

81Don: Y. D. Dong, G. Gregan, and M. G. Scott, "Formation and Stability of Nickel-Zirconium Glasses", *J. Non-Crystalline Solids*, **43**(3), 403-415 (1981). (Meta Phases, Thermo; Experimental; #)

81Kin: H. W. King, "Crystal Structures of the Elements at 25 °C", *Bull. Alloy Phase Diagrams*, **2**(3), 402 (1981). (Compilation)

81Ost: J. Ostatek and H. Matyja, "The Effect of Annealing on the Properties of Metallic Glass Ni₄₀Zr₆₀", Proc.-Conf. 1980 Met. Glasses: Sci. Technol., C. Hargital, I. Bakonyi, and T. Kemeny, Ed., Vol. 2, 305-310 (1981). (Meta Phases, Thermo; Experimental)

81Rav1: A. Ravex, J. C. Lasjaunias, and O. Bethoux, "Effect of Structural Relaxation on the Low-Temperature Thermal Properties of the Superconducting Amorphous Alloy Zr_{0.76}Ni_{0.24}", *Solid State Commun.*, **40**(9), 853-857 (1981). (Meta Phases, Thermo; Experimental)

81Rav2: A. Ravex, J. C. Lasjaunias, and O. Bethoux, "Effect of

Structural Relaxation on Tunneling States in the Superconducting Amorphous Alloy Zr_{0.76}Ni_{0.24}", *Physica B + C*, **107B**(1-3), 397-398 (1981). (Meta Phases, Thermo; Experimental)

82Kin: H. W. King, "Temperature-Dependent Allotropic Structures of the Elements", *Bull. Alloy Phase Diagrams*, **2**(3), 402 (1981). (Compilation)

82Sha: S. K. Shadangik and S. C. Panda, "Structure of the Nickel-Zirconium (Ni₁₁Zr₉) Phase and Its Thermal-Expansion Coefficient", *Acta Crystallogr. B*, **38**(7), 2092-2093 (1982). (Crys Structure; Experimental)

83Gac: J. C. Gachon and J. Hertz, "Enthalpies of Formation of Binary Phases in the Systems FeTi, FeZr, CoTi, CoZr, NiTi, and NiZr by Direct Reaction Calorimetry", *Calphad*, **7**(1), 1-12 (1983). (Thermo, Experimental)

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

Ni-Zr evaluation contributed by P. Nash and C. S. Jayanth, Illinois Institute of Technology, Metallurgical and Materials Engineering, 10 West 33rd Street, Chicago, IL 60616. This work was funded by NASA, Grant No. NAG 3-302, through the American Society for Metals. Literature searched through 1982. Professor Nash is Category Editor for binary nickel alloys.

The Bi-Cu (Bismuth-Copper) System

208.9804

63.546

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Equilibrium Diagram

The Cu-Bi equilibrium diagram is of the eutectic type with the eutectic point located close to pure Bi. In the solid state, the two metals are nearly insoluble in one another. A metastable compound is reported at approximately Cu₅Bi₂ composition. The liquid phase thermodynamics reported in [Hultgren; Binary] are in accord with the experimental phase diagram.

The Bi-Cu system, as contributed in a short version by D. T. Hawkins, was previously published in provisional form in the *Bulletin* [80Haw]. The present evaluation reviews all bibliography and data on the Bi-Cu system available in the literature through 1982 and includes information pertaining to crystal structures, metastable phases, and thermodynamics. The present authors have also performed a thermodynamic assessment of certain phase boundaries. The present evaluation supersedes the earlier work.

The equilibrium phases of the Cu-Bi system are: (1) the liquid, miscible in all proportions; (2) the fcc solid solution, (Cu), with restricted solubility of Bi amounting to 0.003 at.% Bi at 800 °C; and (3) the rhombohedral solid solution, (Bi), with presumably negligible solubility of Cu.

Liquidus. The liquidus in the Cu-Bi system has been studied extensively, and the existence of a eutectic transformation near the composition of pure Bi has been established. The eutectic temperature and composition values obtained by the different authors are presented in Table 1, and the liquidus results from the different works are shown in Fig. 1. Selected data are also tabulated in Table 2, along with the corresponding calculated values obtained from the optimization of thermodynamic and liquidus data for comparison (see "Thermodynamics").

