The Cu-Lu (Copper-Lutetium) System

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Equilibrium Diagram

No equilibrium diagram is available for the Cu-Lu system. However, the general features of the Cu-Lu phase diagram are expected to be similar to those of the other Cu-heavy lanthanide systems [85Gsc]. Moreover, melting and eutectic temperatures in the Cu-lanthanide systems, in general, are known to vary systematically across the lanthanide series (see "The Copper-Rare Earth Systems," in this issue). Accordingly, the invariant temperatures of known Cu-Lu intermediate phases were estimated by extrapolation of corresponding data for those Cu-lanthanide systems for which experimental phase diagrams are already known, using the systematic methods described by [83Gsc]. The Cu-Lu equilibrium diagram was then determined from the extrapolated invariant temperatures, in conjunction with thermodynamic considerations (see "Thermodynamics"). Figure 1 shows the schematic Cu-Lu equilibrium diagram. The melting points of pure Cu and pure Lu are accepted as 1084.87 °C [Melt] and 1663 °C [78Bea, 86Gsc], respectively. In Fig. 1, the existence of Cu_9Lu_2 and Cu_7Lu_2 is proposed solely on the basis of the presence of similar phases in the Cu-Gd [83Car], Cu-Dy [82Fra], and Cu-Er [70Bus] systems. Table 1 shows the various invariant reactions that are expected to occur in the Cu-Lu system.

Crystal Structures and Lattice Parameters

Crystal structure data for the Cu-Lu system are listed in Tables 2 and 3. Data for the pure elements are from [Massalski] and for pure Lu from [78Bea] and [86Gsc].

[71Ian] reported the cubic $AuBe_5$-type structure for Cu_5Lu. [63Sto] reported the formation of Cu_2Lu with the orthorhombic $CeCu_2$-type structure, and [60Dwi]

Fig. 1 Calculated Cu-Lu Phase Diagram

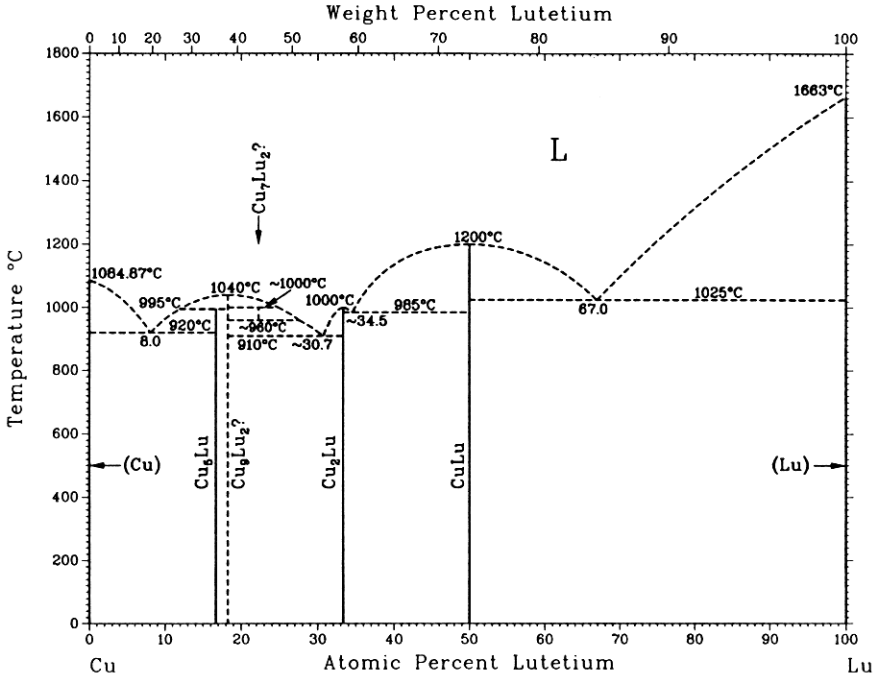

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Table 1 Special Points of the Assessed Cu-Lu Phase Diagram

Reaction	Compositions of the respective phases, at.% Lu			Temperature, °C	Reaction type	Reference
(Cu) ↔ L		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu_5Lu	8.0	~0	16.67	920	Eutectic	(a)
L + Cu_9Lu_2 ↔ Cu_5Lu	~11.8	18.18	16.67	995	Peritectic	(a)
L ↔ Cu_9Lu_2		18.18		1040	Congruent	(a)
L ↔ Cu_9Lu_2 + Cu_2Lu	~30.7	18.18	33.33	910	Eutectic	(a)
L ↔ Cu_2Lu		33.33		1000	Congruent	(a)
L ↔ Cu_2Lu + CuLu	~34.5	33.33	50.0	985	Eutectic	(a)
L ↔ CuLu		50.0		1200	Congruent	(a)
L ↔ CuLu + (Lu)	67.0	50.0	~100	1025	Eutectic	(a)
(Lu) ↔ L		100		1663	Melting point	[78Bea, 86Gsc]

Note: From Fig. 1.
(a) Compositions and temperatures were estimated from systematics of Cu-lanthanide systems, in conjunction with thermodynamic modeling (see text).

