The Solidus Line of the Cu–Bi Phase Diagram

L.-S. Chang, B.B. Straumal*, E. Rabkin, W. Gust, and F. Sommer Max-Planck-Institut für Metallforschung Institut für Metallkunde der Universität Seestrasse 75, D-70174 Stuttgart, Germany

(Submitted 18 September 1996; in revised form 8 November 1996)

The solid solubility of Bi in Cu single crystals has been experimentally determined. It is shown that the solidus line is a retrograde curve without a monotectic transition. The solid and liquid phases are successfully described with simple thermodynamic models. The experimentally measured maximum solubility of 0.0207 at.% Bi at 975°C correlates well with that from the model (0.0193 at.% Bi at 968°C). A linear temperature dependence of the interchange energies is suggested and the values of the optimized coefficients are in accordance with those estimated from the thermal expansion coefficients. The calculated thermodynamic functions are in good agreement with the assessed experimental data.

Introduction

Studies of the Cu-Bi binary phase diagram began more than a century ago. On the basis of numerous investigations, particularly the intensive studies in the first decade of this century [05Hio, 07Jer, 07Por] and in the 1950s and 1960s [52Kle, 57Tay, 61Oel, 62Nat], the liquidus line was collectively established. On the other hand, relatively little attention was given to the determination of the solid solubilities, which generally are not considered in calculations of the thermodynamic properties of the liquid phase. Most of the experimental data on the solubility of Bi in solid Cu are not convincing because they were determined by optical microscopy [07Jer, 27Han, 46Rau, 57Bas] which is not well suited for measurement of very dilute alloys. Other experiments were performed by Voce and Hallowes [47Voc] using mechanical testing. These results suggested that the solidus line is a retrograde curve either with or without a continuous maximum. The continuity on the maximum depends on the occurrence of a monotectic transition proposed by Vasil'ev [81Vas] in a mathematical treatment of these data. This work estimated the maximum solubility as 0.016 at.% Bi at 850 °C. Although this solubility curve, which was constructed by two parabolic lines, was adopted in some research on the Cu-Bi system in recent years, a degenerate monotectic transition

*On leave from the Institute of Solid Physics, Russian Academy of Sciences, Chernogolovka, Moscow District, 142432 Russia.

No.	Specimen thickness, mm	Annealing temperature, °C	Annealing time, ks	Diffusion penetration length, mm
1	0.65	1040	32.8	0.80
2	0.5	1020	25.2	0.61
3	0.4	1000	21.0	0.49
4	0.3	975	10.8	0.30
5	0.3	950	15.7	0.30
6	0.3	925	22.8	0.30
7	3.0	900	1210	1.80
8	0.3	875	50.4	0.30
9	1.2	850	605	0.84
10	0.3	825	119	0.30
11	0.6	800	605	0.54
12	0.3	775	518	0.39
13	0.9	750	2590	0.68
14	0.3	725	864	0.30
15	0.3	700	864	0.23
16	0.3	650	2590	0.21
17	0.1	600	1210	0.07

Table 1 Details of Experimental Conditions

was never experimentally observed in the past. This uncertainty can now be clarified as a result of advances in analyzing very dilute compositions. In the present work, the solubility of Bi in solid Cu was determined in the temperature range from 600 to 1040°C. A recently proposed thermodynamic model of the liquid phase with a demixing tendency [92Sin] was used to reconstruct the Cu-Bi phase diagram over the entire composition range.