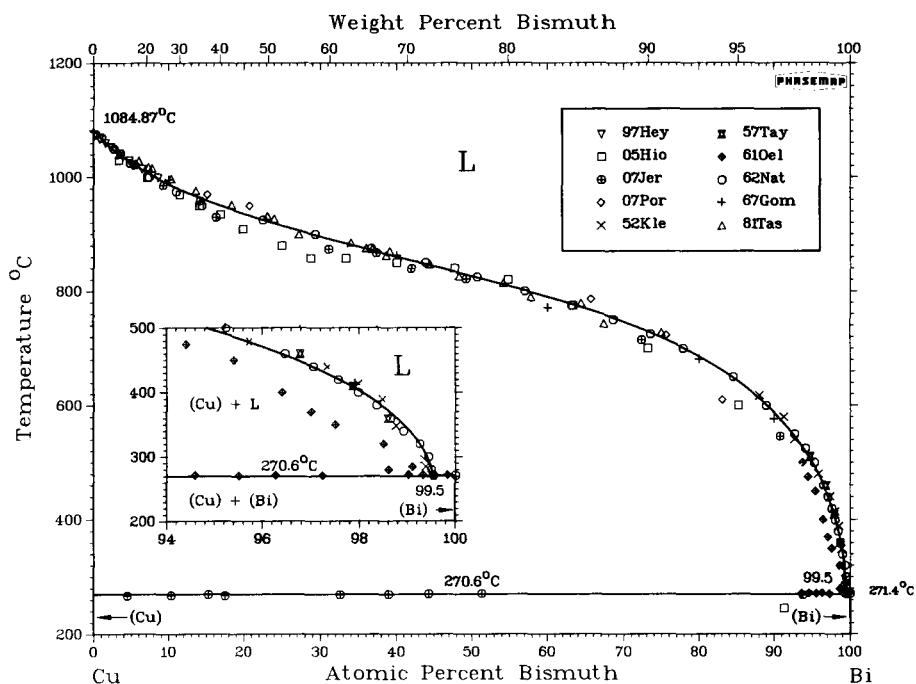
The liquidus accepted in this evaluation is based primarily on the carefully measured data by Nathans and Leider [62Nat], complemented in part by the data of Heycock and Neville [1897Hey] near the Cu-rich end and by the data of

Table 1 Cu-Bi Eutectic Temperature and Composition

Temperature, °C	Composition, at.% Bi	Reference	Method	Material purity
0.6 to 0.8 below melting point of Bi.....	99.3 to 99.4	[1892Hey]	Freezing point depression	...
245	91.3	[05Hio]	Thermal analysis, microscopy	Electrolytic Cu and "pure" Bi
270 ± 2	≥99.5	[07Jer]	Thermal analysis	...
262 ± 3	~99	[07Por]	Thermal analysis, microscopy	...
.....	99.52	[52Kle]	Saturation solubility	...
270	99.31	[61Oel]	Thermal analysis	...
270.6 ± 0.1.....	99.54	[62Nat]	Sampling and thermal analysis	Bi: 99.999% with 0.0001 to 0.001% Mg Cu: OFHC grade with 0.0001 to 0.001% Ag
270.5.....	99.5	[This work]	Calculation using optimized parameters	...

Note: Accepted results are shown in boldface type.

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



Temperatures shown for experimental data are as reported and have not been corrected to the 1968 temperature scale (IPTS-68).

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Kleppa [52Kle] and Taylor [57Tay] at the Bi-rich end of the diagram. In general, there is good agreement among most of the reported results and the corresponding accepted values (Table 2), except for the results of [05Hio] and [61Oel], which show systematically lower values.

Thermal analysis during cooling was employed in all the early studies, complemented at times by metallographic examination of the solidified samples. The existence of a eutectic point near pure Bi (~99.35 at.% Bi) and at ~0.7 °C below the melting point of Bi was suggested in the work of Heycock and Neville [1892Hey]. The melting point for Bi (~266.5 °C) reported in [1892Hey] is, however, lower than the presently accepted value of 271.442 °C [81BAP]. The purity of the Bi used by the authors was not stated.

The Cu-rich end of the liquidus extending up to 8.5 at.% Bi was determined by [1897Hey]. The melting point of Cu reported in that work (1077.2 °C) is considerably lower than the presently accepted value of 1084.87 °C [81BAP]. Thus, although their liquidus data showed consistency and no apparent scatter, the temperature values were most likely systematically low, notwithstanding that the values also were obtained by thermal study during cooling. By contrast, the data of [62Nat], [76Gom], and [81Tas] suggested an upward shift of the liquidus at these compositions. Jeriomin [07Jer] determined the liquidus between 0.7 and 99.5 at.% Bi and established the eutectic transformation to occur at ≥ 99.5 at.% Bi, with the corresponding thermal arrest at 270 ± 2 °C. The liquidus reported by [07Por] lies systematically above that of [07Jer]. [07Por] also confirmed the occurrence of a eutectic transformation between the liquid and the two terminal solid solutions, (Cu) and (Bi).

The observation by [05Hio] of several intermetallic compounds existing in this system is apparently incorrect, as is the contention by [05Hio] of additional "eutectic" transformations occurring at 858 and 1020 °C. A metastable miscibility gap of the liquid exists below the liquidus in this system (see "Thermodynamics" and Fig. 2). The presence of impurities has been known to stabilize such miscibility gaps above the equilibrium liquidus, giving rise to a monotectic transformation [78Ver]. The thermal analysis data of [05Hio] are reminiscent of such a monotectic transformation, which could conceivably arise from impurity contamination effects.

