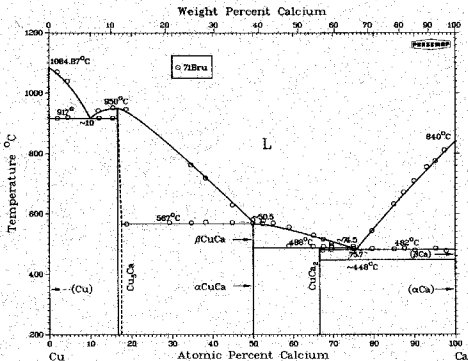# The Ca-Cu (Calcium-Copper) System

40.08   63.546

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Fig. 1   Assessed Cu-Ca Phase Diagram with Selected Experimental Data

The allotropic transition between βCuCa and αCuCa is not known (see text).

D.J. Chakrabarti and D.E. Laughlin, 1984.

The assessed Cu-Ca equilibrium diagram presented in Fig. 1 has been derived primarily from the works of Bruzzone [71Bru]. Crystallographic information on phases in this system is given in Table 1. Cu and Ca are virtually insoluble in one another in the solid state, but are soluble in all proportions in the liquid. The liquidus is characterized by four temperature-invariant transformations, corresponding to two eutectic and two peritectic reactions. Three intermediate phases are present, with stoichiometry Cu_5Ca, $CuCa$, and $CuCa_2$ are present, with Cu_5Ca having a limited solubility field and undergoing congruent melting at 950 °C. The crystal structures of the intermediate phases have been determined, and all of them constitute prototypes of new structures. Except for

several studies on the Cu_5Ca phase, very little thermodynamic data are available on this system.

Equilibrium Diagram

The equilibrium phases in the Cu-Ca system are: (1) the liquid, miscible in all proportions and stable down to 482 °C at 75.7 at.% Ca; (2) the fcc solid solution, (Cu), with limited solubility of Ca; (3) the bcc solid solution, (βCa), with negligible solubility of Cu and stable down to ~448 °C; (4) the fcc solid solution, (αCa), with negligible solubility of Cu and stable below ~448 °C; (5) the hexagonal phase Cu_5Ca, with a composition that includes the stoi-

Table 1 Cu-Ca Crystal Structure and Lattice Parameter Data

Phase	Approximate composition range(a), at.% Ca	Pearson symbol	Space group	Prototype	Lattice parameters, nm a	b	c	Comments	Reference
(Cu)	0	cF4	Fm3m	Cu	0.36147	...	...	(b)	[Landolt-Börnstein]
Cu_5Ca ...	14.1 to 20(c)	hP6	P6/mmm	CaCu₅	0.5074 ± 0.0002	...	0.4074 ± 0.0002	(d, e)	[71Bru]
αCuCa(f)	50	mP20	P2₁/m	CaCu	1.947	0.4271	0.5880	(g, h, j)	[81Mer]
βCuCa(k)	50	oP40	Pnma	CaCu	3.880	0.4271	0.5894	(g, j, m)	[81Mer]
$CuCa_2$ ...	66.67	oP12	Pnma	Ca₂Cu	0.6126	0.4161	1.453	(g, n, p)	[82For]
(αCa)	100	cF4	Fm3m	Cu	0.5592	...	...	(q, r)	[61Pet]
(βCa)	100	cI2	Im3m	W	0.4480	...	...	(q, s)	[59Smi]

(a) From the phase diagram. (b) At 18 °C, on elemental Cu. (c) Based on a small, but progressive, variation of the lattice parameters observed in this range by [71Bru]. A much narrower homogeneity range (approximately 16 to 17 at.% Ca) was indicated, however, in the phase diagram presented by [71Bru]. (d) On 16.6 at.% Ca sample, furnace cooled to room temperature from 800 °C; lattice parameters previously reported by [40Hau] and [42Now]. (e) Previously reported as Cu_4Ca by [11Bau] and as Cu_5Ca by [31Sny]. (f) High temperature; 96.3° interaxial angle. (g) Alloys made from 99.9 wt.% Ca and 99.999 wt.% Cu, melted in Fe crucibles, sealed under Ar. (h) On samples annealed at 370 °C for three months. (j) Stacking variant of the FeB-CrB type. (k) Low temperature. (m) On samples quenched from 600 °C in water. (n) On sample annealed at 450 °C for two months. (p) Orthorhombic structure also reported by [81Mer]. (q) On 99.94% Ca, containing 120 to 240 ppm H. (r) At room temperature. (s) At 467 °C.

