The Cu-Eu (Copper-Europium) System

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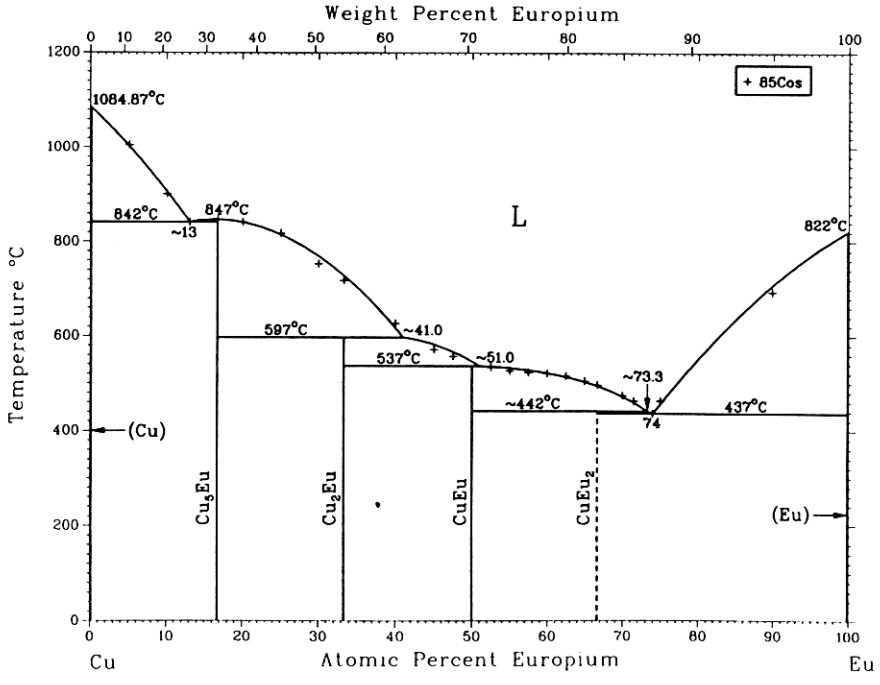
Equilibrium Diagram

The present assessment of the Cu-Eu system is based primarily on the recent phase diagram investigation of [85Cos], who reported the existence of four intermediate phases (Cu_5Eu, Cu_2Eu, CuEu, and $CuEu_2$). Of these, the existence of $CuEu_2$ has hitherto been unreported, whereas the existence of Cu_5Eu, Cu_2Eu, and CuEu has been established by other researchers. The Cu-Eu phase diagram of [85Cos] is based on differential thermal analysis (DTA), metallography, and X-ray analysis. Thermal analyses were carried out using

Fig. 1 Assessed Cu-Eu Phase Diagram



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several thermal cycles with varying heating and cooling rates to ensure reproducibility. Eu is chemically very active, and according to [85Cos], alloys containing >30 at.% Eu were oxidizable in air, the tendency to oxidize decreasing with increasing Cu content. The assessed Cu-Eu equilibrium diagram, shown in Fig. 1, has been derived from [85Cos], with minor adjustments in the elemental melting points. The phase diagram of the Cu-Eu system deviates from the systematics of Cu with the other light lanthanides in that Cu_6Eu and Cu_4Eu are absent, Cu_5Eu melts congruently, and Cu_2Eu melts peritectically. In contrast, for the other light lanthanides, the 6-to-1 as well as the 4-to-1 phases do occur, the 5-to-1 phases melt peritectically, and the 2-to-1 phases melt congruently. These differences are attributable to the fact that Eu is one of the two lanthanides that is divalent in its standard state.

Terminal Solid Solubility

[85Cos] concluded that the solid solubility of Cu in Eu is negligible, because the lattice parameter of Eu does not change significantly on alloying with Cu. Similarly, there is no evidence of any terminal solid solubility of Eu in Cu.

Table 1 Cu-Eu Experimental Liquidus Data

Composition, at.% Eu	Temperature, °C	Composition, at.% Eu	Temperature, °C
5.0	1005	55.0	527
10.0	901	57.5	523
13.0	842	60.0	521
16.7	847	62.5	516
20.0	842	65.0	505
25.0	818	66.7	497
30.0	753	70.0	475
33.3	718	71.5	464
40.0	627	74.0	437
45.0	571	75.0	464
47.5	557	90.0	694
52.5	534		

From [85Cos].