Extending from above approximately 90 at.% Bi, the liquidus boundary has an increasingly steep slope and, consequently, is not amenable to accurate determination by the thermal analysis method. This part of the liquidus was studied nearly 45 years later by Kleppa [52Kle], followed by Taylor [57Tay] and Nathans and Leider [62Nat], all of whom employed the more accurate method of sampling from the liquid. Both [52Kle] and [57Tay] added Cu to Bi and measured the composition of the sampled liquid after it had been saturated by the partial dissolution of the Cu at various temperatures. [62Nat] formed a liquid of known composition by the complete dissolution of Cu into liquid Bi. This liquid was subsequently equilibrated in the two-phase region at successively lower temperatures, and the corresponding compositions of the liquid were determined by the sampling method. There is good agreement between these determinations, as seen in Fig. 1 and in Table 2. The resultant liquidus is also thermodynamically consistent, in that the partial molar enthalpy of fusion of Cu determined from this liquidus by [62Nat] was found to be within 6% of the literature value. [61Oel] determined

Table 2 Cu-Bi Liquidus Data

Temperature, °C	Liquidus composition, at.% Bi			Reference	Liquidus temperature(a), °C
	Accepted in this work	Optimization calculation	Literature selected data		
1074	0.286	[1897Hey]	...
1070	1.05	...	1.05	[62Nat]	1072.4
1060	...	2.1	1.51	[1897Hey]	...
1052	2.65	...	2.65	[62Nat]	1054.5
1042	3.5	[07Jer]	...
1030	...	5.1	4.68	[1897Hey]	...
1026	5	1023.5
1014.9	6.36	[1897Hey]	...
1000	...	8.8
986	10	988.6
975	11.0	[62Nat]	...
957	15	956.5
950	16.4	[62Nat]	...
935	20	932.0
900	...	30.6	29.3	[62Nat]	...
897	30	896.6
864	40	863.9
850	43.8	[62Nat]	...
828	50	826.5
800	...	60.0	57.0	[62Nat]	...
789	60	790.3
750	68.6	[62Nat]	...
744	70	746.0
700	...	78.6	77.9	[62Nat]	...
685	80	683.2
681	80	[76Gom]	...
650	84.5	[62Nat]	...
645	85	641.5
588	90	591.2
577	90	[76Gom]	...
550	92.7	[76Gom]	...
505	95
500	...	95.1	95.24	[62Nat]	...
460	96.78	[57Tay]	...
400	97.9	97.9	97.97	[62Nat]	...
360	98.6	[57Tay]	...
300	99.4	99.3	99.44	[62Nat]	...
270.6	99.54	...	99.54	[62Nat]	...
270.5	...	99.5

(a) Temperatures are calculated using Eq 1 or 2 and are based on the accepted composition values appearing in the respective rows.

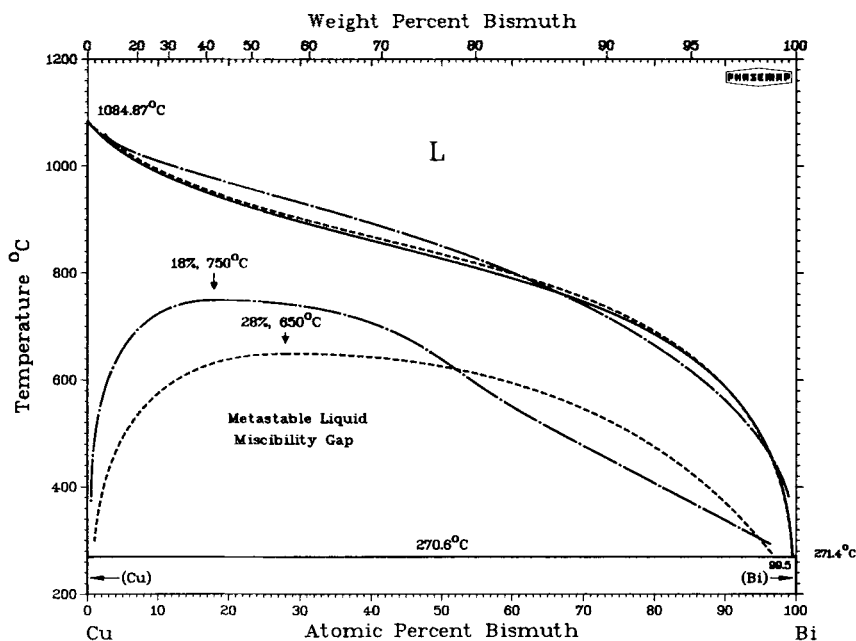
the liquidus above 93 at.% Bi by quantitative thermal analysis. The results, although consistent with each other, are systematically below the liquidus obtained by the sampling method (see inset in Fig. 1).

