The Cu-Pm (Copper-Promethium) System

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

Equilibrium Diagram

No equilibrium diagram is available for the Cu-Pm system. However, the general pattern of Cu-Pm phase relationships is expected to be compatible with those of the other Cu-light lanthanide systems [85Gsc]. Accordingly, the existence of Cu_6Pm, Cu_5Pm, Cu_4Pm, Cu_7Pm_2, Cu_2Pm, and CuPm is proposed, because of the presence of similar phases in the Cu-Ce, Cu-Pr, Cu-Nd, and Cu-Sm systems (in this issue). Moreover, melting and eutectic temperatures in the Cu-lanthanide systems show a systematic variation across the lanthanide series (see "The Copper-Rare Earth Systems," in this issue). On this basis, invariant temperatures were estimated for the proposed Cu-Pm intermediate phases by interpolation of corresponding data for the Cu-Ce, Cu-Pr, Cu-Nd, and Cu-Sm systems. The interpolated invariant temperatures were then combined with thermodynamic modeling to derive the Cu-Pm phase diagram. Figure 1 shows the resulting Cu-Pm equilibrium diagram. The melting points of pure Cu and pure αPm are accepted as 1084.87 °C [Melt] and 1042 °C [78Bea, 86Gsc], respectively. The α ↔ β transformation temperature of Pm is accepted as 890 °C [78Bea, 86Gsc].

Table 1 Cu-Pm Crystal Structure Data

Phase	Composition, at.% Pm	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Cu_6Pm	~14.2	*oP*28	*Pnma*	...	$CeCu_6$
Cu_5Pm	~16.67	*hP*6	*P*6/*mmm*	$D2_d$	$CeCu_5$
Cu_4Pm	~20.0	*oP*20	*Pnnm*	...	$CeCu_4$
Cu_2Pm	~33.3	*oI*12	*Imma*	...	$CeCu_2$
CuPm	~50	*oP*8	*Pnma*	*B*27	FeB
(αPm)	100	*hP*4	$P6_3/mmc$	*A*3′	αLa
(βPm)	100	*cI*2	$Im\bar{3}m$	*A*2	W

Fig. 1 Calculated Cu-Pm Phase Diagram

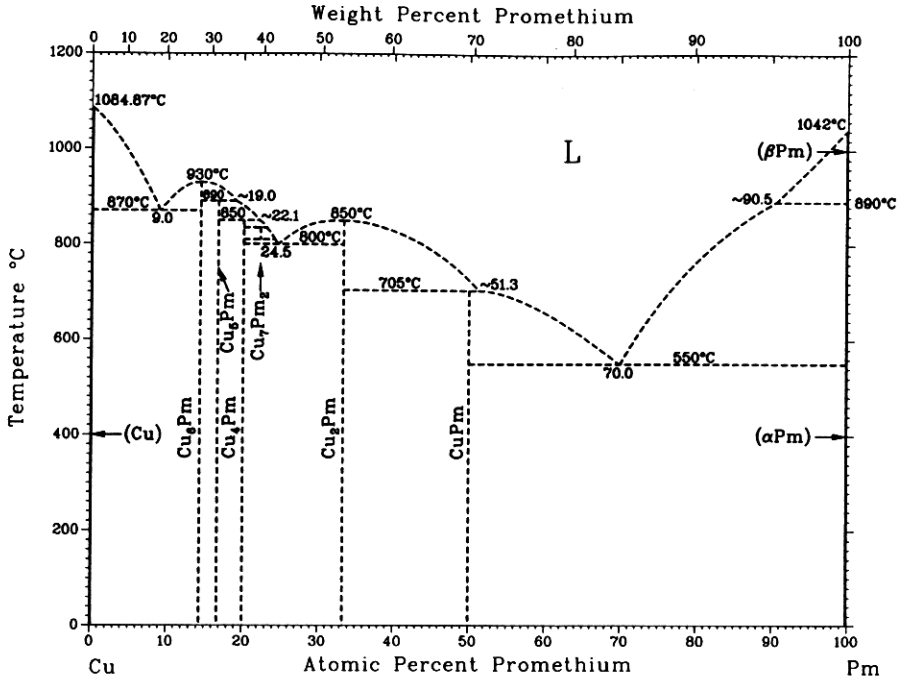

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Table 2 Cu-Pm Lattice Parameter Data

Phase	Composition, at.% Pm	Lattice parameters, nm a	b	c	Comment	Reference
(Cu)	0	0.36146	...	...	At 24 °C	[Massalski]
Cu_6Pm	~14.2	0.807	0.505	1.008	...	(a)
Cu_5Pm	~16.67	0.509	...	0.410	...	(a)
Cu_4Pm	~20.0	0.446	0.803	0.910	...	(a)
Cu_2Pm	~33.3	0.437	0.696	0.740	...	(a)
CuPm	~50	0.722	0.454	0.553	...	(a)
(αPm)	100	0.365	...	1.165	At 25 °C	[78Bea, 86Gsc]
(βPm)	100	...	...	...	...	[78Bea, 86Gsc]

(a) Lattice parameters were estimated from the systematics of crystallographic data for the Cu-lanthanide systems (see text).