Fig. 2 Assessed vs Calculated Cu-Ca Phase Boundaries
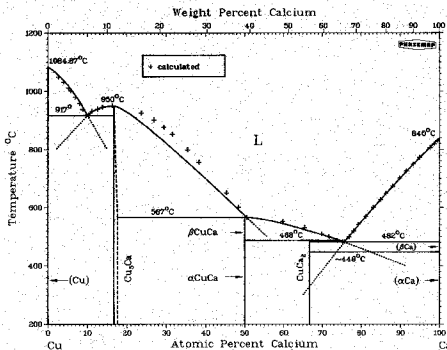
D.J. Chakrabarti and D.E. Laughlin, 1984.

chiometric composition, stable below 950 °C; (6) the orthorhombic stoichiometric phase βCuCa, stable below 567 °C and some undefined lower temperature; (7) the monoclinic low-temperature modification of the CuCa phase, αCuCa, whose temperature limits of stability have not been defined; and (8) the orthorhombic stoichiometric phase CuCa$_2$, which forms peritectically at 488 °C.

Ca is very reactive in air, and the Cu-Ca alloys behave similarly. Thus, the problem of contamination is ever present with these alloys, particularly in the liquid. The Ca used by Bruzzone [71Bru] was purified by distillation. The purities of Ca and Cu used were 99.9 and 99.999%, respectively [83Bru]. The melting point (839 °C) of βCa and lattice parameter value (0.55884 nm) of αCa, the melts were stirred prior to cooling. The temperature ported in [71Bru], are comparable with the conventional literature data (840 °C [81BAP] and 0.5592 nm [61Pet], respectively). The same is also true for the Cu that was used.

The alloys were prepared under an argon atmosphere, using Fe crucibles for compositions above 60 at.% Ca and Mo crucibles for Cu-rich compositions [71Bru]. The liquidus and the temperature invariant phase boundaries were determined by direct thermal analysis on specimens during cooling. The rate of cooling was 2 to 4 °C/min, and the melts were stirred prior to cooling. The temperature was measured to an accuracy of ±1 °C, and the composition was determined by chemical analysis. The crystal structures of the phases were studied by X-ray diffraction.

Liquidus and Solidus. The assessed liquidus in this evaluation has been based on the data of Bruzzone [71Bru] for the alloys above 9.5 at.% Ca and on the compilation in [81BAP] for the melting points of Ca and Cu at 840 and 1084.87 °C, respectively (see Fig. 1). Between 0 and 9.5 at.% Ca, the assessed liquidus has been obtained from thermodynamic modeling calculations (see under Thermodynamics and Fig. 2). The resultant liquidus is in agreement with the limited differential thermal analysis (DTA) data of [80Kuz] and thermodynamically consistent with the rest of the phase diagram, as discussed below.

The Cu-Ca phase diagram proposed by [71Bru] indicates negligible mutual solid solubility between Cu and Ca. No report of the solubility of Ca in Cu is available. The solubility of Ca in Cu was reported by [80Kuz], from X-ray and microscopic analysis, to be 0.015 to 0.047 at.% Ca at

850 °C and less than 0.015 at.% Ca at 700 °C. Using samples of H annealed at 800 °C for 1 h, [30Sch] observed (presumably, at room temperature) a two-phase structure in a 0.1 at.% Ca alloy, implying a solubility less than this value. Thus, the solubility of Ca in Cu is extremely limited, and the same appears to be also true for Cu in Ca. The claim of a single-phase structure in a 0.74 at.% Ca sample by [31Ssy] is apparently not correct.

