The Cu-Sc (Copper-Scandium) System

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Equilibrium Diagram

[70Zak] determined the solid solubility of Sc in Cu in the range 600 to 865 °C from hardness measurements on alloys prepared from 99.6% pure Sc. They reported a maximum solubility of ~0.5 at.% Sc at the eutectic temperature of 865 °C, and their solubility data are shown in Table 1.

[70Sav] investigated the Cu-Sc system by means of metallography, differential thermal analysis (DTA), dilatometry, and X-ray diffraction. The authors observed the congruent formation of Cu_4Sc and CuSc at 925 and 1125 °C, respectively, and the peritectic formation of Cu_2Sc at 890 °C. Three eutectics were reported: Cu-Cu_4Sc (865 °C, ~13 at.% Sc); Cu_4Sc-Cu_2Sc (875 °C, ~30 at.% Sc), and CuSc-(αSc) (875 °C, ~71 at.% Sc). [70Sav] reported the terminal solid solubility of Sc in Cu to be ~0.5 at.% Sc and that of Cu in Sc to be <1 at.% Cu.

[78Mar] investigated the Cu-Sc system in the region 0 to 80 at.% Sc and proposed the congruent formation of Cu_4Sc, Cu_2Sc, and CuSc at 975, 990, and 1125 °C, respectively. The authors also reported that Cu_4Sc forms over a wide range of homogeneity (~4 at.%) and

Table 1 Solubility of Sc in (Cu)

Temperature, °C	Solubility(a), at.% Sc
600	0.04
700	0.13
800	0.28
850	0.42
865(b)	0.49

From [70Zak].
(a) Solid solubility limits based on hardness measurements on alloys with compositions of 0.05, 0.2, 0.4, 0.47, and 1.05 wt.% Sc. (b) Cu-rich terminal eutectic temperature.

Fig. 1 Assessed Cu-Sc Phase Diagram

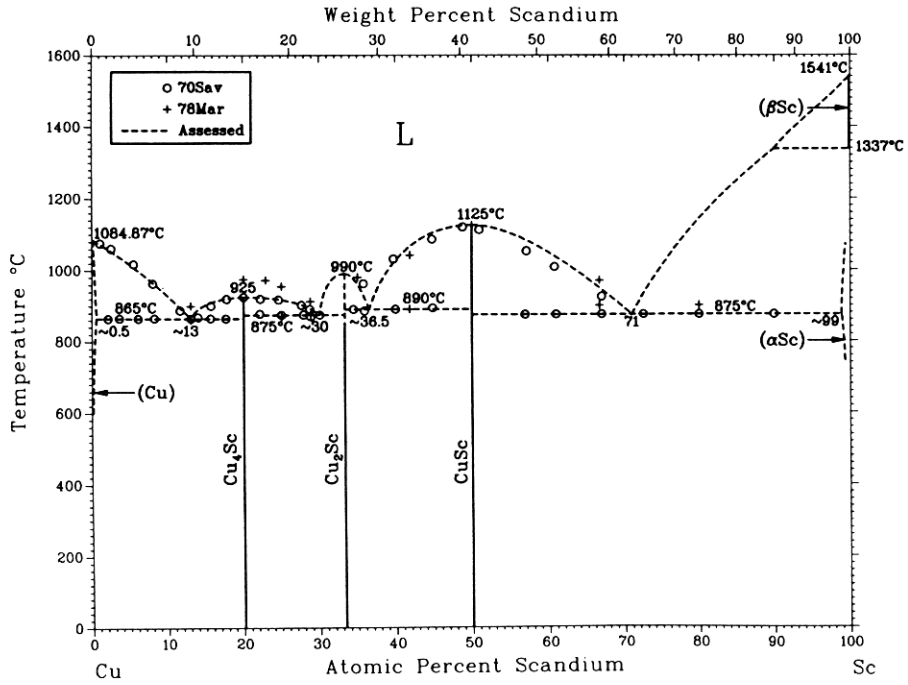

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Table 2 Special Points of the Assessed Cu-Sc Phase Diagram