The liquidus along the entire composition range was determined with great care and precision by Nathans and Leider [62Nat]. The samples were made from 99.999% pure Bi and OFHC Cu containing 0.0001 to 0.001% Ag as the major impurity. Sampling was done following equilibration during both heating and cooling sequences. Care was taken to ensure attainment of equilibrium in the bath and to prevent contamination by oxygen from the atmosphere. A porous graphite filter was used during sampling to prevent the intake of particles of solid (Cu) phase, which was in equilibrium with the liquid. Thermal analysis measurements additionally were made by [62Nat]. These results were in essential agreement with the sampling data, although the liquidus based on the latter was reported to be displaced systematically to slightly higher temperatures. Notably, these observations point to the general reliability of the sampling results, because any entrapment of second-phase particles during sampling would have displaced the liquidus to lower temperatures, corresponding to the increased Cu content in the sample. The

accepted liquidus in this evaluation was, therefore, based on the data of [62Nat] from their smoothed liquidus (see Table 2). These data are in good agreement with those of [52Kle] and [57Tay] below 600 °C and lie within the scatter limits of other reported data above this temperature. The accepted liquidus is also in good agreement with the equilibrium data of [76Gom]. The liquidus data of [81Tas], based on the activity measurements using a liquid electrolyte galvanic cell, also support the accepted liquidus, although they are somewhat less consistent and show scatter. Above 1000 °C, the accepted liquidus is in reasonable agreement with the thermal analysis data of [1897Hey], but is displaced slightly above their data. This is consistent with the possibility that the temperature data of [1897Hey] were slightly in error, as discussed earlier.

The eutectic composition (99.5 at.% Bi) obtained by [62Nat] is in agreement with those obtained by [52Kle] and [07Jer], whereas the composition given by [61Oel] is slightly lower (99.3 at.%) (see Table 1). Regarding the eutectic temperature, there is good agreement (~270 °C) among [62Nat], [61Oel], and [07Jer]. The accepted eutectic temperature of 270.6 °C is, however, taken from [62Nat], to be consistent with the accepted liquidus data also taken from the same source.

Fig. 2 Calculated (Optimized) vs Assessed (Experimental) Liquidus and Metastable Miscibility Gap of Liquid



— = assessed liquidus; ---- = calculated (optimized data from [Hultgren, Binary] and assessed liquidus); - · - · = calculated (optimized data from [81Tas] and assessed liquidus).
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An analytic representation of the accepted liquidus at two composition ranges is presented below in Eq 1 and 2, and the calculated temperatures using these equations are shown in Table 2 for comparison. For 0 to 45 at.% Bi:

$$T(^{\circ}\text{C}) = 1084.9 - 1222.6 X + 2907 X^2 - 3080 X^3 \pm 3^{\circ}\text{C} \quad (\text{Eq 1})$$

For 40 to 90 at.% Bi:

$$T(^{\circ}\text{C}) = 1253.4 - 1788.8 X + 2745 X^2 - 1750 X^3 \pm 3^{\circ}\text{C} \quad (\text{Eq 2})$$

where X is the atomic fraction of Bi.

Solid Solubility. The solid solubility of Bi in (Cu) was estimated by optical microscopy to lie between 0.25 and 0.50% by [07Jer]. [30Ehr] inferred, from the lack of change in the lattice parameter values of (Cu) phase alloys, that the solubility of Bi was below 0.50 at.%, corresponding to the detection limits for observing such changes by X-ray diffraction. [07Por] indicated the solubility to be negligibly small. The large size difference between Bi and Cu atoms would suggest restricted mutual solubility, and this was supported in the subsequent studies.

From metallographic examination of samples quenched from 980 °C following annealing for four days, [27Han] estimated the solubility to be no greater than 0.0006 at.% Bi. The alloys were made from 99.96% pure Cu and P-free Bi and deoxidized by melting under a hydrogen atmosphere. [57Bas] studied, by optical microscopy, the precipitation behavior of samples following deformation and annealing, and he estimated the solubility of Bi to be at least 0.005 at.% at 500 °C. Using the indirect method of hot and cold notched bar test to determine the minimum temperature above which the embrittlement effect of Bi in

Table 3 Solid Solubility of Bi in (Cu)

Reference	Composition at.% Bi	Experimental method
[07Jer]	0.25 to 0.50	Optical microscopy
[07Por]	~0	...
[27Han]	<0.0006	Optical microscopy
[30Ehr]	<0.5	X-ray diffraction
[46Rau]	0.06 max	Optical microscopy
[47Voc]	0.003 (at 800 °C) 0.0003 (at 600 °C)	Mechanical testing
[57Bas]	At least 0.005 (at 500 °C)	Optical microscopy
[81Vas]	0.016 (at 850 °C) (estimated maximum solubility)	Calculation

Note: Accepted results are shown in boldface type.

