic fraction of Yb. Mol refers to the atom as the elementary entity.
(**a**) From [Hultgren,E]. (**b**) From [83Cha]; melting and transformation temperatures are from [78Bea] and [86Gsc]. (**c**) From the phase diagram [this work].

ture resembling a tetragonal cell. Hence, lattice parameters reported for Cu_9Yb_2 in Table 3 should be regarded as tentative.

[84Tsv] reported the synthesis of the phase $Cu_{23}Yb_6$ by the application of a pressure of 7.7 GPa at high temperature to a stoichiometric mixture of the constituent elements. The resultant phase had a cubic structure with a = 1.203 nm and could be indexed on the basis of the Th_6Mn_{23}-type structure with space group $Fm\bar{3}m$.

Cu_2Yb has the orthorhombic $CeCu_2$ structure, and the accepted lattice parameters in Table 4 represent an average of the data of [68Ian] and [71Ian]. The lattice parameters reported for Cu_2Yb by [63Sto] are in discord with the values of [68Ian] and [71Ian], and this could be due to the use of lower purity Yb by [63Sto].

The equiatomic phase CuYb is the most Yb-rich phase in the Cu-Yb system and forms with the orthorhombic FeB structure. This is in contrast to the behavior of CuRE phases formed by the trivalent heavy lanthanides, which form with the cubic CsCl crystal structure. Due to the divalent state of Yb, CuYb adopts a structure type that is characteristic of equiatomic alloys of the larger size trivalent light lanthanides. Lattice parameters reported for CuYb by [76Deb] are in excellent agreement with the data of [71Ian].

Thermodynamics

No experimental thermodynamic data are available for the Cu-Yb system. In the present modeling, therefore, the experimental Cu-Yb liquidus data were utilized to derive analytical expressions for the Gibbs energy function of the liquid, as well as the Gibbs energies of formation of the various Cu-Yb intermediate phases. The basic assumptions behind the modeling are discussed in earlier evaluations (see Cu-Ce and Cu-Pr, in this issue).

In the present evaluation, data for the two eutectic points at 10 at.% Yb, 859 °C and 73.5 at.% Yb, 472 °C were utilized for deriving the integral molar excess Gibbs energy of the liquid. The resultant expression for the integral Gibbs energy of the liquid is given in Table 6. The integral molar Gibbs energies of the intermediate phases were next derived by solving for equilibrium between the liquid and the respective intermediate phases at various invariant temperatures. The Gibbs energies of the phases at various temperatures were then fitted by least-squares analysis to give the analytic expressions that are listed in Table 6.

To assess the internal consistency of the Gibbs energy functions in Table 6, the liquidus boundaries were, in turn, generated from the evaluated thermodynamic functions. The calculated liquidus, shown in Fig. 2, is in excellent agreement with the experimental phase boundaries. The Gibbs energy functions generated in the present modeling, therefore, are adequate to reproduce the phase boundaries of the experimental equilibrium diagram.

The enthalpy data from the present thermodynamic analysis are compared in Table 7 with the enthalpies of formation estimated with the semi-empirical model of Miedema [80Mie, 83Nie]. As seen in Table 7, the results from the two different approaches are in excellent agreement.

Table 7 Calculated Enthalpies of Formation of Cu-Yb Intermediate Phases vs Theoretical Estimates Based on Miedema's Model

Phase	Enthalpy of formation, kJ/mol: Present modeling	Miedema model(a)
Cu_5Yb	−23.6	−24.2
Cu_9Yb_2	−28.2	−25.2
Cu_7Yb_2	−32.8	−27.7
Cu_2Yb	−33.7	−32.2
CuYb	−31.3	−31.4

Note: Standard states are liquid Cu and liquid Yb.
(**a**) From [83Nie]. Yb is assumed to be in the divalent state in all of the phases.