Liquidus and Solidus

Experimental data for the Cu-Eu liquidus boundaries are listed in Table 1. The melting points of (Cu) and (Eu) are accepted as 1084.87 °C [Melt] and 822 °C [78Bea, 86Gsc], respectively. However, the melting point reported by [85Cos] for Eu is 7 °C lower than the accepted melting point. This is attributable to the presence of impurities in Eu, because their Eu sample was reported to be only 99% pure.

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

Intermediate Phases

Cu_5Eu

Cu_5Eu is the most Cu-rich intermediate phase, and it forms congruently at 847 °C. The eutectic temperature at the Cu-rich end is very close to the melting temperature of Cu_5Eu. The phase adjacent to Cu_5Eu on the Eu-rich side is Cu_2Eu, which forms from the liquid and Cu_5Eu through a peritectic reaction at 597 °C. As indicated earlier, the melting behaviors of Cu_5Eu and Cu_2Eu are anomalous with regard to those of the corresponding phases formed by the trivalent light lanthanides, and this could be explained by the conclusion of [69Gsc] that Eu behaves like a divalent element in both Cu_5Eu and Cu_2Eu. Accordingly, the melting temperatures of Cu_5Eu and Cu_2Eu fall well below the values obtained by interpolation of melting data for the corresponding trivalent lanthanide phases, because the divalent state of Eu produces weaker bonding in the solid state (see "The Copper-Rare Earth Systems," in this issue).

CuEu

CuEu forms from the liquid and Cu_2Eu through a peritectic reaction at 537 °C. [69Gsc] indicated that Eu is in the trivalent state in CuEu, based on the reported lattice for this compound by [66Mor]. More recent X-ray data [76Mie1, 80Bus, 85Cos] indicate that Eu is divalent in CuEu. This is in agreement with [76Mie1], who reported that Eu should show divalent behavior in CuEu, and is further supported by the fact that the

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

Reaction		Compositions of the respective phases, at.% Eu		Temperature, °C	Reaction Type	Reference
(Cu) ↔ L		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu_5Eu	~13	~0	16.7	842	Eutectic	[85Cos]
L ↔ Cu_6Eu		16.7		847	Congruent	[85Cos]
L + Cu_5Eu ↔ Cu_2Eu	~41	16.7	33.3	597	Peritectic	[85Cos](a)
L + Cu_2Eu ↔ CuEu	~51	33.3	50	537	Peritectic	[85Cos](a)
L + CuEu ↔ $CuEu_2$	~73.3	50	66.7	~442	Peritectic	[85Cos](a)
L ↔ $CuEu_2$ + (Eu)	74	66.7	~100	437	Eutectic	[85Cos]
(Eu) ↔ L		100		822	Melting point	[78Bea, 86Gsc]

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

Table 3 Cu-Eu Experimental Lattice Parameters

Phase	Crystal structure	Lattice parameters, nm a	b	c	Reference
Cu_5Eu	Hexagonal	0.5134	...	0.4111	[67Pal](a)
		0.5138	...	0.4114	[75Ste](b)
		0.5160	...	0.4081	[85Cos](c)
Cu_2Eu	Orthorhombic	0.445	0.725	0.754	[63Sto](d)
		0.4434	0.7250	0.7553	[68Ian](e)
		0.4434	0.7234	0.7539	[85Cos](c)
CuEu	Cubic	0.3479	...	...	[66Mor](f)
	Orthorhombic	0.798	0.441	0.609	[76Mie1]
		0.7980	0.4424	0.6049	[80Bus](g)
		0.7976	0.4407	0.6054	[85Cos](c)
$CuEu_2$	Orthorhombic	0.640	0.421	1.508	[85Cos](c)

(a) Alloys made from electrolytic Cu and >99.5% pure Eu. (b) Alloys prepared from 99.99% pure Cu and 99.9% pure Eu; alloy sample contained trace amounts of elemental Cu and Eu_2O_3 as impurity phases. (c) Alloys made from 99.999% pure Cu and 99% pure Eu. (d) Alloys made from 99.999% pure Cu and 99+% pure Eu. (e) Alloys prepared from 99.9% pure Cu and 99.5 to 99.7% pure Eu. (f) Alloys prepared from >98.5% pure Cu and at least 99.8% pure Eu. (g) Alloys prepared from 99.9% pure starting materials; 5 to 10 at.% excess Eu used to compensate for Eu lost due to evaporation during arc melting.