Cu disappeared through the formation of solid solution, [47Voc] observed a solubility of 0.0003 at.% Bi up to 600 °C. Above 600 °C, the solubility increased, reaching the tentatively accepted value of 0.003 at.% at 800 °C.

The possible existence of a retrograde-type solidus, resulting from the restricted mutual solubility between Cu and Bi, was hypothesized by Hume-Rothery [43Hum]. From an analysis of the solubility data of [47Voc] and of the shape of the Cu-Bi liquidus, [81Vas] also discussed the possible existence of a retrograde solubility of Bi in Cu. They calculated the maximum solid solubility of 0.016 at.% Bi to occur at 850 °C, commensurate with the temperature at which an inflection occurs in the liquidus. The solubility values given by [46Rau] at unspecified temperatures are unacceptably high. The results from the different works, summarized in Table 3, thus far indicate a very restricted solubility of Bi in Cu, but in view of the

controversies existing, a detailed careful measurement of the solidus is required.

No report on the solubility of Cu in Bi is available, but it is expected to be negligibly small, for considerations similar to those for Bi in Cu stated earlier.

Metastable Phases

A metastable compound of the probable composition Cu_5Bi_2 was reported to occur in the Cu-Bi system by [60Cov]. The work was based on the alloys made under vacuum from 99.999% Cu and +99.99% purity Bi. The compound reportedly forms only at temperatures below $\sim 300^\circ\text{C}$ and in the absence of Cu nuclei, through precipitation from liquid Bi supersaturated with Cu. The structure of the precipitates, as judged from the marked variations in the intensity under polarized light, was inferred by [60Cov] to be noncubic.

Crystal Structure and Lattice Parameters

Bi has a rhombohedral structure with two atoms per unit cell (or a hexagonal unit cell with six atoms per unit cell), which is isostructural with αAs . The structure was found to be stable at atmospheric pressure, from its melting point down to 4 K [60Bar]. Reports of several high-pressure modifications of Bi, studied by Bridgman [35Bri] and others, are given in [74Don], one of which, the βBi , was indexed by [67Bru] on the basis of a monoclinic unit cell containing four atoms.

[30Ehr] studied X-ray diffraction patterns of several alloys of Cu and Bi, prepared from electrolytic Cu and (unspecified) "high-purity" Bi metals. The authors failed to observe any change in the lattice parameter values between the elements (Cu and Bi) and their corresponding primary solid solution phases. The details of the structure and lattice parameter values for Cu and Bi are presented in Table 4.

Thermodynamics

Thermodynamic Measurements. Selected values of the thermodynamic partial and integral quantities for the Cu-Bi liquid alloys at 1200 K are given in [Hultgren; Binary], based on the analysis of the previously reported thermodynamic and phase diagram data. The selected $\Delta\bar{G}_{\text{Cu}}$ and $\Delta\bar{G}_{\text{Bi}}$ values, according to [Hultgren; Binary], are generally within ± 600 J/mol of the values obtained by emf [59Nik, 64Lom] and vapor pressure [67Aza] measure-

ments, respectively. The selected enthalpy of mixing (ΔH) values are reported to be less endothermic (0 to 840 J/mol) than the corresponding experimental values by [61Oel] at 1416 K or the direct calorimetric results of [30Kaw] at 1473 K (0 to 1500 J/mol), but are more endothermic (0 to ~ 1300 J/mol) than the values of [64Lom] at 1215 K.

Recently, Cu activities at 1173 to 1373 K were measured carefully by [81Tas] by the emf method on liquid Cu-Bi alloys made from 99.99% Cu and 99.9% Bi. The results indicated that both the enthalpy (ΔH) and the entropy of mixing (ΔS) for these liquid alloys are independent of temperature. The activity values (a) reported by [73Pre] from vapor pressure measurements at 1373 K were systematically lower (0 to 0.08) than the corresponding values by [81Tas]. ΔH values for the Cu-Bi liquid alloys were measured by [74Tak] at 1090°C . The data showed approximately parabolic variation with composition and fell in between the corresponding selected values given by [Hultgren; Binary] and the computed values from the measured a_{Cu} data given by [81Tas].

The enthalpy of mixing for the liquid as a function of composition was calculated by [52Kle], based on the interaction parameter of Cu ($\Omega_{\text{Cu}}^{\text{L}} = 19200$ J/mol) derived from the Cu-Bi phase diagram. [54Pta] reported the composition variation of the activity coefficient of the liquid Cu-Bi alloys that followed the regular solution model, and the corresponding value for the interaction parameter was given as $\Omega_{\text{L}} = 6900$ J/mol. The enthalpy of solution of Cu in liquid Bi at 625 K, as determined by [73Ske] in an isoperibol liquid Bi solution calorimeter (i.e., a calorimeter in which the wall is maintained at a constant temperature, contrasted to an adiabatic calorimeter, in which the temperature of the wall equals the temperature of the bath), is 4140 ± 200 J/mol. Additional reports correlating thermodynamic parameters with the equilibrium diagram in the Cu-Bi system are given in [43Sch] and [67Ans].