Crystal Structure and Lattice Parameters

Crystal structure and lattice parameter data are listed in Tables 1 and 2. Lattice parameters for the proposed Cu-Pm intermediate phases were estimated on the basis of the systematics of crystallographic data in the Cu-lanthanide systems (see "The Copper-Rare Earth Systems," in this issue). Crystal structure and lattice parameter data for pure Cu are from [Massalski] and for pure αPm are from [78Bea] and [86Gsc]. There is no lattice parameter data for high-temperature cubic βPm.

Thermodynamics

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

- Terminal solid solubilities are negligible.
- The liquid behaves like a subregular solution.
- Eutectic and melting temperatures represent values interpolated from experimental data for the other Cu-lanthanide systems. On this basis, the Cu-Cu_6Pm, Cu_4Pm-Cu_2Pm, and CuPm-αPm eutectic temperatures were estimated to be 870, 800, and 550 °C, respectively. For a first approximation, the corresponding compositions were assumed to be close to 9, 25, and 70 at.% Pm, respectively. These compositions were inferred from the Cu-Ce, Cu-Pr, Cu-Nd, and Cu-Sm phase diagrams.

Table 3 Cu-Pm Thermodynamic Properties

Lattice stability parameters for Cu(a)

$G^0(Cu, L) = 0$

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

Lattice stability parameters for Pm(b)

$G^0(Pm, L) = 0$

$G^0(Pm, bcc) = -7550 + 5.741\,T$

$G^0(Pm, dcph) = -10\,450 + 8.234\,T$

Integral molar Gibbs energies(c)

$G(L) = X(1-X)(-96\,042 + 58\,830\,X) + RT[X \ln X + (1-X) \ln (1-X)]$

$\Delta_f G(Cu_6Pm) = -21\,148 + 5.25\,T$

$\Delta_f G(Cu_5Pm) = -22\,304 + 5.06\,T$

$\Delta_f G(Cu_4Pm) = -18\,484 + 0.24\,T$

$\Delta_f G(Cu_2Pm) = -39\,583 + 14.83\,T$

$\Delta_f G(CuPm) = -31\,238 + 9.13\,T$

Note: Standard states: pure liquid Cu and pure liquid Pm. Free energies are expressed in J/mol, and temperatures are in K. X is the atomic fraction of Pm. 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].

The thermodynamic functions associated with elemental Cu, αPm, and βPm are listed in Table 3. These functions were used in conjunction with the above assumptions to derive the excess Gibbs energy of mixing of the liquid phase. The Gibbs energies of formation of the Cu-Pm phases were then evaluated by solving for equilibrium between the liquid and the respective alloy phases at the various interpolated invariant temperatures. In all instances, the phases were assumed to be line compounds. The resulting thermodynamic functions are summarized in Table 3. The Cu-Pm liquidus boundaries generated from the Gibbs energy functions in Table 3 are shown in Fig. 1.

The enthalpy data obtained in the present modeling are compared in Table 4 with the enthalpies of formation calculated on the basis of the semi-empirical model of Miedema and co-workers [80Mie, 83Nie]. In all instances, the Miedema values are much more exothermic than the data obtained in the present calculation.

Table 4 Calculated Enthalpies of Formation of the Cu-Pm Intermediate Phases vs Theoretical Estimates Based on Miedema's Model.