Under the condition of zero mutual solid solubility between Cu and Ca, the theoretical maximum initial slopes of the liquidus at pure Cu and pure Ca, calculated from the Van't Hoff relation, are, respectively, −11.74 and −12.1 °C per atomic percent of solute. The enthalpy of fusion values for Cu and Ca used in these calculations were 13 054 and 8535 J/mol, respectively [Hultgren, Elements]. The corresponding initial slopes of the liquidus, estimated from the experimental data by [71Bru], agree with the above value at the Ca end of the diagram (~−12 °C/at.% Cu), but this value is too low for the Cu end, in that it would require an unacceptably large terminal solid solution field. The DTA data of [80Kuz] at the Cu-rich end appear more compatible with the theoretical limiting slope value and, thus, support the liquidus obtained from the thermodynamic modeling calculations in this evaluation.

The assessed solidus boundaries also have been based on the results of [71Bru]. The existence of four temperature invariant transformations was indicated by [71Bru] from the occurrence of primary thermal arrests. These corresponded to the two eutectic transformations at 917 and 482 °C and the two peritectic transformations at 567 and 488 °C, respectively.

Figure 1 also shows a temperature invariant line at ~448 °C, corresponding to the (βCa) $\rightleftharpoons$ (αCa) transformation. The type of transformation would be either eutectoid or peritectoid, depending on whether the (βCa) $\rightarrow$ (αCa) transition temperature is lowered or raised in alloys, with respect to that of pure Ca (448 °C [61Pet]). Another temperature invariant transformation occurs in this system, associated with the orthorhombic-to-monoclinic transition of the CuCa phase. However, because the precise transformation temperature is not known, it has not been indicated in Fig. 1. Selected invariant temperatures and compositions are shown in Table 2.

Table 2 Temperature-Invariant Transformations in the Cu-Ca System

Transformation	Temperature, °C	Compositions, at.% Ca		
Eutectic				
L $\rightleftharpoons$ (Cu) + Cu$_6$Ca	917	~10	~0	~16.7
L $\rightleftharpoons$ CuCa$_2$ + (βCa)	482	75.7	66.67	~100
Peritectic				
L + Cu$_6$Ca $\rightleftharpoons$ βCuCa	567	~50.5	~16.7	~50
L + βCuCa $\rightleftharpoons$ CuCa$_2$	488	~74.5	~50	~66.67
Eutectoid (either)				
(βCa) $\rightleftharpoons$ CuCa$_2$ + (αCa)	~448	~100	66.67	~100
Peritectoid (or)				
(βCa) + CuCa$_2$ $\rightleftharpoons$ (αCa)	~448	~100	66.67	~100
Congruent				
L $\rightleftharpoons$ Cu$_6$Ca	950	~16.7	~16.7	