Thermodynamic Calculations. The ΔH values given by both [74Tak] and [81Tas] show an asymmetric shift with respect to composition from the parabolic relation envisaged in the data by [Hultgren; Binary] (Fig. 3). To judge if the above shift in the ΔH values is significant and to ascertain which of these representations best represent the measured phase diagram, the following thermodynamic calculations were performed.

The $Q (= \Delta H/X(1 - X))$ and $\beta (= {}^E\Delta S/X(1 - X))$ values derived from the data tabulated by [Hultgren; Binary] were fitted into polynomial expressions parabolic in com-

Table 4 Cu-Bi Crystal Structure and Lattice Parameter Data

Phase	Approximate composition(a), at.% Bi	Pearson symbol	Prototype	Space group	Lattice parameters, nm			Reference
					a	b	c	
(Cu).....	0 to 0.003	<i>cF4</i>	Cu	<i>Fm3m</i>	0.36147	[Landolt-Bornstein](b)
(Bi) or (αBi)	100	<i>hR2</i>	αAs	<i>R3m</i>	0.47461(c)	[62Cuc](d)
					0.45333	...	1.1807	[60Bar](e)
(βBi).....	100	(f)	...	<i>c2/m</i>	0.6674	0.6117	0.3304	[67Bru](g)
Metastable phase								
Cu_5Bi_229

(a) From the phase diagram. (b) At 18°C , for elemental Cu; composition of (Cu) phase is given corresponding to 800°C . (c) $\alpha = 57.23^\circ$. (d) At 25°C , on zone-refined Bi containing <0.03 ppm spectroscopically detectable impurity; lattice parameter values are given for rhombohedral unit cell (2 atoms/cell); corresponding values based on hexagonal unit cell (6 atoms/cell) are $a = 0.45461$ nm, $c = 1.18629$ nm. (e) At 4 K on high-purity Bi; values on the basis of hexagonal unit cell. (f) Monoclinic. (g) High-pressure allotropic form of Bi at 26 kbar; powder pattern indexed on the basis of monoclinic unit cell with $\beta = 110.33^\circ$ and 4 atoms/cell.

Table 5 Thermodynamic Properties of Liquid Cu-Bi Alloys
X is the atomic fraction of Bi

$Q = \Delta H/X(1 - X)$ (J/mol)	$\beta = {}^E\Delta S/X(1 - X)$ (J/mol·K)	Reference	Source
$32200 - 33400X + 24400X^2 \pm 130$ (Eq A)	$13.8 - 21.1X + 16.9X^2 \pm 0.1$ (Eq B)	[Hultgren; Binary]	Selected data from [59Nik, 61Oel, 64Lom, 67Aza] emf measurements
$17350 - 18000X_{Cu} + 43500X_{Cu}^2$ (Eq C)	$4.8 - 12.7X_{Cu} + 28.3X_{Cu}^2$ (Eq D)	[81Tas]	
$30060 - 27400X + 17550X^2$ (Eq E)	$10.7 - 14.3X + 92X^2$ (Eq F)	This work	Optimization of data from [Hultgren] and phase diagram(a) Q data from [81Tas]; β from optimization of Q data of [81Tas] with liquidus data(b)
$17350 - 18000X_{Cu} + 43500X_{Cu}^2$ (Eq C)	$18.4 - 38.3X + 20.0X^2$ (Eq G)	This work	

(a) rms deviation of the optimization fit to ${}^E\Delta G^L$: 180 J/mol.

(b) rms deviation of the optimization fit to ${}^E\Delta G^L$: 550 J/mol.

position (see Eq A and B, Table 5), analogous to the similar fit of the data given by [81Tas] (Eq C and D, Table 5). [Hultgren]'s thermodynamic data, in combination with the accepted liquidus data from the phase diagram determinations (Table 2), were utilized in a computer program to arrive at a set of optimized expressions for the composition dependence of Q and β for the liquid alloys (Eq E and F, Table 5). The optimized Q and β values are plotted in Fig. 3 and 4, respectively, for comparison.