Table 4 Cu-Eu Crystal Structure Data

Phase	Composition, at.% Eu	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF4*	$Fm\bar{3}m$	*A1*	Cu
Cu_5Eu	~16.67	*hP6*	*P6/mmm*	$D2_d$	$CaCu_5$
Cu_2Eu	~33.3	*oI2*	*Imma*	...	$CeCu_2$
CuEu	~50	*oP8*	*Pnma*	*B27*	FeB
$CuEu_2$	~66.67	*oP12*	*Pnma*	...	Ca_2Cu
(Eu)	100	*cI2*	$Im\bar{3}m$	*A2*	W

Table 5 Cu-Eu Lattice Parameter Data

Phase	Composition, at.% Eu	Lattice parameters, nm a	b	c	Comment	Reference
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
Cu_5Eu	~16.67	0.5136	...	0.4113	...	[67Pal, 75Ste]
Cu_2Eu	~33.3	0.4439	0.7245	0.7544	...	[63Sto, 68Ian, 85Cos]
CuEu	~50	0.7978	0.4416	0.6052	...	[80Bus, 85Cos]
$CuEu_2$	~66.67	0.640	0.421	1.508	...	[85Cos]
(Eu)	100	0.45827	...	...	At 25 °C	[78Bea, 86Gsc]

melting temperature of CuEu lies well below the systematic trend observed for the melting temperatures of the normal trivalent lanthanide phases.

$CuEu_2$

$CuEu_2$ is reported by [85Cos] to be the most Eu-rich intermediate phase in the Cu-Eu system. Phases with this stoichiometry have not been reported for any of the other rare earths. According to [85Cos], the existence of this phase was revealed by micrographic examination of alloys with compositions between 60 and 74 at.% Eu, and subsequently corroborated by powder X-ray diffraction and microprobe analysis of homogeneous alloys containing ~67 at.% Eu. The peritectic melting temperature of $CuEu_2$ is close to the eutectic temperature at the Eu-rich end, and this was cited by [85Cos] as the reason why initial thermal analysis failed to distinguish two separate thermal effects. Subsequent thermal analysis of Cu-67 at.% Eu alloys, annealed for two months at ~407 °C, revealed thermal arrests at 442 °C, corresponding to the formation of $CuEu_2$. According to [85Cos], such behavior is analogous to that observed in the Ca-Cu system [84Cha], where the temperature of formation of the isostoichiometric phase Ca_2Cu is close to the eutectic temperature at the Ca-rich end.

Crystal Structures and Lattice Parameters

Table 3 gives the experimental values for the lattice parameters of the four Cu-Eu intermediate phases. The accepted lattice parameter and crystal structure data for the four phases are summarized in Tables 4 and 5.