Table 3 Experimental vs Calculated Liquidus in the Cu-Ca System

Experimental liquidus			Calculated liquidus [This work]	
Composition, at.% Ca	Temperature(a), °C	Reference(b)	Composition(c), at.% Ca	Temperature(d), °C
Liquid/(Cu) equilibrium			**Liquid/(Cu) equilibrium**	
0.	1084.87	[81BAP]	...	1085.7
1.2	1070	[This work]	1.2	1068.2
2.5	1067	[71Bru]	...	(e)
1.4	1067	[This work]	1.5	1065.4
2.6	1050	[This work]	2.7	1049.1
3.9	1031	[This work]	4.0	1031.2
5.0	1029	[71Bru]	4.1	(e)
5.2	1010	[This work]	5.2	1011.7
5.8	1000	[This work]	5.8	1001.7
7.0	980	[This work]	7.0	979.4
8.0	960	[This work]	8.0	957.5
8.8	940	[This work]	8.8	937.5
~10.	917	...	10.3	917.8
Liquid/Cu$_5$Ca equilibrium			**Liquid/Cu$_5$Ca equilibrium**	
~10.	917	...	9.6	916.9
11.0	930	...	11.1	930.9
12.5	940	[71Bru]	12.6	939.2
14.0	945	...	13.8	945.1
16.0	950	[71Bru]	16.3	950.0
19.0	944	[71Bru]	20.0	(e)
20.7	925	...	23.7	924.7
23.2	900	...	26.9	901.0
25.5	875	...	29.4	875.7
27.5	850	...	31.6	851.8
29.5	830	[71Bru]	33.2	...
31.7	800	...	35.5	798.7
35.0	758	[71Bru]	38.4	756.0
38.5	716	[71Bru]	41.2	(e)
43.5	650	...	45.4	650.2
45.0	625	[71Bru]	46.9	(e)
47.6	600	...	48.5	601.5
50.0	576	[71Bru]	49.9	(e)
50.5	567	...	50.5	566.7
Liquid/CuCa equilibrium			**Liquid/CuCa equilibrium**	
55.0	565	[71Bru]	...	562.7
59.0	550	[71Bru]	59.8	551.5
64.2	530	...	65.5	530.9
69.0	510	...	69.8	509.3
71.3	500	...	71.7	499.3
75.0	488	[71Bru]	73.8	486.7
Liquid/CuCa$_2$ equilibrium			**Liquid/CuCa$_2$ equilibrium**	
75.5	485	...	75.2	483.3
75.7	482	...	75.8	482.6
Liquid/(Ca) equilibrium			**Liquid/(Ca) equilibrium**	
76.8	500	...	76.3	499.5
78.2	520	...	78.1	520.5
79.5	540	[71Bru]	79.3	542.8
81.2	570	...	81.2	569.7
83.2	600	...	83.1	600.6
85.0	628	[71Bru]	84.9	628.1
86.5	650	...	86.3	649.1
88.1	675	...	88.0	674.2
90.0	704	[71Bru]	89.8	701.9
91.6	725	...	91.5	725.5
93.4	750	...	93.3	750.1
95.	771	[71Bru]	94.9	772.2
97.5	806	[71Bru]	97.6	806.1
98.5	820	...	98.7	819.4
99.3	830	...	99.5	830.0
100.	840	[81BAP]	...	839.1

(a) Temperatures shown for experimental data are as reported and have not been corrected to the 1968 temperature scale (IPTS-68).   (b) Experimental liquidus data without any indicated reference correspond to values obtained from Fig. 1 by interpolation of experimental data.   (c) Compositions are calculated using thermodynamic parameters in Table 6 and with respect to temperatures given in the second column in each respective row. (d) Temperatures are calculated using analytic expressions in Eq 1 to 5 and with respect to compositions given in the first column in each respective row. No calculations are made with data from [71Bru] showing scatter.   (e) These experimental data of [71Bru] did not fall on the assessed phase boundaries shown in Fig. 1, and therefore, they are not suitable for comparison with our calculated values.

The invariant compositions of the liquidus at various transformation temperatures have been ascertained from the interpolation of the experimental liquidus data or from the results of modeling calculations (see Table 3).

Among the earlier studies on the Cu-Ca system, Baar [11Baa] determined part of the Cu-Ca phase diagram by thermal analysis, and Haucke [40Hau] and Nowotny [42Now] identified the stoichiometry and structure of the intermediate phase Cu_5Ca by X-ray analysis. Various aspects of phase equilibria were also studied by [06Sto] and [08Don]. In recent times, the Cu-rich side of the phase diagram was studied experimentally and theoretically by [80Kuz], and the occurrence of the intermediate phases was studied by [70Myl]. The Cu-rich side of the diagram given by [11Baa] is roughly in agreement with the accepted diagram, but the Ca-rich side of his proposed diagram is thermodynamically incorrect. The eutectic temperatures on the Cu side, reported by the different authors, were approximately 910 °C by [11Baa], 920 °C by [08Don], and 906 °C by [80Kuz], compared to the accepted value of 917 °C by [71Bru].

The experimental data, from which the assessed liquidus in Fig. 1 has been drawn, are presented in Table 3. The detailed thermal analysis results of [71Bru] are presented in Table 4 (see also [83Bru]).

Analytic representations of the liquidus temperature, in terms of the polynomials of composition, have been obtained by the least-squares analysis of the experimental data in the different composition ranges. These are shown in Eq 1 to 5 below, where X is the atomic fraction of Ca, and T is in °C. The fit between the calculated and the experimental liquidus is within ±2 °C in most of the ranges, as can be seen in Table 3 and Fig. 2.