Reaction	Compositions of the respective phases, at.% Sc			Temperature, °C	Reaction type	Reference
(Cu) ↔ L		0.0		1084.87	Melting point	[Melt]
L ↔ (Cu) + Cu_4Sc	~13	~0.5	20	865	Eutectic	[70Sav]
L ↔ Cu_4Sc		20		925	Congruent	[70Sav]
L ↔ Cu_4Sc + Cu_2Sc	~30	20	33.3	875	Eutectic	[70Sav]
L ↔ Cu_2Sc		33.3		990	Congruent	[78Mar]
L ↔ Cu_2Sc + CuSc	36.5	33.3	50	890	Eutectic	[70Sav, 78Mar](b)
L ↔ CuSc		50		1125	Congruent	[70Sav, 78Mar]
L ↔ CuSc + (αSc)	71	50	~99	875	Eutectic	[70Sav]
(αSc) ↔ (βSc)		~100		1337	Allotropic	[78Bea, 86Gsc1]
(βSc) ↔ L		100		1541	Melting point	[78Bea, 86Gsc1]

(a) Compositions for the phases are given in the order they appear in column 1. (b) Liquidus composition was estimated from Fig. 1.

that CuSc occurs at an off-stoichiometric composition of ~35 at.% Sc. [78Mar] observed the formation of four eutectics: Cu-Cu_4Sc (860 °C, ~11 at.% Sc); Cu_4Sc-Cu_2Sc (870 °C, ~32 at.% Sc); Cu_2Sc-CuSc (890 °C, ~39 at.% Sc); and CuSc-(αSc) (900 °C, ~71 at.% Sc). According to [78Mar], the terminal solid solubility of Sc in Cu is negligible, whereas the solubility of Cu in Sc is estimated to be ~1.6 at.% Cu at 800 °C.

The Cu-Sc phase relationships of [70Sav] are in general agreement with those of [78Mar], with the exception of the region 30 to 40 at.% Sc. The major point of contention is the melting behavior of Cu_2Sc; [70Sav] reported the peritectic formation of Cu_2Sc at 890 °C, whereas [78Mar] reported the congruent formation of Cu_2Sc at 990 °C, as well as the occurrence of a Cu_2Sc-CuSc eutectic at 39 at.% Sc and 890 °C. In the absence of other experimental phase diagram information, one has to rely on the systematics of alloying behavior of Cu with the rare earths [85Gsc] to resolve the conflicting data (see also "The Copper-Rare Earth Systems," in this issue). In this context, the melting behavior of Cu_2Sc, as reported by [78Mar], is in agreement with the data of Cu_2Gd [83Car], Cu_2Dy [82Fra], and Cu_2Y [61Dom] (also see "The Copper-Rare Earth Systems" and Cu-Gd, in this issue, and [81Cha], respectively). The alloying behavior of Sc is expected to be analogous to that of Y and Gd (a member of the heavy lanthanide group). As such, Cu_2Sc is accepted as a congruently melting phase, with the melting temperature accepted from [78Mar] as 990 °C. The presence of Cu_2Sc as a congruently melting phase is corroborated by the results of [84Wat], who reported the synthesis of Cu_2Sc by heating appropriate amounts of pure Cu and pure Sc in a high-temperature calorimeter.

Figure 1 shows a composite of the available experimental data from [70Sav] and [78Mar]. The assessed Cu-Sc equilibrium diagram, also shown in Fig. 1, is drawn from the data of [70Sav], primarily because of the presence of a larger number of data points in their investigation. Because of the lack of experimental data points for the liquidus in the regions L/L + Cu_2Sc, Cu_2Sc + L/L, and L/L + (Sc), these phase boundaries were calculated from thermodynamic analysis (discussed in a later section). Further experimental work needs to be done in the region close to the stoichiometry of Cu_2Sc in order to delineate the L/L + Cu_2Sc and Cu_2Sc + L/L liquidus boundaries. Elemental melting points have been adjusted in Fig. 1 in accordance with the accepted values listed in [Melt] for Cu and in [78Bea] and [86Gsc1] for Sc. The (α → β) transformation temperature of Sc is accepted as 1337 °C [78Bea, 86Gsc1]. Table 2 shows composition and temperature data at the various invariant points.