Fig. 2 Assessed vs Calculated Cu-Eu Phase Diagram

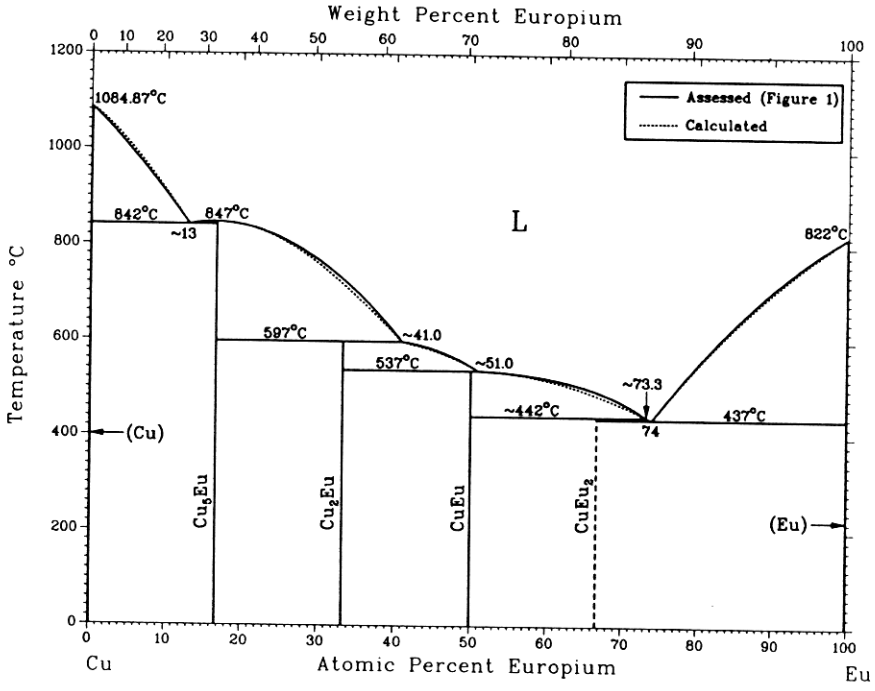

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Table 6 Cu-Eu Thermodynamic Properties

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 Eu(b)

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

$G^0(\text{Eu, bcc}) = -9210 + 8.41\,T$

Integral molar Gibbs energies(c)

$G(\text{L}) = X(1-X)(-48\,406 + 18\,100\,X + RT[X \ln X + (1-X)\ln(1-X)]$

$\Delta_f G(\text{Cu}_5\text{Eu}) = -23\,578 + 11.65\,T$

$\Delta_f G(\text{Cu}_2\text{Eu}) = -29\,800 + 17.73\,T$

$\Delta_f G(\text{CuEu}) = -30\,317 + 19.51\,T$

$\Delta_f G(\text{CuEu}_2) = -14\,008 + 2.72\,T$

Note: Standard states: pure liquid Cu and pure liquid Eu. Gibbs energies are expressed in J/mol, and temperatures are in K. X is the atomic fraction of Eu. Mol refers to the atom as the elementary entity.

(**a**) From [Hultgren,E]. (**b**) From [83Cha]; melting temperatures from [78Bea] and [86Gsc]. (**c**) From the phase diagram [this work].

Cu_5Eu has the hexagonal $CaCu_5$ structure, and the lattice parameters reported for this phase by [67Pal] and [75Ste] are in close agreement. However, the data of [85Cos] is in discord with the values of [67Pal] and [75Ste]; [85Cos] attributed this to the existence of solid solubility in Cu_5Eu. Moreover, the Eu used by [85Cos] had a lower purity.

Cu_2Eu has the orthorhombic $CeCu_2$ structure, and in this instance, the lattice parameters reported by the various authors are in reasonably good accord.

[66Mor] reported that the equiatomic phase CuEu forms with the cubic CsCl structure. However, subsequent reports by [76Mie1], [80Bus], and [85Cos] show that CuEu is isostructural with the corresponding 1-to-1 phases of the light lanthanides and crystallizes with the orthorhombic FeB structure. It was shown that the formula unit volumes of the Cu-lanthanide 1-to-1 phases with the FeB structure, as well as those with the CsCl structure, lie on straight lines and increase linearly with increasing trivalent ionic radius of the lanthanide element (see "The Copper-Rare Earth Systems," in this issue). In the present system, the data point for CuEu with the CsCl structure from [66Mor] shows a deviation in the opposite direction to that expected for the larger size divalent Eu or even trivalent Eu (its lattice parameter is slightly smaller than that of CuTb), whereas the data for CuEu with the FeB structure show a deviation in the correct direction, i.e., toward larger formula unit volumes. It is most likely that the CsCl structure observed for CuEu by [66Mor] is due to stabilization by impurities and therefore, is not an equilibrium structure for

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

Phase	Enthalpy of formation, kJ/mol Present modeling	Miedema model(a)
Cu_5Eu	−23.6	−22.6
Cu_2Eu	−29.8	−28.8
CuEu	−30.3	−27.4
$CuEu_2$	−14.0	−21.6

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

CuEu. As such, the FeB structure is accepted for CuEu, and the accepted lattice parameters in Table 5 represent an average of the data of [80Bus] and [85Cos].

[85Cos] have indicated that the X-ray pattern for $CuEu_2$ could be indexed on the basis of the orthorhombic Ca_2Cu-type structure and that the volume contraction on formation of this phase is similar to that observed for Ca_2Cu.