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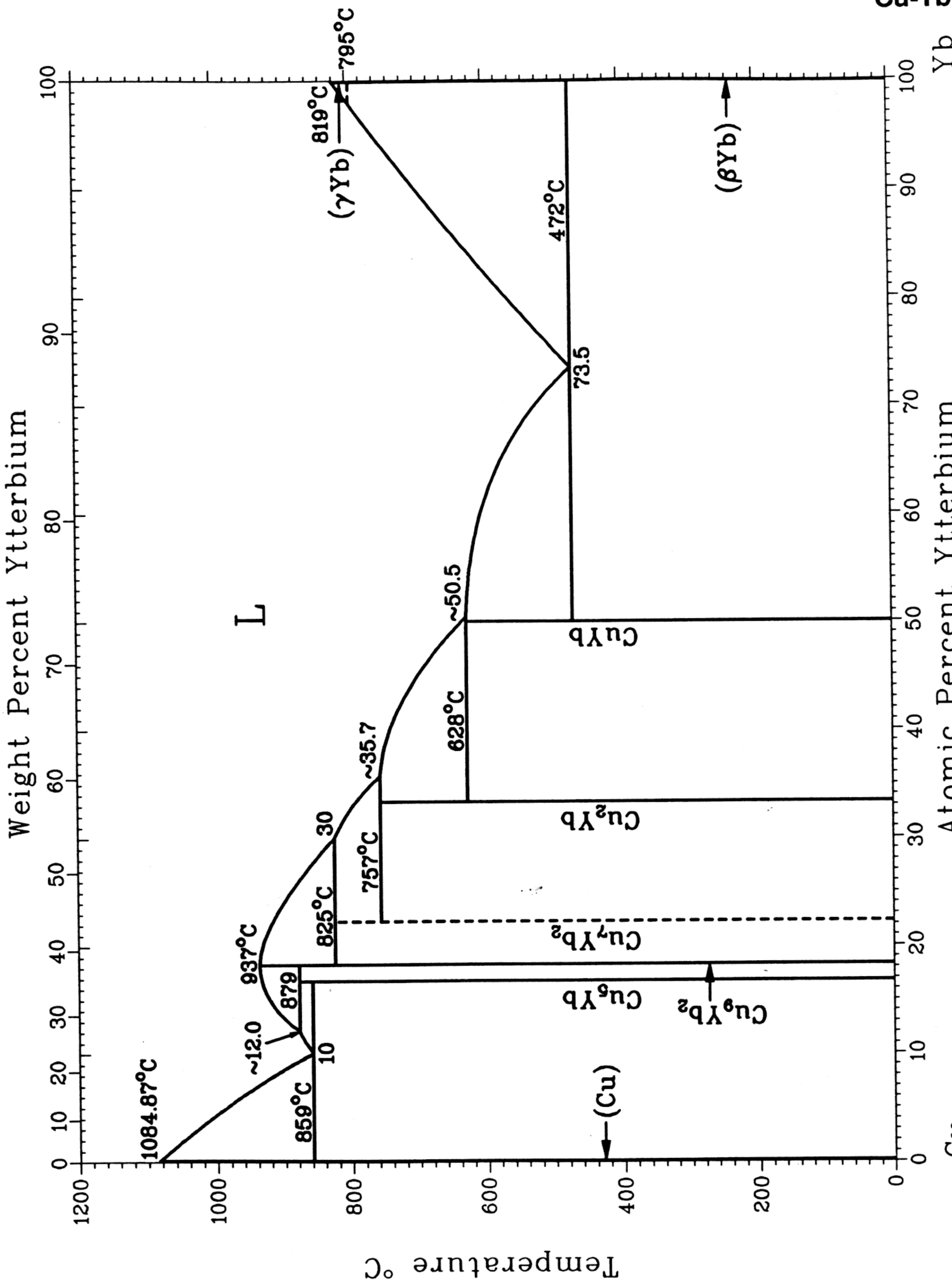