(as quoted in [Elliott]) reported the cubic CsCl-type structure for CuLu.

[84Tsv] obtained a phase with the stoichiometry $Cu_{23}Lu_6$ by the application of a constant pressure of 7.7 GPa at high temperatures to a stoichiometric mixture of the constituent elements. The resulting phase was indexed on the basis of the cubic Th_6Mn_{23} structure with space group $Fm\bar{3}m$ and with a lattice parameter a = 1.20 nm.

Thermodynamics

Thermodynamic Data

[84Wat] determined the enthalpy of mixing of liquid Cu in solid Lu at 1373 K and over the range 0 to 10.04 at.% Lu by means of high-temperature reaction calorimetry. The resulting enthalpy of mixing for liquid Cu-Lu alloys from [84Wat] are listed in Table 4. [84Wat] determined the limiting enthalpy of solution of liquid Lu in liquid Cu to be –120 kJ/mol at 1373 K.

Table 2 Cu-Lu Crystal Structure Data

Phase	Composition, at.% Lu	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF4*	$Fm\bar{3}m$	*A1*	Cu
Cu_5Lu	~16.67	*cF24*	$F\bar{4}3m$	$C15_b$	$AuBe_5$
Cu_2Lu	~33.3	*oI12*	*Imma*	...	$CeCu_2$
CuLu	~50	*cP2*	$Pm\bar{3}m$	$\bar{B}2$	CsCl
(Lu)	100	*hP2*	$P6_3/mmc$	*A3*	Mg

Table 3 Cu-Lu Lattice Parameter Data

Phase	Composition, at.% Lu	Lattice parameters, nm			Comment	Reference
		a	*b*	*c*		
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
Cu_5Lu	~16.67	0.6970	...	...	...	[71Ian]
Cu_2Lu	~33.3	0.4245	0.6627	0.7220	...	[63Sto]
CuLu	~50	0.3390	...	...	...	[Elliott]
(Lu)	100	0.35052	...	0.55494	At 25 °C	[78Bea, 86Gsc]

Table 4 Enthalpy of Mixing of Liquid Cu-Lu Alloys at 1373 K

Composition, atomic fraction Lu	Enthalpy of mixing, J/mol
0.0138	1 580
0.0425	5 010
0.0664	7 550
0.0861	9 480
0.1004	11 030

From [84Wat].

Table 5 Cu-Lu 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 Lu(b)

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

$G^0(\text{Lu, cph}) = -18\,650 + 9.633\,T$

Integral molar Gibbs energies(c)

$G(\text{L}) = X(1-X)(-79\,178 + 46\,599\,X) + RT[X \ln X + (1-X)\ln(1-X)]$

$\Delta_f G(Cu_5Lu) = -24\,862 + 7.75\,T$

$\Delta_f G(Cu_9Lu2) = -28\,462 + 9.72\,T$

$\Delta_f G(Cu_2Lu) = -15\,194 + 4.47\,T$

$\Delta_f G(CuLu) = -29\,290 + 4.64\,T$

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

Thermodynamic Modeling

Because there is no experimental phase diagram information for the Cu-Lu system, the calculation of the Cu-Lu phase relationships involved the following assumptions:

- Terminal solid solubilities are negligible.
- The liquid behaves like a subregular solution.
- Eutectic and melting temperatures represent values extrapolated from experimental data for the other Cu-lanthanide systems.

On this basis, the Cu-Cu_5Lu and CuLu-Lu eutectic temperatures were estimated to be 920 and 1025 °C, respectively, and for a first approximation, the corresponding compositions were assumed to be close to 10 and 70 at.% Lu, respectively. These compositions were inferred from experimental data for the Cu-Gd [83Car], Cu-Dy [82Fra], and Cu-Er [70Bus] systems, and the application of systematics of Cu-lanthanide systems [83Gsc] (see also "The Copper-Rare Earth Systems," in this issue). Moreover, the compositions were allowed to vary within ±3 at.% to produce a phase diagram that is generally compatible with those of the other Cu-heavy lanthanide systems.