Crystal Structures and Lattice Parameters

Crystal structures, accepted lattice parameter data, and related parameters for the various phases are summarized in Tables 3 and 4. Data for pure Cu are from [Massalski], and for pure Sc from [78Bea] and [86Gsc1].

Crystal structure and lattice parameter data have not been reported for Cu_4Sc. [67Dwi] reported that Cu_2Sc forms with the tetragonal $MoSi_2$-type structure. Although CuSc is confirmed to crystallize with the cubic CsCl structure, there is some disagreement in the reported lattice parameter data for this phase. [64Gla] determined the lattice constant of CuSc to be 0.324 nm; their investigations were conducted on arc-melted alloys prepared from electrolytic Cu and 98.2 wt.% pure Sc. On the other hand, [74Mar] reported an unusually large value of 0.48 nm for the lattice parameter of CuSc; no alloy purity was given. The CuSc lattice parameter data of [62Ald] and [77Sie] concur; their alloys were prepared from metals with a purity of at least 99.95%, which is considerably higher than that of [64Gla]. As such, their data are accepted in Table 4.

Thermodynamics

Thermodynamic Data

[84Wat] determined enthalpies of mixing of liquid Cu in solid Sc at 1373 K and over the range 0 to 72.25 at.% Sc by means of high-temperature reaction calorimetry.

Table 3 Cu-Sc Crystal Structure Data

Phase	Composition, at.% Sc	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF4*	$Fm\bar{3}m$	*A1*	Cu
Cu_2Sc	~33.3	*tI6*	*I4/mmm*	$C11_b$	$MoSi_2$
CuSc	~50	*cP2*	$Pm\bar{3}m$	*B2*	CsCl
(αSc)	100	*hP2*	$P6_3/mmc$	*A3*	Mg
(βSc)	100	*cI2*	$Im\bar{3}m$	*A2*	W

Table 4 Cu-Sc Lattice Parameters

Phase	Composition at.% Sc	Lattice parameters, nm *a*	*c*	Comment	Reference
(Cu)	0	0.36146	...	At 25 °C	[Massalski]
Cu_2Sc	~33.3	0.3290	0.8388	...	[67Dwi]
CuSc	~50	0.3256	...	...	[62Ald, 77Sie]
(αSc)	100	0.33088	0.52680	At 25 °C	[78Bea, 86Gsc1]
(βSc)	100	...	...	>1337 °C(a)	[78Bea, 86Gsc1]

(a) [Massalski] reported a value of 0.4541 nm for the lattice parameter of (βSc). This value is almost 0.1 nm larger than the lattice parameter of bcc Sc estimated by [86Gsc2] (~0.368 nm).

Table 5 Enthalpy of Mixing of Liquid Cu-Sc Alloys

Composition, atomic fraction Sc	Enthalpy of mixing, J/mol	Composition, atomic fraction Sc	Enthalpy of mixing, J/mol
0.00693	830	0.2000	16 550
0.0179	1 900	0.2699	21 340
0.0367	3 470	0.3335	22 490
0.0588	5 300	0.4066	24 660
0.0789	6 870	0.6376	21 910
0.1199	10 910	0.7225	18 450

Note: At 1373 K. From [84Wat].

The resulting enthalpies of mixing for liquid Cu-Sc alloys from [84Wat] are listed in Table 5. [84Wat] also determined the enthalpies of formation of the congruently melting phases Cu_4Sc, Cu_2Sc, and CuSc by calorimetry. These data are listed in Table 6, along with the enthalpies obtained by thermodynamic modeling, which is described in the subsequent section.