Experimental Procedure

The vapor transfer method was used to obtain Cu saturated with Bi. Pure Cu single crystal cylinders were produced by the Bridgman method and cut into thin disks with various thicknesses (0.1 to 3 mm). These disks were etched in an aqueous solution of 50% HNO₃ to remove the oxidized film. Each disk was then sealed separately in a silica tube with a Bi vapor source. In contrast to the pure Bi source used by Li and Zhang [95Li], Cu-Bi alloys were prepared as Bi vapor sources. The compositions of these alloys were Cu-4.5 at.% Bi for temperatures lower than 850°C and Cu-0.3 at.% Bi for the higher temperatures. Alloys of these compositions are in the (Cu) + liquid two-phase region at the annealing temperature so that the formation of a liquid phase in the Cu single crystal could not occur during annealing. A pure liquid Bi source, even in a small amount, can produce a liquid phase on a Cu target. Seventeen different temperatures between 600 and 1040°C were chosen. At temperatures lower than 600°C the diffusion rate of Bi in (Cu) is too slow to yield equilibrium in a reasonable time. It is expected that at lower temperatures the Bi solubility in Cu (a few ppm) is much smaller than that at higher temperatures. Because the purity of the Cu single crystals was not better than 99.999 wt.%, it was inappropriate to perform experiments at temperatures lower than 600°C. The silica tubes were positioned in the furnace such that the Cu crystals were kept at the desired temperature while the temperature of the Cu-Bi alloy was about 5°C lower in the temperature range 600 to 1000°C and about 5°C higher in the temperature range 1000 to 1040 °C. The annealing times for a complete vapor transfer were chosen by estimating the time, at which the diffusion penetration depth of Bi in solid Cu, $2\sqrt{Dt}$, considerably exceeds the thickness of the sample. In the calculation of the penetration depth, D is the volume diffusion coefficient of Bi in solid Cu [90Meh] and t is the annealing time. Details of the experimental conditions are given in Table 1.

After long annealing the specimens were etched again to remove the liquid film or liquid particles which may have condensed from the Bi vapor during water quenching. Finally, the solute contents in the Cu-Bi single crystals were measured by atomic absorption spectroscopy (AAS). A Perkin–Elmer (model 5000) spectrometer was used with a relative accuracy of 10^{-9} g/g. Because only a small amount of the specimen mass was needed for the measurement (≈ 10 mg), it was possible to analyze thin disks (0.1 mm) and thus decrease the time required for complete saturation with Bi at low temperatures. For the analysis, the specimens were cut into three or four pieces and the Bi concentration in each piece was determined independently.

Thermodynamic Modeling

Solid Phase

The Cu-Bi solid solution is described by the regular solution model. This is a satisfactory assumption as the mutual solubility of Cu and Bi is so small that foreign atoms are statistically distributed in the matrix. Regular solutions were considered for the face-centered cubic (fcc) and rhombohedral (rhomb) structure of the Cu-rich and Bi-rich solid solutions, respectively. The activities of Cu and Bi in the different crystal structures can be expressed in the form:

$$\ln a_{Cu}^{s} = \ln x_{Cu}^{s} + \left(X_{Bi}^{s}\right)^{2} \frac{\Omega^{s}}{RT}$$

$$\ln a_{Bi}^{s} = \ln x_{Bi}^{s} + \left(X_{Cu}^{s}\right)^{2} \frac{\Omega^{s}}{RT}$$
(Eq 1)

where a^s and X^s are the activity and mole fraction of the element Cu or Bi in the solid solution, *R* is the gas constant, *T* is the absolute temperature, and Ω^s is the interchange energy between Cu and Bi atoms in the solid phase.

Liquid Phase

It is impossible to fit the experimentally observed strong increase of the solubility of Bi in the temperature range from 600 to 800°C with the regular solution model for the liquid phase. Otherwise, the asymmetry of the metastable miscibility gap in the liquid phase calculated by Chakrabarti and Laughlin [84Cha] and Taskinen and Niemelä [81Tas] showed that the classical regular model and its improvements cannot be used to represent satisfactorily the Cu-Bi phase diagram. The selfas-sociate model developed recently by Singh and Sommer [92Sin] represents a relevant tool for the description of a liquid phase exhibiting an asymmetric miscibility gap. Singh and Sommer emphasized that such an asymmetric demixing behavior occurs mainly in systems exhibiting a large difference in atomic volumes and a small difference in electronegativities. This is expected in the Cu-Bi system because of the large ratio of the atomic volumes and the small difference in the electronegativities of the Cu and Bi atoms.