Thermodynamics

No experimental thermodynamic data are available for the Cu-Eu system. In the present modeling, therefore, the experimental Cu-Eu 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-Eu 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 13 at.% Eu, 842 °C and 74 at.% Eu, 437 °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 the 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. The enthalpies of formation of Cu_5Eu, Cu_2Eu, CuEu, and $CuEu_2$, evaluated with the semi-empirical model of Miedema [76Mie2, 80Mie, 83Nie], are compared in Table 7 with the data obtained in the present modeling. The results show excellent agreement, except for $CuEu_2$, for which the two estimates differ by ~9 kJ/mol.

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

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

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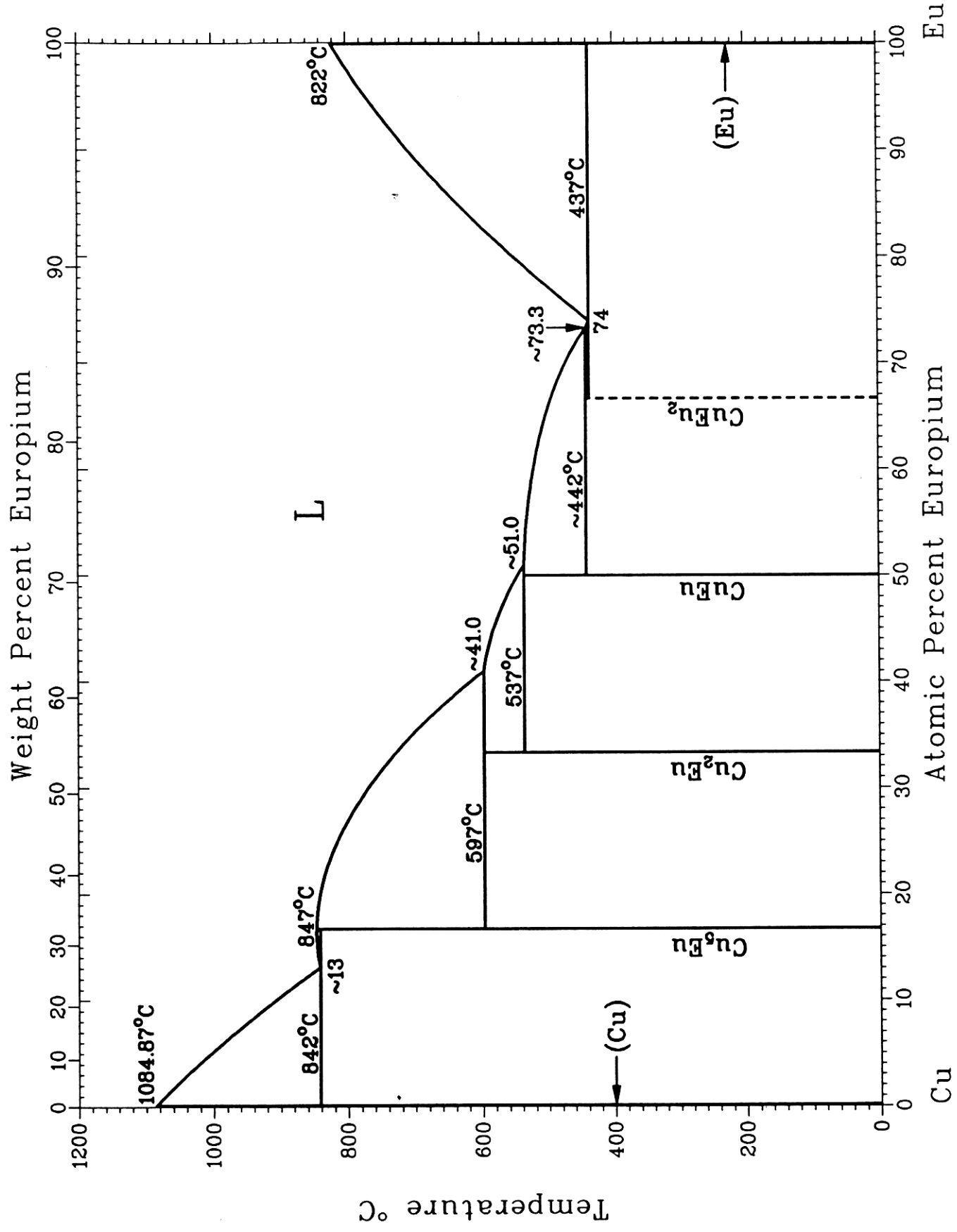