Thermodynamic Modeling

The enthalpy of mixing values of [84Wat], listed in Table 5, were fitted to a polynomial of the form:

$$H(\mathrm{L}) = X_{\mathrm{Sc}}(1 - X_{\mathrm{Sc}})\,(A + BX_{\mathrm{Sc}} + CX^2_{\mathrm{Sc}}) \qquad \text{(Eq 1)}$$

The resulting equation is:

$$H(\mathrm{L}) = X_{\mathrm{Sc}}(1 - X_{\mathrm{Sc}})\,(-105\,142 + 11\,710\,X_{\mathrm{Sc}} + 6903\,X_{\mathrm{Sc}})^2 \text{ J/mol} \qquad \text{(Eq 2)}$$

Equation 2 was then combined with the terminal eutectic data from Fig. 1 (13 at.% Sc, 865 °C and 71 at.% Sc, 875 °C), as well as the elemental lattice stability parameters listed in Table 7, to derive the following expression for the excess entropy of the liquid phase:

$$S^{\mathrm{ex}}(\mathrm{L}) = X_{\mathrm{Sc}}(1 - X_{\mathrm{Sc}})\,(-51.79 + 10.891\,X_{\mathrm{Sc}}) \text{ J/mol} \qquad \text{(Eq 3)}$$

Equations 2 and 3 were utilized in conjunction with the liquidus temperatures from Fig. 1 to derive Gibbs energy of formation values for the phases Cu_4Sc, Cu_2Sc, and CuSc. Table 7 shows the values of the various parameters.

Liquidus boundaries evaluated from the expressions in Table 7 do not show overall agreement with experimental data in the region 20 to 71 at.% Sc. This is not surprising, considering the approximate nature of the Cu-Sc phase diagram. Moreover, the experimental enthalpy of mixing data of [84Wat] are based on a limited range of composition and show a large degree of scatter, especially in the Cu-rich region. As such, the experimental phase boundaries, as shown in Fig. 1, are preferred over the calculated phase boundaries. There is a lack of experimental data for the L/L + Cu_2Sc, Cu_2Sc + L/L, and the L/L + Sc phase boundaries. These boundaries were, therefore, estimated from the thermodynamic functions listed in Table 7.

The enthalpy data from the present modeling are compared in Table 6 with the experimental results of [84Wat], as well as with the values calculated with the semi-empirical model of Miedema [80Mie, 83Nie]. As seen in Table 6, the present calculations are in excellent agreement with the experimental data of [84Wat] for Cu_4Sc and CuSc. The poor agreement for Cu_2Sc is primarily due to the lack of experimental data in the vicinity of Cu_2Sc. In all instances, the Miedema estimates are more exothermic than the data of [84Wat], as well as the data from the present thermodynamic analysis.

Table 6 Experimental and Calculated Enthalpy of Formation Values for Cu-Sc Intermediate Phases

Phase	Enthalpy of formation, kJ/mol		
	Experimental(a)	Calculated	
		Present modeling	Miedema model(b)
Cu_4Sc	-14.0	-13.6	-22.1
Cu_2Sc	-17.4	-8.4	-33.3
CuSc	-20.9	-20.8	-35.6

Note: Standard states are pure solid Cu and pure solid αSc.
(a) From [84Wat]. **(b)** From [80Mie] and [83Nie].

Table 7 Cu-Sc 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 Sc(b)

$G^0(Sc, L) = 0$
$G^0(Sc, bcc) = -14\,100 + 7.772\,T$
$G^0(Sc, cph) = -18\,110 + 10.263\,T$

Integral molar Gibbs energies(c)

$G^{ex}(L) = X(1-X)[(-105\,142 + 11\,710\,X + 6903\,X^2) - T(-51.79 + 10.891\,X)]$
$\Delta_f G(Cu_4Sc) = -27\,676 + 13.16\,T$
$\Delta_f G(Cu_2Sc) = -23\,183 + 6.09\,T$
$\Delta_f G(CuSc) = -36\,340 + 14.40\,T$

Note: Standard states: pure liquid Cu and pure liquid Sc. Gibbs energies are expressed in J/mol, and temperatures are in K. X is the atomic fraction of Sc. Mol refers to the atom as the elementary entity.
(a) From [Hultgren,E]. **(b)** From [83Cha]; melting and transformation temperatures are from [78Bea] and [86Gsc1]. **(c)** From the present modeling.