It is supposed that Cu and Bi have the tendency to self–aggregate and form atomic clusters in the liquid alloy. It can be expressed as follows:

 $iCu \leftrightarrow Cu_i$ $jBi \leftrightarrow Bi_i$

where i and j are the numbers of atoms in the Cu and Bi clusters. The thermodynamic functions were derived from the quasi–lattice statistical mechanical theory [92Sin]. The expressions of the Gibbs energy, enthalpy and entropy of mixing are:

$$\Delta_{mix}G = RT[X_{Cu}^{L} \ln X_{Cu}^{L} + X_{Bi}^{L} \ln X_{Bi}^{L} - X_{Cu}^{L} \ln n + \ln \eta] + X_{Cu}^{L} X_{Bi}^{L} \eta W$$
(Eq 2)

Section I: Basic and Applied Research

$$\Delta_{mix}H = X_{Cu}^{L}X_{Bi}^{L}\eta W - X_{Cu}^{L}X_{Bi}^{L}\eta T \frac{\partial W}{\partial T}$$
(Eq 3)

$$\Delta_{mix}S = -R[X_{Cu}^{L}\ln X_{Cu}^{L} + X_{Bi}^{L}\ln X_{Bi}^{L} - X_{Cu}^{L}\ln n + \ln\eta] - X_{Cu}^{L}X_{Bi}^{L}\eta\frac{\partial W}{\partial T}$$
(Eq 4)

From Eq 2 the expressions for the activities can be obtained:

$$\ln a_{Cu}^{L} = \ln \left[X_{Cu}^{L} \eta (1 - \beta) \right] + X_{Bi}^{L} \eta \beta + \left(X_{Bi}^{L} \right)^{2} \eta^{2} \frac{W}{RT}$$
$$\ln a_{Bi}^{L} = \ln \left(X_{Bi}^{L} \eta \right) + X_{Cu}^{L} (1 - \beta) \eta (1 - n) + n \left(X_{Cu}^{L} \right)^{2} \qquad (\text{Eq 5})$$
$$(1 - \beta)^{2} \eta^{2} \frac{W}{RT}$$

where X^{L} is the mole fraction of Cu or Bi in the liquid phase, n = j/i which has been assumed to be temperature–independent, $\beta = 1 - 1/n$, $\eta = 1/(1 - \beta X_{Cu}^{L})$ and $W = i\Omega^{L}$, Ω^{L} being the interchange energy in the liquid alloy.

The equilibrium relationships between the solidus and liquidus lines are expressed as:

$$\ln X_{Bi}^{s} = \frac{\Delta G_{Bi}^{0}}{RT} + \ln \left(X_{Bi}^{L} \eta \right) + X_{Cu}^{L} (1 - \beta) \eta (1 - n) + n \left(X_{Cu}^{L} \right)^{2} (1 - \beta)^{2} \eta^{2} \frac{W}{RT} - \frac{\Omega^{s}}{RT} (1 - X_{Bi}^{s})^{2}$$
(Eq 6)

$$\ln X_{Cu}^{s} = \frac{\Delta G_{Cu}^{0}}{RT} + \ln \left[X_{Cu}^{L} \eta (1 - \beta) \right] + X_{Bi}^{L} \beta \eta + \left(X_{Bi}^{L} \right)^{2} \eta^{2} \frac{W}{RT} - \frac{\Omega^{s}}{RT} \left(1 - X_{Cu}^{s} \right)^{2}$$
(Eq 7)

The term *S* indicated the fcc or rhombohedral structure on the Cu-rich and Bi-rich side, respectively. $\Delta G_i^0 = G_i^{0,L} - G_i^{0,S}$, $G_i^{0,L}$ and $G_i^{0,S}$ being the Gibbs energies for the liquid and solid phase of the pure element *i* (*i* = Cu, Bi) in the fcc or rhombohedral structure. As compiled by Dinsdale [91Din], the Gibbs energy can be formulated as a function of temperature

$$G^{0}(T) = H^{SER}(25^{\circ}C) + a + bT + cT \ln T + dT^{2} + eT^{3} + fT^{7} + g/T + h/T^{9}$$
(Eq 8)

 $H^{SER}(25^{\circ}C)$ is the enthalpy of the pure element at the standard reference temperature of 25°C in its stable state. The coefficients *a* to *h* are different in different temperature ranges (Table 2).