For 0 to 9.5 at.% Ca:

$$T = 1084.87 - 1540X + 7828X^2 - 107684X^3 \quad \text{(Eq 1)}$$

For 9.5 to 16.67 at.% Ca:

$$T = 801.3 + 1735.2X - 5057X^2 \quad \text{(Eq 2)}$$

For 16.67 to 50.5 at.% Ca:

$$T = 723.3 + 3937.1X - 20789X^2 + 35942X^3$$
$$- 22633X^4 \quad \text{(Eq 3)}$$

For 50.5 to 75.7 at.% Ca:

$$T = 571.8 - 1395.6(1 - X) + 5614(1 - X)^2$$
$$- 5684(1 - X)^3 \quad \text{(Eq 4)}$$

For 75.7 to 100 at.% Ca:

$$T = 840 - 1303.2(1 - X) - 692(1 - X)^2 \quad \text{(Eq 5)}$$

Intermediate Phases. Three intermediate phases are present in the Cu-Ca system; CuCa and $CuCa_2$ are believed to be stoichiometric phases, but Cu_5Ca has a limited solubility field. The Cu_5Ca phase, wrongly quoted as Cu_4Ca by [11Baa] and as Cu_5Ca by [31Ssy], was assigned the correct stoichiometry by [40Hau] and by [42Now], who also determined its crystal structure. The phase melts congruently at 950 °C. The presence of a homogeneity range in Cu_5Ca was suggested by [Hansen] from the report of coring, and its probable approximate range was investigated from X-ray lattice parameter data by [71Bru] (see Table 1). The CuCa phase reported by [42Now] and the $CuCa_2$ phase by [70Myl] were

Table 4 Thermal Analysis Results of Cu-Ca Alloys(a)

Composition, at.% Ca	Liquidus temperature, °C	Secondary arrest temperatures, °C		
0	1084	...	...	...
2.5	1067	915	...	...
5	1029	918	...	...
12.5	940	916	...	...
16	950	915	...	...
19	944	...	564	...
29.5	830	...	567	...
35	758	...	567	...
38.5	716	...	567	...
45	625	...	567	...
50	576	...	567	...
52.5	572	...	565	...
55	565	...	565	...
59	550	...	...	488
65	524	...	...	488
67.5	510	...	488	476
69.5	497	...	488	479
75	488	...	...	482
79.5	540	...	...	482
85	628	...	...	480
87.5	668	...	...	480
90	704	...	...	476
93	750	...	...	...
95	771	...	...	482
97.5	806	...	...	475
100	839	...	...	455

(a) Data from Bruzzone [83Bru].

observed by [71Bru] to melt incongruently via peritectic transformations at 567 and 488 °C, respectively.

Crystal Structure and Lattice Parameters

The crystal structures and accepted lattice parameters of Cu, Ca, and of the intermediate phases Cu_5Ca, CuCa, and $CuCa_2$ are shown in Table 1. Ca has an fcc structure, αCa, at room temperature that transforms to the bcc structure, βCa, at 448 °C [61Pet]. The cph and other complex forms of Ca observed at intermediate temperatures in the early works were shown by Smith, Carlson, and Vest [56Smi] to result from the presence of impurities. Hydrogen was found to stabilize the cph phase [59Smi, 61Pet], whereas N or C stabilized the complex structures of Ca [59Smi]. High-pressure studies by [63Jay] also showed that only the bcc and fcc structures exist. Measurements at much higher pressures by [63Sta] indicated two transitions at 25 °C at pressures ~150 kbar and ~300 kbar, respectively. The phases have unknown crystal structures.