The integral Gibbs energy of mixing of the liquid phase was derived from the extrapolated data, in conjunction with the elemental lattice stability parameters listed in Table 5. The Gibbs energies of formation of the Cu-Lu phases were then determined at the various extrapolated invariant temperatures from the Gibbs energy of mixing of the liquid. In all instances, the phases were assumed to be line compounds. Table 5 summarizes the various thermodynamic functions. The resultant Cu-Lu phase boundaries are shown in Fig. 1.

Alternately, the heat of mixing values of [84Wat] from Table 4 were optimized in conjunction with a sub-

Table 6 Calculated Enthalpies of Formation of the Cu-Lu Intermediate Phases vs Theoretical Estimates Based on Miedema's Model

Phase	Enthalpy of formation, kJ/mol Present modeling	Miedema model(a)
Cu_6Lu	-24.9	-33.4
Cu_9Lu_2	-28.5	-35.2
Cu_2Lu	-15.2	-48.8
CuLu	-29.3	-50.5

Note: Standard states are liquid Cu and liquid Lu.
(a) From [83Nie].

regular approximation to derive the following expression for the excess Gibbs energy of mixing of the liquid:

$$G^{ex}(L) = X_{Lu}(1 - X_{Lu})(-117\,757 - 47\,915\,X_{Lu}) \text{ J/mol}$$

This function is valid only in the range 0 to 10 at.% Lu, and the Cu-rich liquidus computed from this function is also shown in Fig. 1.

The enthalpies of formation from the present modeling are compared in Table 6 with those evaluated with the semi-empirical model of Miedema and co-workers [80Mie, 83Nie]. In all the cases, the Miedema values are much more exothermic than the data obtained in the present calculation.

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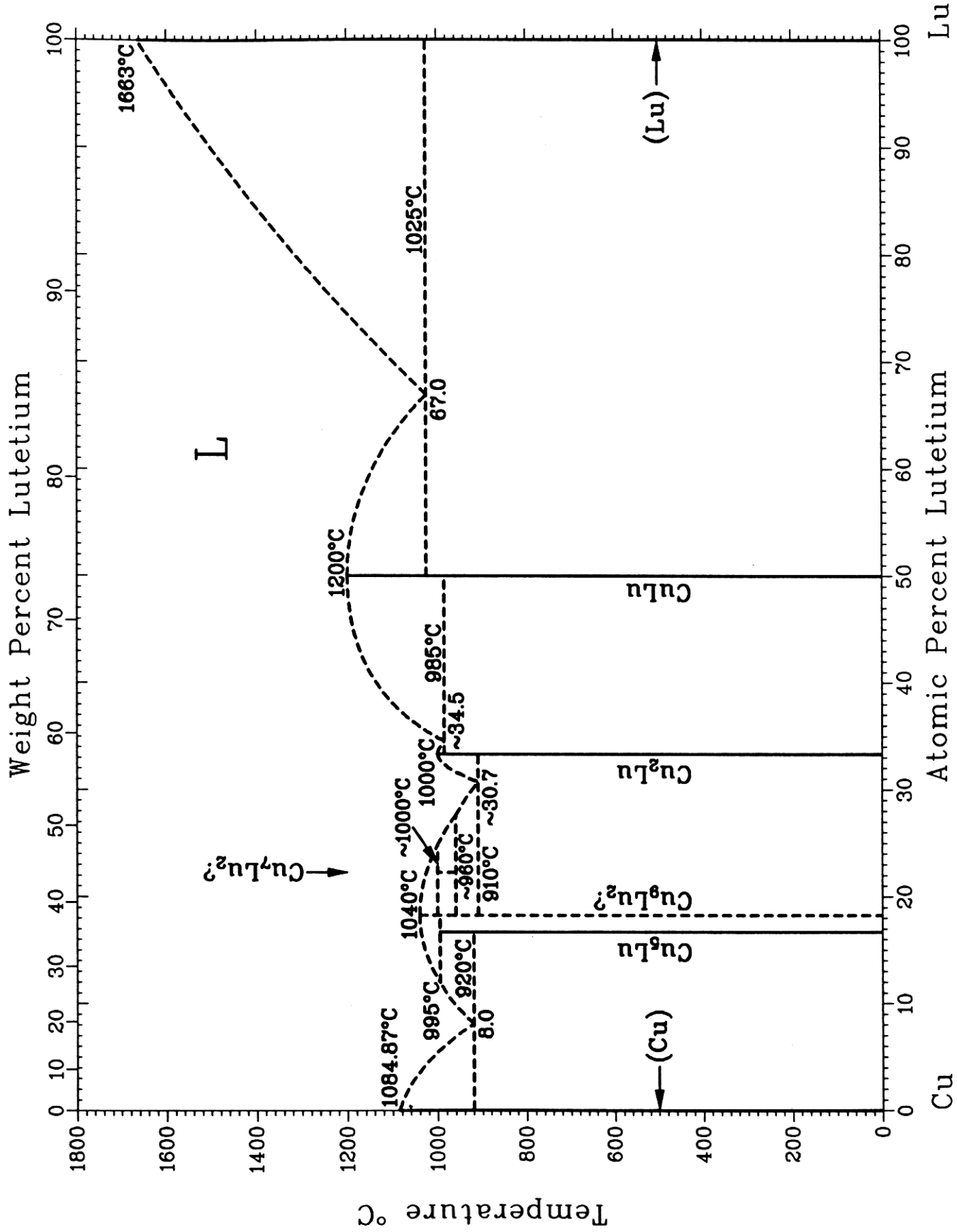