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*Indicates key paper.

#Indicates presence of a phase diagram.

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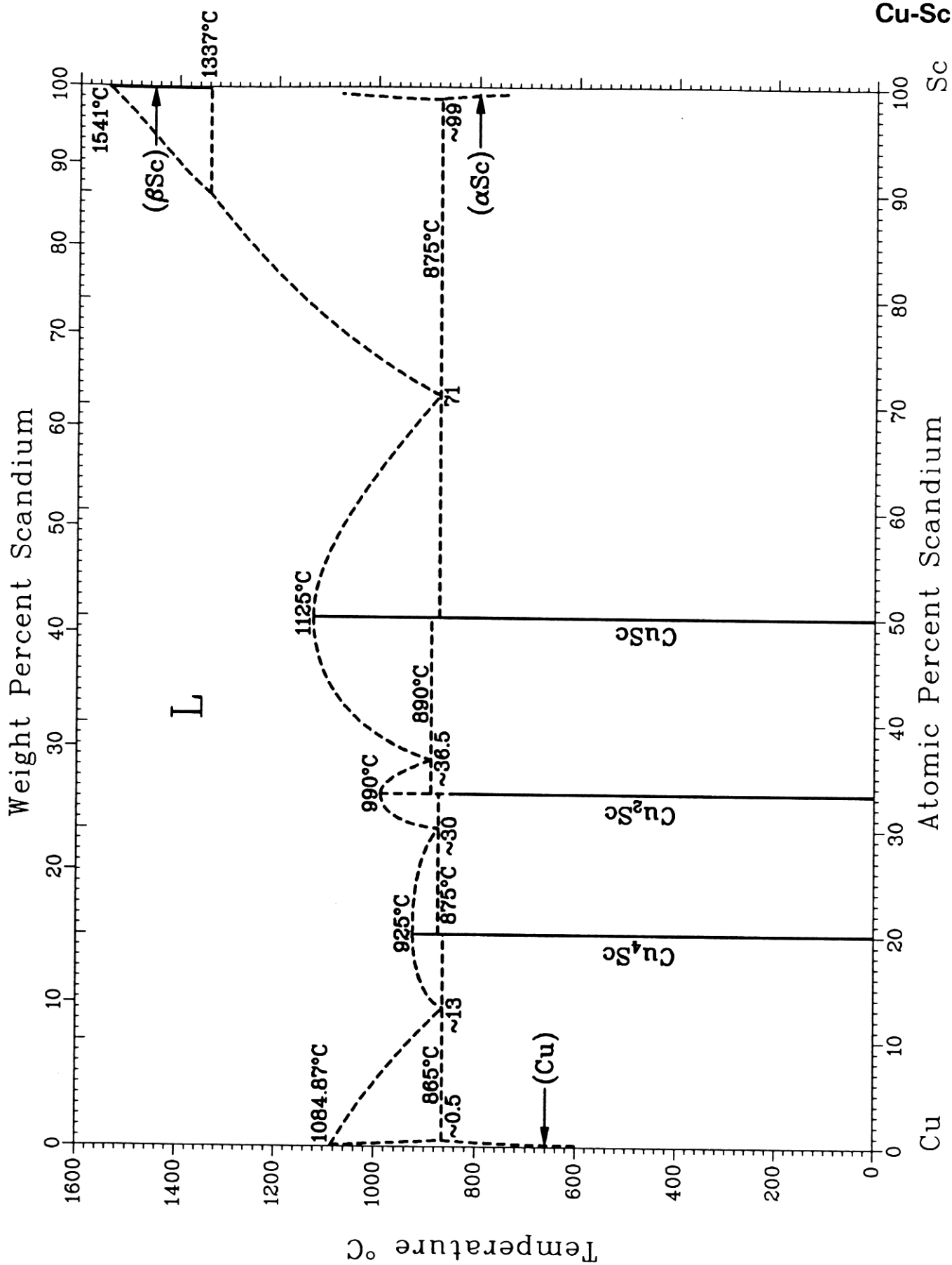