Thermodynamics

The free energy of formation of Cu_5Ca between 25 and 780 °C (298 and 1053 K) was determined by [64Chi] from equilibrium hydrogen vapor pressure measurements and between 523 and 873 °C (800 and 1150 K) by [79Not], using the emf method. The enthalpy of formation (ΔH) of Cu_5Ca was obtained by [80Dja], directly from calorimetric measurements. The results are presented in Table 5, where also are shown the integral molar Gibbs free energy for the Cu-26 at.% Ca liquid at 873 °C (1150 K) reported by [79Not] and the enthalpy and entropy of formation data of Cu_5Ca reported by [64Chi], [79Not],

Table 5   Thermodynamic Properties of Phases in the Cu-Ca System

Experimental Data and Comparison with Calculated Results

	Integral molar Gibbs free energy(a)		
		Gibbs free energy, J/mol	
Temperature, K	Experimental		Calculated
	[79Not]	[79Not](b)	[This Work(b,c)]
Liquid (Cu-26 at.% Ca) at 1150 K			
1150	−10600(d)	−12100	−12700
Cu₅Ca			
800	−8975(e)	−13893	−14038
900	−8625(e)	−12611	−13099
1000	−8350(e)	−11403	−12160
1100	−8150(e)	−11559	−11221
1150	−8100(e)	−9755	−10752

Enthalpy and entropy of formation of Cu₅Ca(a)			
	Enthalpy(e),	Entropy(e),	
Reference	J/mol	J/mol	Method
[64Chi](f)	−7300 ± 2000	−0.63 ± 1.3	Equilibrium H₂ pressure
[79Not]	−10500 ± 1000	−2.2 ± 1	emf
[80Dja](g)	−7800 ± 1300	⋯	Solution calorimetry

Lattice stability parameters [Hultgren]

$$^0G^L_{Cu} - {^0G^{Cu(\alpha)}_{Cu}} = 13054 - 9.613\,T$$
$$^0G^L_{Ca} - {^0G^{Ca(\alpha)}_{Ca}} = 8535\,(\pm418) - 7.68\,(\pm0.38)\,T$$

(a) The entities for the mole are the atom (for the liquid phase and the compounds).   (b) Standard states: Liquid Cu and liquid Ca.   (c) Calculated using the equations in Table 6.   (d) Standard states: Solid Cu and liquid Ca.   (e) Standard states: Solid Cu and solid Ca.   (f) Between 800 and 1000 K, as compiled in [Hultgren] from the data of [64Chi].   (g) At room temperature.

and [80Dja]. Apart from this limited information, no other thermodynamic data are available on the Cu-Ca alloys.

Because the Cu-Ca phase diagram is reasonably well established, the equilibrium boundaries between the coexisting phases can be utilized to derive expressions for the thermodynamic variables of the different phases. The variables, in turn, can be used to reproduce the phase boundaries as a check for self-consistency and also to calculate the regions of the phase diagram not determined experimentally. Both of these aspects have been attempted in this evaluation, following the approach described below.

Because both the (Cu) and the (Ca) phases display virtually zero solubility, they have been assumed to be line phases, and the representation of their molar free energy has been obtained from the respective lattice stability parameter values for the solid → liquid transition, as given in [Hultgren; Elements]. The resultant expressions relative to pure liquid Cu and pure liquid Ca as standard states (used throughout the calculation) are presented in Table 5.

The liquidus boundaries between 1084.87 and 917 °C and between 840 and 482 °C have been utilized to estimate the integral molar excess free energy expressions for the liquid. The latter has been expressed as a polynomial with composition in the following form:

$$^E\Delta G^L = X(1-X)\sum_{i=1}^{N}(a_i^H X^{i-1} - T \cdot b_i^S X^{i-1}) \qquad (Eq\ 6)$$

where a_i^H and b_i^S are, respectively, the coefficients of the enthalpy $(\Delta H/X(1-X))$ and entropy $(^E\Delta S/X(1-X))$

Table 6   Calculated Thermodynamic Properties of Phases in the Cu-Ca System

Integral molar Gibbs free energies

$$G^L = X(1-X)(-26480 + 12550X - 12.28T) + RT[X \ln X + (1-X)\ln(1-X)]$$
$$G^{Cu_5Ca} = -21550 + 9.39T$$
$$G^{CaCa} = -28650 + 19.35T$$
$$G^{CeCa_2} = -14510 + 5.56T$$

Note: X is atomic fraction of Ca, and all units are in J/mol. Standard states: pure liquid Ca and pure liquid Cu. Mole for Cu₅Ca, CuCa, and CuCa₂, refers to the atom as the elementary entity. This work from the assessed phase diagram, Fig. 1.