Phase	Enthalpy of formation, kJ/mol Present modeling	Miedema model(a)
Cu_6Pm	−21.2	−29.5
Cu_5Pm	−22.3	−32.1
Cu_4Pm	−18.5	−35.7
Cu_2Pm	−39.6	−45.2
CuPm	−31.2	−44.5

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

Cited References

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80Mie: A.R. Miedema, P.F. de Chatel, and F.R. de Boer, "Cohesion in Alloys-Fundamentals of a Semi-Empirical Method," *Physica B, 100*, 1-28 (1980). (Thermo; Theory)

83Cha: M.W. Chase, "Heats of Transition of the Elements," *Bull. Alloy Phase Diagrams, 4*(1), 123-124 (1983). (Thermo; Compilation)

83Nie: A.K. Niessen, F.R. de Boer, R. Boom, P.F. de Chatel, W.C.M. Mattens, and A.R. Miedema, "Model Predictions for the Enthalpy of Formation of Transition Metal Alloys II," *Calphad, 7*(1), 51-70 (1983). (Thermo; Theory)

85Gsc: K.A. Gschneidner, Jr., private communication (1985). (Equi Diagram; Review)

86Gsc: K.A. Gschneidner, Jr. and F.W. Calderwood, "Intra Rare Earth Binary Alloys: Phase Relationships, La tice Parameters and Systematics," in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 8, K.A. Gschneidner, Jr. and L. Eyring, Ed., North-Holland Physics Publishing Co., Amsterdam, 1-161 (1986). (Equi Diagram, Crys Structure; Compilation)

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

Cu-Pm evaluation contributed by **P.R. Subramanian,** Materials Science Division, Universal Energy Systems, Incorporated, 4401 Dayton, OH 45435 and **D.E. Laughlin,** Department of Metallurgical Engineering and Materials Science, Carnegie Mellon University, Pittsburgh, PA 15213.

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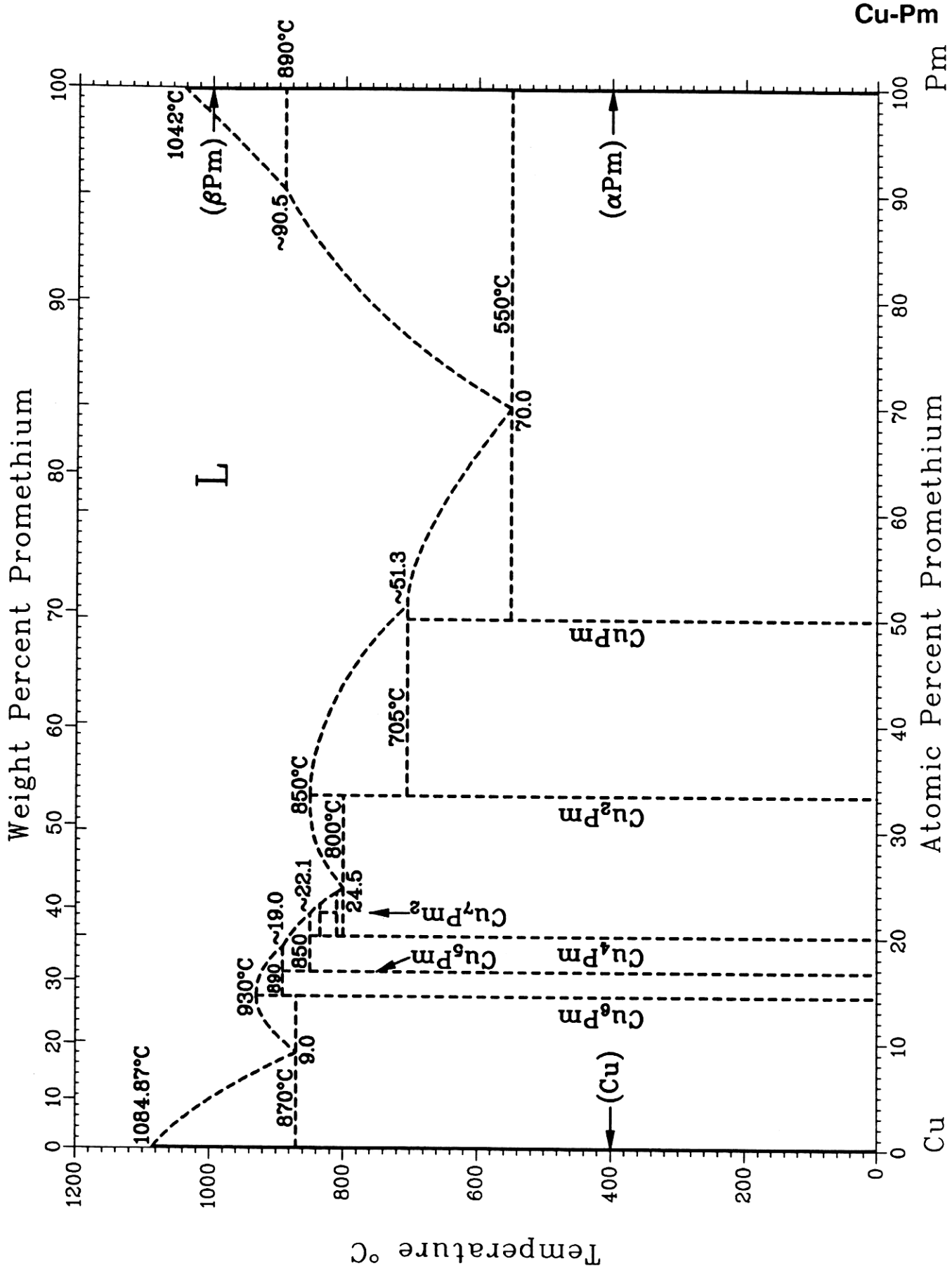