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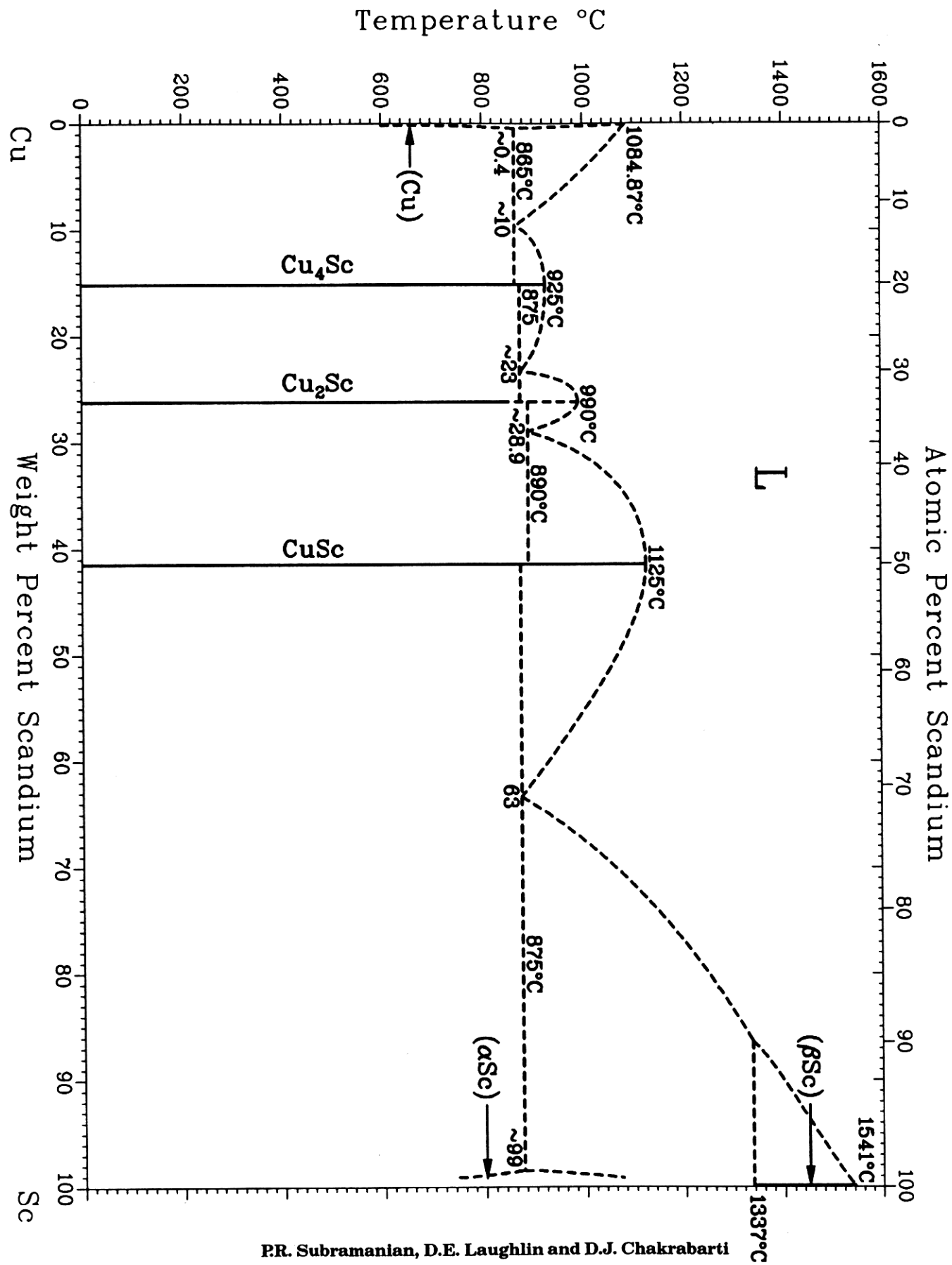

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