Using this optimized expression for the liquid and assuming negligible solubility of Bi in Cu, the liquidus was calculated as a function of temperature. Both the ΔH and the ${}^E\Delta S$ were assumed to be independent of temperature [81Tas]. The values for the free energy of fusion of Cu and Bi were derived from [77Bar] and were as follows:

$$\Delta G_{Cu}^f = 7683 + 38.844T + 1.8933 \times 10^{-3}T^2 - 6.527T \ln T \quad (\text{J/mol}) \quad (\text{Eq 3})$$

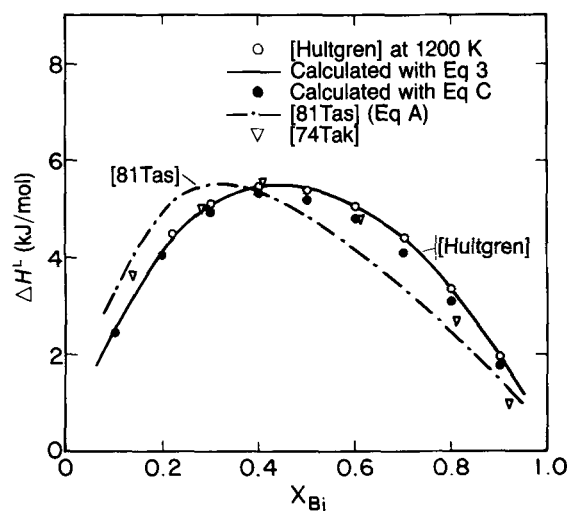
$$\Delta G_{Bi}^f = 13642.5 + 17.238T + 10.048 \times 10^{-3}T^2 + 0.665 \times 10^{-6}T^3 - 7.167T \ln T - 8.318 \times 10^5 T^{-1} \quad (\text{J/mol}) \quad (\text{Eq 4})$$

The calculated liquidus (Fig. 2) agrees to within 7 °C of the assessed liquidus and is displaced above the latter, except above 90 at.% Bi where the two liquidus curves essentially coincide (Table 2). The calculated eutectic temperature and composition values obtained were 270.5 °C and 99.5 at.% Bi, in excellent agreement with the experimental values (Table 1).

In the other calculation using the data of [81Tas], the Q vs composition expression was accepted as given by the author (Eq C, Table 5), and the corresponding expression for β was calculated from optimization with the experimental liquidus data (Fig. 4 and Eq G in Table 5). The composition variation of ΔH , as given by [81Tas], was retained here in order to study its effect on the shape of the liquidus being calculated. The calculated liquidus (Fig. 2) indicates a deviation from the assessed liquidus much larger than that obtained with the previous calculation. The rms deviation of the optimization fit of the data reported by [Hultgren; Binary] is three times lower than that of [81Tas] (see footnote in Table 5). Thus, [Hultgren]'s thermodynamic data are more consistent with the experimental Cu-Bi phase diagram than are those of [81Tas].

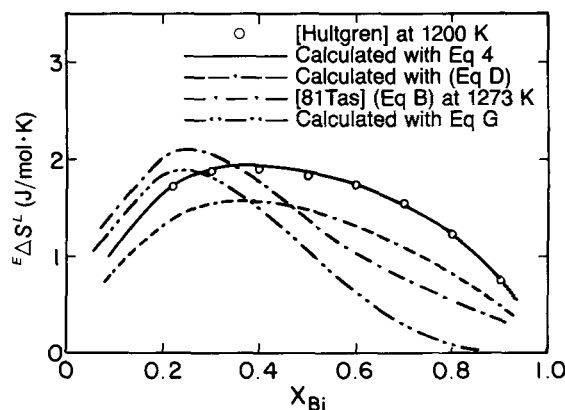
Next, the liquidus was directly calculated, without the incorporation of any optimization from the liquidus data, by using the Q and β expressions alone, as given by [Hultgren; Binary] (Eq A and B, Table 5) and by [81Tas]