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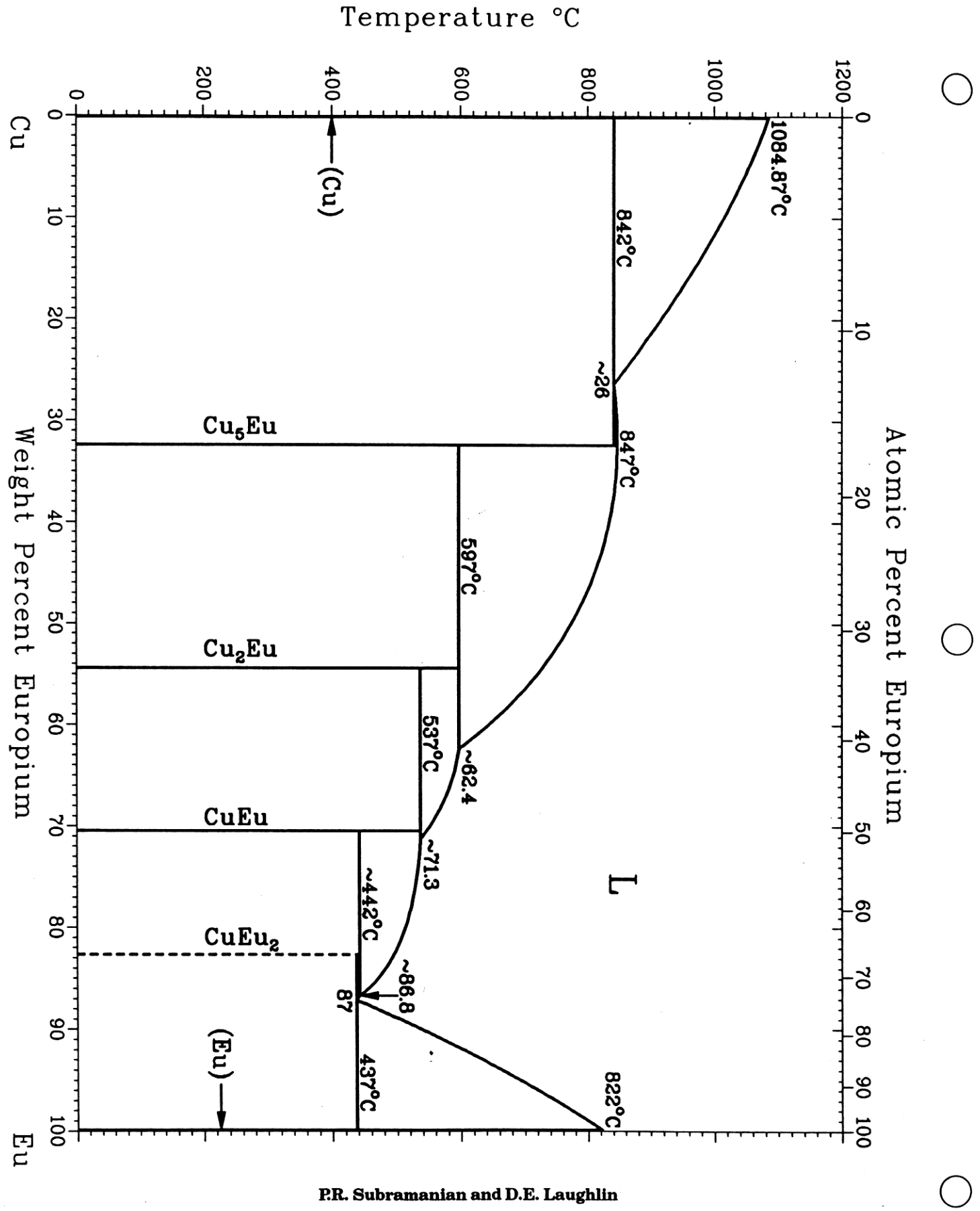

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