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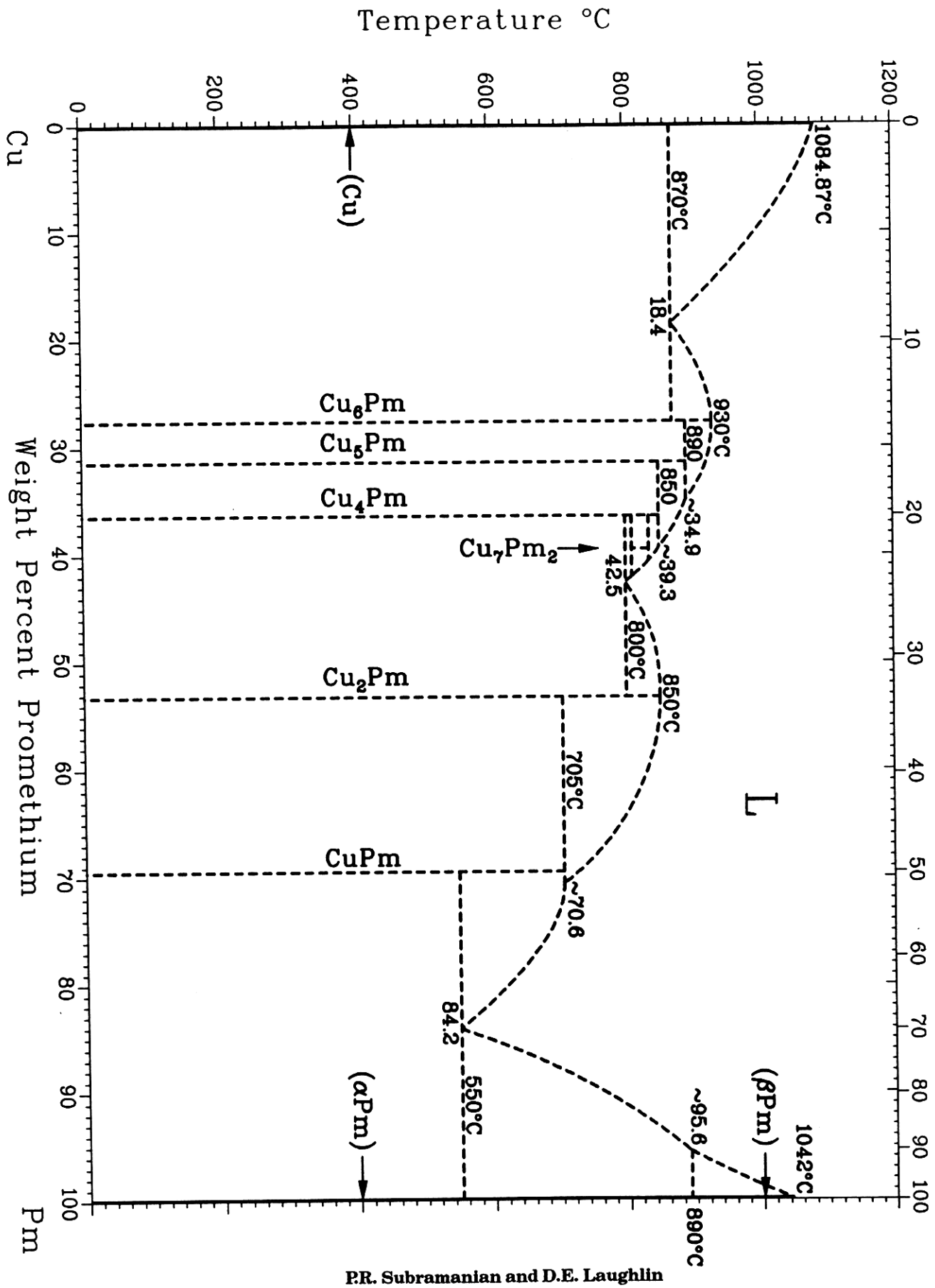

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