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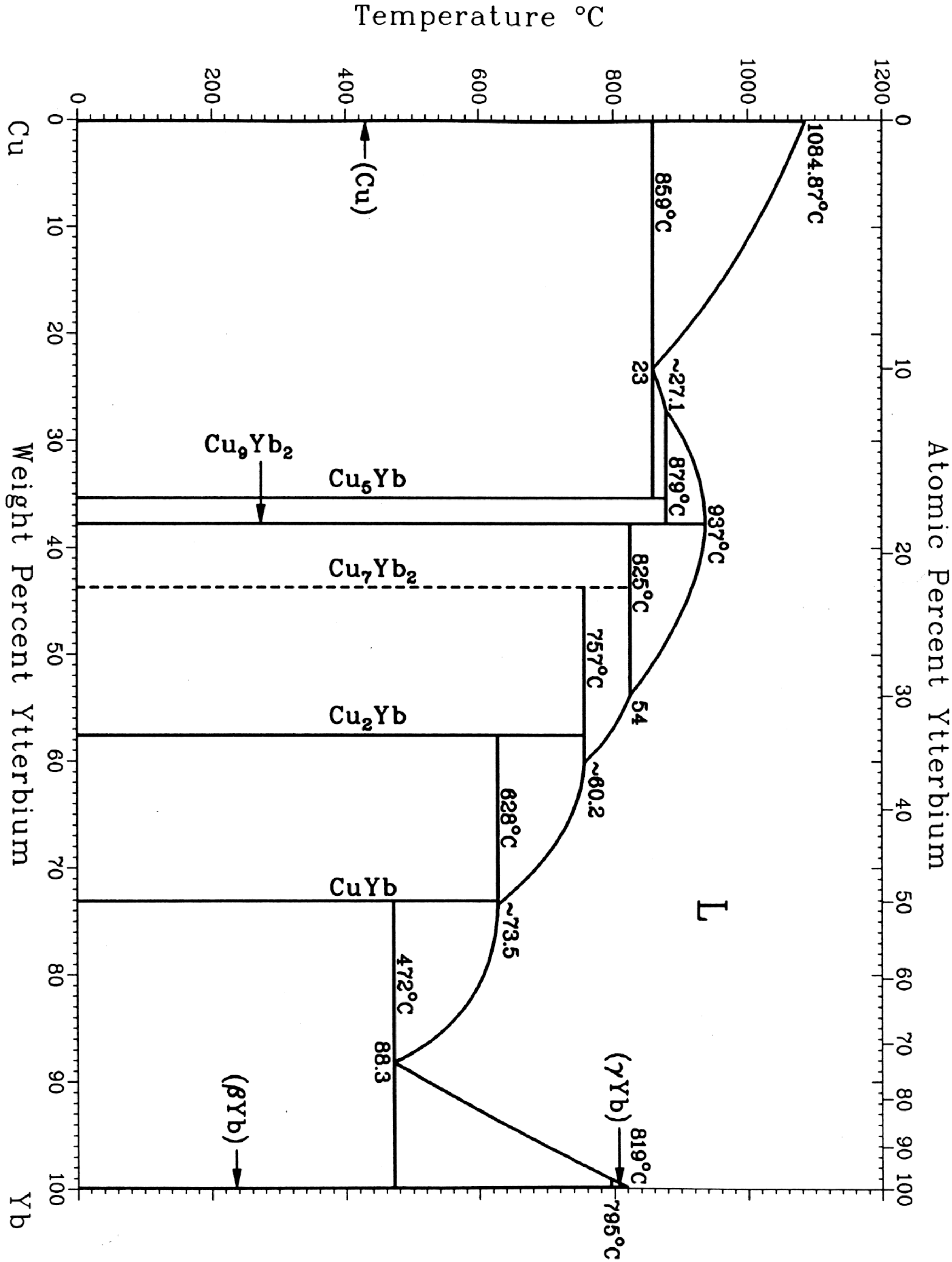

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