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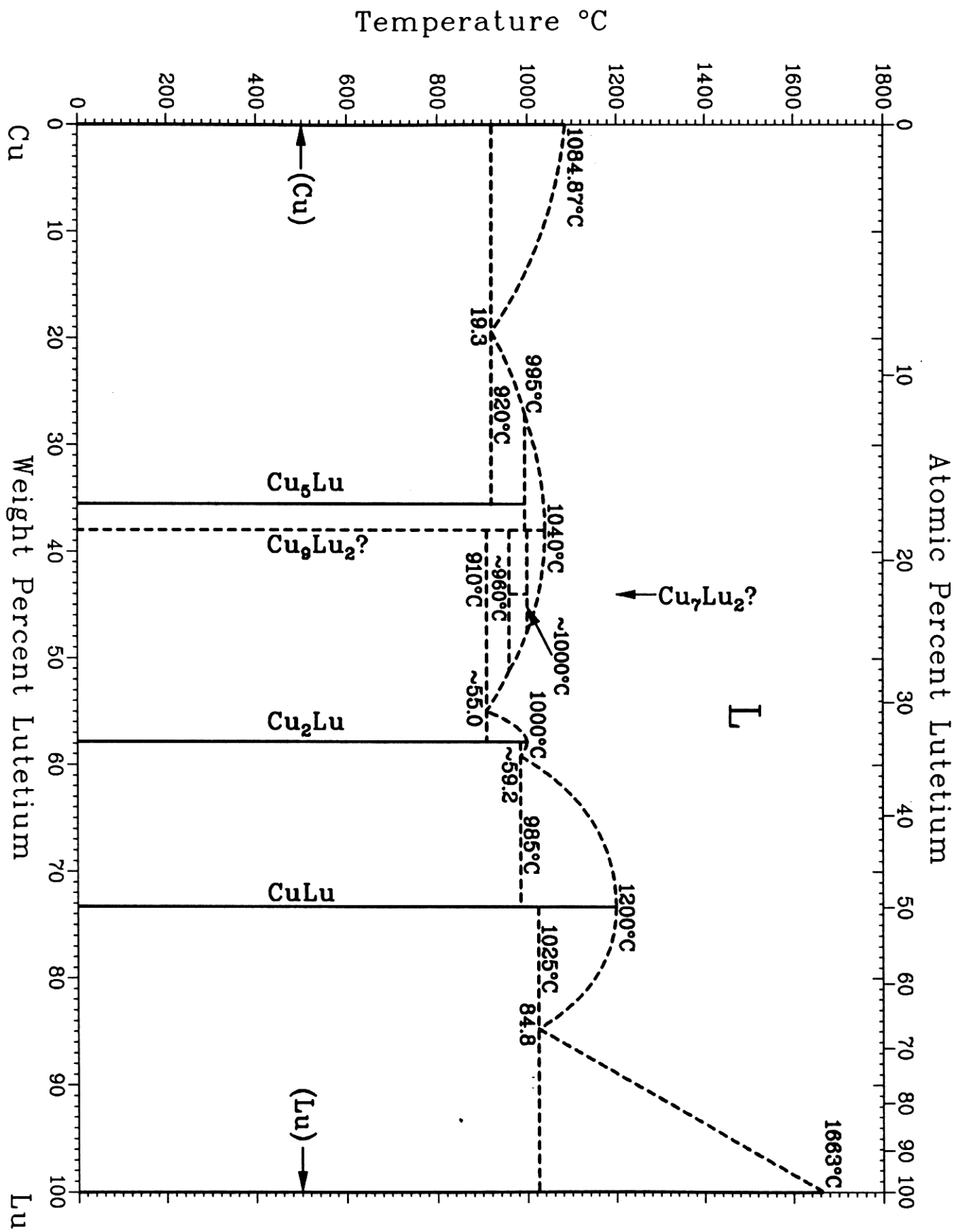

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