Table 2 Coefficients of Gibbs Energy (J/mol) of the Pure Components According to Eq 8 [91Din]

			2		21		25
a	b	с	$d \cdot 10^3$	$e \cdot 10^{\circ}$	$f \cdot 10^{21}$	g	$h \cdot 10^{-25}$
-7817.776	128.418925	-28.4096529	12.338888	-8.381598			
30208.022	-393.650351	51.8556592	-75.311163	13.499885		-3616168	1.661
-11045.664	182.548971	-35.9824	7.4266	-1.046			1.661
-7581.312	124.77144	-27.196					1.661
2082.224	115.918925	-28.4096529	12.338888	-8.381598			
40108.022	-406.150351	51.8556592	-75.311163	13.499885		-3616168	1.661
-1145.664	170.048971	-35.9824	7.4266	-1.046			1.661
2318.688	112.27144	-27.196					1.661
3428.29	107.782415	-28.4096529	12.338888	-8.381598	-595.5		
41544.282	-414.460769	51.8556592	-75.311163	13.499885		-3616168	
290.595	161.738553	-35.9824	7.4266	-1.046			
3754.947	103.961022	-27.196					
-7770.458	130.485235	-24.112392	-2.65684	0.129223		52478	
-13542.026	183.803828	-31.38					36420
5194.277	120.973331	-24.112392	-2.65684	0.129223	-5.849	52478	
-46.545	173.881484	-31.38					
	<i>a</i> -7817.776 30208.022 -11045.664 -7581.312 2082.224 40108.022 -1145.664 2318.688 3428.29 41544.282 290.595 3754.947 -7770.458 -13542.026 5194.277 -46.545	a b -7817.776 128.418925 30208.022 -393.650351 -11045.664 182.548971 -7581.312 124.77144 2082.224 115.918925 40108.022 -406.150351 -1145.664 170.048971 2318.688 112.27144 3428.29 107.782415 41544.282 -414.460769 290.595 161.738553 3754.947 103.961022 -7770.458 130.485235 -13542.026 183.803828 5194.277 120.973331 -46.545 173.881484	abc -7817.776 128.418925 -28.4096529 30208.022 -393.650351 51.8556592 -11045.664 182.548971 -35.9824 -7581.312 124.77144 -27.196 2082.224 115.918925 -28.4096529 40108.022 -406.150351 51.8556592 -1145.664 170.048971 -35.9824 2318.688 112.27144 -27.196 3428.29 107.782415 -28.4096529 41544.282 -414.460769 51.8556592 290.595 161.738553 -35.9824 3754.947 103.961022 -27.196 -7770.458 130.485235 -24.112392 -13542.026 183.803828 -31.38 5194.277 120.973331 -24.112392 -46.545 173.881484 -31.38	abc $d\cdot 10^3$ -7817.776128.418925-28.409652912.33888830208.022-393.65035151.8556592-75.311163-11045.664182.548971-35.98247.4266-7581.312124.77144-27.19612.33888840108.022-406.15035151.8556592-75.311163-1145.664170.048971-35.98247.42662318.688112.27144-27.19612.33888841544.282-414.46076951.8556592-75.311163290.595161.738553-35.98247.42663754.947103.961022-27.1967.4266-7770.458130.485235-24.112392-2.65684-13542.026183.803828-31.38-2.656845194.277120.973331-24.112392-2.65684-46.545173.881484-31.38-2.65684	abc $d \cdot 10^3$ $e \cdot 10^6$ -7817.776128.418925-28.409652912.338888-8.38159830208.022-393.65035151.8556592-75.31116313.499885-11045.664182.548971-35.98247.4266-1.046-7581.312124.77144-27.19612.338888-8.3815982082.224115.918925-28.409652912.338888-8.38159840108.022-406.15035151.8556592-75.31116313.499885-1145.664170.048971-35.98247.4266-1.0462318.688112.27144-27.19612.338888-8.38159841544.282-414.46076951.8556592-75.31116313.499885290.595161.738553-35.98247.4266-1.0463754.947103.961022-27.196-2.656840.129223-7770.458130.485235-24.112392-2.656840.129223-13542.026183.803828-31.38-2.656840.129223	abc $d \cdot 10^3$ $e \cdot 10^6$ $f \cdot 10^{21}$ -7817.776128.418925-28.409652912.338888-8.38159830208.022-393.65035151.8556592-75.31116313.499885-11045.664182.548971-35.98247.4266-1.046-7581.312124.77144-27.196-28.409652912.338888-8.38159840108.022-406.15035151.8556592-75.31116313.499885-1145.664170.048971-35.98247.4266-1.0462318.688112.27144-27.196-28.409652912.338888-8.381598-31.868112.27144-27.196-1.0463428.29107.782415-28.409652912.338888-8.381598-1.04651.8556592-75.31116313.499885290.595161.738553-35.98247.4266-1.046-7770.458130.485235-24.112392-2.656840.129223-7770.458130.485235-24.112392-2.656840.129223-5194.277120.973331-24.112392-2.656840.129223-5.849	abc $d \cdot 10^3$ $e \cdot 10^6$ $f \cdot 10^{21}$ g-7817.776128.418925-28.409652912.338888-8.381598-8.38159830208.022-393.65035151.8556592-75.31116313.499885-3616168-11045.664182.548971-35.98247.4266-1.046-36161682082.224115.918925-28.409652912.338888-8.381598-361616840108.022-406.15035151.8556592-75.31116313.499885-3616168-1145.664170.048971-35.98247.4266-1.046-36161683428.29107.782415-28.409652912.338888-8.381598-595.52318.688112.27144-27.196-75.31116313.499885-36161683428.29107.782415-28.409652912.338888-8.381598-595.5290.595161.738553-35.98247.4266-1.046-3616168-7770.458130.485235-24.112392-2.656840.12922352478-15542.026183.803828-31.38-2.656840.129223-5.84952478