Fig. 3 Experimental vs Optimized ΔH

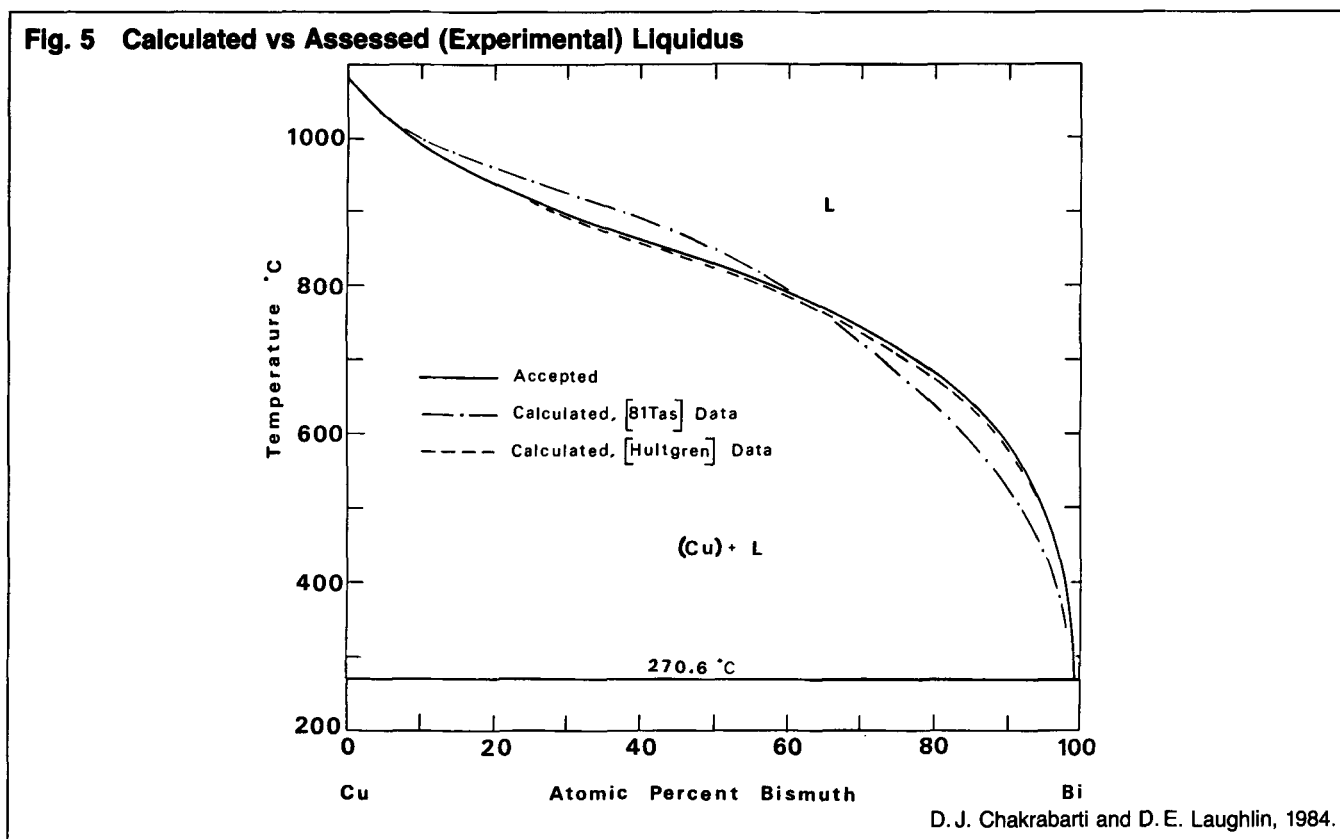


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Fig. 4 Experimental vs Optimized ${}^E\Delta S$



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(Eq C and D, Table 5). This was done to evaluate the comparative appropriateness of the thermodynamic parameters from these two sources in relation to the measured phase diagram. The results shown in Fig. 5 indicate that the liquidus based on the data of [81Tas] deviates much more from the assessed liquidus than the corresponding one of [Hultgren; Binary]. The latter, in fact, shows very close agreement with the experimental liquidus, comparable to the optimization calculation results in the midcomposition ranges. Thus, the results in Fig. 2 and 5 demonstrate that the thermodynamic parameters of the liquid Cu-Bi alloys given by [Hultgren; Binary], including the near-symmetric parabolic variation of ΔH with composition, agree quite satisfactorily with the phase diagram data.

The moderately high positive values of ΔH for the liquid at 1200 K and the gentle slope of the liquidus, having an inflection point in the midcomposition range, suggest the possible development of a miscibility gap in the liquid at temperatures not far removed from the liquidus [81Goo]. This metastable miscibility gap was calculated using the optimized thermodynamic parameters of the liquid based on [Hultgren] (Eq E and F, Table 5) and is shown in Fig. 2. The gap shows an asymmetric shift in composition, with the critical point at ~ 28 at.% Bi and ~ 650 °C. Figure 3 shows that the optimized ΔH values (Eq E, Table 5) are mildly asymmetric with respect to composition, similar to [Hultgren]'s reported values (Eq A, Table 5). The corresponding $^E\Delta S$ values shown in Fig. 5 (Eq B and F, Table 5), however, show much greater asymmetry and are mainly responsible for the asymmetry in the miscibility gap. By contrast, both the ΔH and $^E\Delta S$ values from [81Tas] (Eq C and D, Table 5), as well as the optimized values for the $^E\Delta S$ (Eq G, Table 5) showed pronounced

asymmetry (Fig. 3 and 4). The resultant metastable miscibility gap of the liquid, shown in Fig. 2, has a shape very similar to the corresponding $^E\Delta S$ curve in Fig. 4. The shifts of the calculated liquidus based on these data with respect to the assessed experimental liquidus also bear resemblance to the contour of the $^E\Delta S$ curve. Thus, the $^E\Delta S$ of the liquid has a pronounced effect on the shape of both the liquidus and the metastable miscibility gap in the Cu-Bi system.

Suggestions for Future Experimental Work

Work is needed to establish the (Cu) solidus and to determine the possible occurrence of a retrograde solubility in the (Cu) phase.

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*Indicates key paper.

#Indicates presence of a phase diagram.

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