functions of the liquid, and X is the atomic fraction of Ca. The coefficients have been assumed to be independent of temperature. The simultaneous linear equations, set up from the equilibrium between the liquid and the solid phases at several temperatures, have been solved by the conventional multiple least-squares regression analysis (and the Gauss-Jordan reduction algorithm) to derive the values of the coefficients a_i^H and b_i^S, respectively. The number of the a^H and b^S terms have been limited to a minimum in these calculations, as a compromise between the reproducibility of the calculated diagram, which improves with their increased numbers, and the simplicity of the model. A total of 35 data points have been used to derive two coefficients for a^H and one for b^S that could reproduce the phase diagram satisfactorily. The resultant expression for the $^E\Delta G^L$ is as follows:

$$^E\Delta G^L = X(1-X)(-26480 + 12550X - 12.28T) \qquad (J/mol) \qquad (Eq\ 7)$$

where X is atomic fraction of Ca, and T is in kelvin.

The maximum value of ΔH, according to Eq 7, is −5168 J/mol at $X = 0.43$, and the corresponding ΔG value, estimated at 1000 K, is −13 847 J/mol. The only available experimental result for the Gibbs free energy of the liquid was reported by [79Not]. This value, when normalized relative to pure liquid Cu and pure liquid Ca as standard states, agrees to within 5% of the value calculated from Eq 7 (see Table 5). Thus, Eq 7 represents a realistic approximation to the thermodynamics of the liquid in this instance.

From a knowledge of the molar free energy of the liquid, the molar free energy of Cu₅Ca, expressed in the form $(A + BT)$, has been estimated by considering equilibrium of the phase with the liquid at temperatures 950 and 567 °C, corresponding to the invariant liquid compositions of 16.67 and 50.5 at.% Ca, respectively. For these calculations, Cu₅Ca has been represented as a line phase, and its small solubility field has been neglected. In a similar manner, the molar free energies of CuCa and CuCa₂ have been estimated from the least-squares fitting of the liquidus data at 567, 525, 488, and at 488, 482 °C, respectively. The results for these phases are presented in Table 6. The molar free energy of Cu₅Ca has been calculated at several temperatures, based on the derived expressions in Table 6, and are compared in Table 5 with the experimental results of [79Not], normalized relative to pure liquid Cu and pure liquid Ca as standard states. The agreement between the two sets of results is better than 10% at most temperatures. This, together with the aforementioned agreement in the liquid, demonstrates that the approach of deriving thermodynamic expres-

sions of phases from equilibrium phase diagrams, can produce a realistic representation of free energies of the phases.

The liquidus (composition), calculated at selected temperatures based on these derived expressions (Table 6) and the lattice stability parameters for Cu and Ca (Table 5), is shown in Fig. 2 and is tabulated in Table 3 for quantitative comparison with the experimental liquidus. The agreement between these results, for the most part, is very good, suggesting good consistency between the thermodynamic parameters of the different phases as derived from the phase diagram. As for the Ca-enriched liquidus coexisting with Cu_5Ca, it is possible to obtain a closer fit between the experimental and calculated liquidus in the range 16.7 and 50 at.% Ca, if the G^{Cu_5Ca} is derived from phase equilibria data at several intermediate temperatures between 950 and 567 °C. However, the associated congruent point shifts down by 20 to 30 °C, and the Cu-rich side of the calculated liquidus, between 9.5 and 16.7 at.% Ca, also shows a poor fit. The accepted value of G^{Cu_5Ca} (see Table 6), by contrast, shows excellent agreement in both these respects. The presence of the discrepancy between the calculated and experimental Ca-enriched liquidus coexisting with Cu_5Ca can be understandable, because the solubility field in Cu_5Ca has been neglected for the simplified calculations above. Conversely, because the liquidus has been measured by thermal analysis during cooling, the possibility of a downward shift of the liquidus, caused by undercooling effects, also cannot be ruled out.

Suggestions for Future Experimental Work

The Cu_5Ca phase is known to have a narrow homogeneity range. However, its precise boundaries are not known and need determination.

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