Temperature,	Solidus data at. pp	, this work, m Bi	Liquidu at.%	us data, 6 Bi	
°C	Experimental	Calculated	Literature	Calculated	Reference
1070			1.1		[62Nat]
1052			2.7		[62Nat]
1042			3.5		[07Jer]
1040	109 ± 12				
1020	147 ± 12				
1000	183 ± 9	182		8.7	
975	207 ± 17		11.0		[62Nat]
950	188 ± 9		16.4		[62Nat]
925	176 ± 9				. ,
900	$99 \pm 2*$	161	29.3	26.4	[62Nat]
875	132 ± 6				. ,
850	97 ± 6		43.8		[62Nat]
825	81 ± 4				. ,
800	65 ± 3	75	57.0	58.7	[62Nat]
775	58 ± 3				
750	$26 \pm 2*$		68.6		[62Nat]
725	38 ± 3				
700	22 ± 1	24	77.9	78.0	[62Nat]
681			80.0		[76Gom]
650	12 ± 1.4		84.5		[62Nat]
600	7.6 ± 1.5	5.4		88.5	
577			90.0		[76Gom]
550			92.7		[76Gom]
500		0.8	95.2	94.4	[62Nat]
460			96.8		[57Tay]
400		0.06	98.0	97.7	[62Nat]
360			98.6		[57Tay]
300		0.007	99.4	99.3	[62Nat]
270.6			99.5		[62Nat]
(a) Not accepted in the optimiz	ation				

Table 3 Cu–Bi solidus and liquidus Data

Interchange Energy

The interchange energy Ω between two atoms in the solid or liquid is as follows:

$$\Omega = z \left(\varepsilon_{CuBi} - \frac{\varepsilon_{CuCu} + \varepsilon_{BiBi}}{2} \right)$$

where ε_{CuBi} , ε_{CuCu} and ε_{BiBi} are the binding energies for Cu-Bi, Cu-Cu, and Bi-Bi pairs in the solid (fcc or rhombohedral) or liquid phase. They are assumed to depend only on the interatomic distance *r* and can be roughly expressed in terms of a sixtwelve Lennard–Jones potential:

$$\Omega = -\frac{A}{r^6} + \frac{B}{r^{12}}$$
(Eq 9)

where *A* and *B* are constants. From $\Delta r/r = \alpha \Delta T$, where α is the thermal expansion coefficient, we obtained as $\alpha T \ll 1$:

$$\Omega^{s} \approx \Omega_{0}^{s} + \lambda^{s} T$$
 and $\Omega^{L} \approx \Omega_{0}^{L} + \lambda^{L} T$ (Eq 10)

Table 4 Optimized Parameters for the Cu-BiBinary System

Phase	Model	Parameter
Solid(fcc) Liquid	Regular Self–associate	$\Omega^{fee} = 1.12 \times 10^5 - 35 \times T \text{ J/mol}$ $n = 1.4$ $W = 2.10 \times 10^4 - 8 \times T \text{ J/mol}$

where

$$\Omega_0 = \frac{1}{r_0^6} \left(\frac{B}{r_0^6} - A \right)$$

and

$$\lambda = -\frac{6\alpha}{r_0^6} \left(\frac{2B}{r_0^6} - A\right) \approx -12\alpha\Omega_0 \qquad \text{for } A \ll \frac{B}{r_0^6}$$

 r_0 is the interatomic distance at T = 0 K under the assumption of constant α . From Eq 10 and the definition of W in Eq 5, $W = W_0 + \lambda^L T$ (where $\lambda^L = -12\alpha W_0$) was obtained.



Optimization of the Model Parameters

The five parameters *n*, W_0 , Ω_0^{fcc} , λ^L' and λ^{fcc} were optimized by the least-squares method. For lack of data on the experimental solubility of Cu in solid Bi the parameters Ω_0^{rhomb} and λ^{rhomb} could not be optimized. The data for the solubility of Bi in solid Cu, obtained in this study, and the liquidus concentrations obtained by different authors and selected in the work of [84Cha], except the data from Heycock and Neville [1897Hey], were used to perform the optimization (Table 3). It is also noted that the calculated eutectic temperature and concentration using the optimized parameters should also agree within $\pm 1^{\circ}$ C and ± 0.1 at.%, respectively. After the optimization of the solidus and liquidus data, the optimized parameters were further checked by comparing the calculated thermodynamic values (the integral Gibbs energy, enthalpy, entropy of mixing and component activities) with the experimental data. The activities of Cu and Bi in the liquid phase have been investigated by different groups. The experimental data of Lomov and Krestovnikov [64Lom] obtained by electromotive force measurements at 927°C, of Azakami and Yazawa [67Aza] obtained by vapor pressure measurements at 927°C, and of Predel and Emam [73Pre] at 1100°C were used. The integral Gibbs energy, enthalpy and entropy of mixing at 927°C that were calculated by the Gibbs-Duhem integration by Hultgren et al. [73Hul] and that calculated by Niemelä et al. [86Nie] were also taken. The measured concentration dependence of



the activity of Bi at 1100°C from Taskinen *et al.* [81Tas] was not accepted in this work because it lies too close to the line from Hultgren *et al.* at 927°C and is incompatible with the results obtained by Predel and Emam [73Pre] at 1100°C. The final values of the optimized parameters are listed in Table 4.

Results and Discussion

Estimation of λ

The thermal expansion coefficient of Cu in the solid state is $\alpha^{s} \approx 2 \times 10^{-5}$ /°C for *T*> 800°C [72Gra]. The expansion coefficient in the liquid phase near the melting point can be estimated from the density(ρ) change with temperature:

$$\alpha^{L} = -\frac{1}{3\rho_{0}} \frac{d\rho}{dT}$$

where ρ_0 is the density of the liquid at the melting temperature. The values of $d\rho/dT$ for liquid Cu and Bi are -0.801 and -1.33 mg/cm³ °C [92Bra]. The average value of the thermal expansion coefficients for these two elements $(3.5 \times 10^{-5})^{\circ}$ C) were taken. By combining this value with the thermal expansion coefficient of solid Cu and the Ω_0^{fcc} and W_0 values from the optimization, one obtains the values -26.88 and -8.8 J/mol·K for the coefficients λ^{fcc} and λ^{L} for the solid and liquid phases, respectively. These values are in reasonable agreement with the final fitted values of -35 and -8 J/mol·K.

Phase Diagram

Good agreement between the calculated solidus line and the authors' experimental data is achieved (see Fig. 1), while the liquidus line is in good agreement with the accepted data (Fig. 2). The experimental solubilities of Bi in solid Cu according to [47Voc] are apparently too low. The error bars in Fig. 1 repre-



sent the standard deviation of the experimental values. This deviation may result from the inhomogeneity of the distribution of Bi in the specimens. The rapid increase of the solubility between 600 and 800°C, which could not be explained by the regular solution model, was successfully described by the self-associate model in the liquid state with a simple linear temperature dependence of the interchange energy in the solid and liquid phases. The calculated solubility exhibits a maximum of 0.0193 at.% Bi at 968°C, which is different from 0.016 at.% at 850°C suggested by Vasil'ev [81Vas]. In addition, the continuity at the maximum is maintained. It was noticed during the optimization that this continuity may be lost when W_0 is larger

or Ω_0^s is smaller than some critical values. With the optimized parameters, however, a monotectic reaction does not exist. In this respect, the metastable miscibility gap in the liquid phase was also calculated with the same set of parameters and is shown in Fig. 2. It lies under the liquidus line with the critical values of 37.7 at.% Bi and 674.8°C.

The region around the fitted eutectic point is presented in Fig. 3 in a small temperature range. The concentration of this point is 99.5 at.% Bi which agrees well with the data listed in [84Cha], whereas the value of eutectic temperature of 270.3° C is 0.3° C lower than that in [84Cha]. The calculated solubilities of Bi in solid Cu or Cu in solid Bi at the eutectic point are both approximately 10^{-9} with the assumption that the interchange energy in the rhombohedral structure is similar to that in the fcc structure. This small amount cannot be detected with modern spectroscopy, and the material is normally treated as a pure material. In contrast to the liquidus line on the Cu-rich side, the liquidus concentration on the Bi–rich side changes linearly with temperature.

Thermodynamic Properties

Figure 4 shows the concentration dependencies of the activities at four temperatures. The experimental values lie close to



the calculated lines. The Gibbs energy, and the enthalpy and entropy of mixing were also calculated with the optimized parameters and compared with the experimental data. The results are shown in Fig. 5. They all lie within the range of the experimental error with the Gibbs energy of mixing showing the best agreement. It should be noted that the authors' calculated values of the enthalpy and entropy of mixing are in excellent agreement with those calculated by Niemelä et al. [86Nie]. The asymmetry of these functions is interpreted successfully by the self-associate model. The minimum value of the Gibbs energy of mixing occurs at 58 at.% Bi, or equivalently a Bi-Cu mole ratio of 1.38. This is in agreement with the optimized nvalue of 1.4, which suggests that the most stable associate configurations in liquid Cu-Bi alloys are Cu₅ and Bi₇, or Cu₁₀ and Bi14, and so forth. The different sizes of associates result in an asymmetry in the concentration dependence of the enthalpy and entropy of mixing. It should be mentioned that from the linear temperature dependence of the interchange energy, a temperature independent ΔH of the liquid phase results from the self-associate model. A nonlinear temperature dependence of the interchange energy could be determined only if the heat capacity at least at one concentration is known [94Som].

In an alternative approach to optimizing the Cu–Bi system the Redlich–Kister formalism has been used with five optimization parameters, while the temperature dependence of the in-



Fig. 5 Calculated and experimental thermodynamic data of the liquid phase at 927°C: (a) Gibbs energy, (b) enthalpy, and (c) entropy of mixing.

terchange energy in the solid phase [86Nie, 90Tep] was ignored. This assumption, together with the absence of reliable information about the solubility of Bi in solid Cu, may be the reason for the poor agreement between the calculated and measured activities in these assessments. To obtain better agreement between experimentally determined and calculated activities in the framework of the Redlich–Kister formalism obviously more than five parameters should be considered. Moreover, contrary to the Redlich–Kister formalism, the parameters used in the present thermodynamic model have physical meanings. These parameters could be very useful in modeling selected material properties such as interfacial segregation.

Conclusions

From the results of the present study the following conclusions can be drawn.

- The solidus line obtained experimentally from 600 to 1040°C in the present work and the liquidus line from the literature are successfully fitted using a recently developed self-associate model of binary alloys with a demixing tendency in the liquid state under the assumption of a linear temperature dependence of the interchange energy between the atoms in the liquid and solid phases.
- The solidus line has the form of a retrograde curve and exhibits no monotectic reaction. This is supported by the fact that the calculated miscibility gap in the liquid phase with the maximum at 37.7 at.% Bi and 674.8°C lies below the liquidus line. The calculated eutectic temperature (270.3°C) is 0.3°C lower than the previously assessed value, while the calculated and previously accepted eutectic concentrations are in agreement (99.5 at.% Bi).
- The optimized model parameters provide a good description of the thermodynamic properties of liquid Cu–Bi alloys at 927 and 1100°C. The agreement between optimized and experimentally measured activities of Cu and Bi in the liquid phase is superior to the agreement obtained using the Redlich–Kister formalism with five optimization parameters. The optimized temperature dependence of the interchange energy in the solid and liquid phases is consistent with the estimation from the relative thermal expansion coefficients.

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft (contract Gu 258/12–1) and the INTAS Programme (contract 93-1451).

Cited References

- 1897Hey: C.T. Heycock and F.H. Neville, *Philos. Trans. R. Soc. (London)A*, 189, 25 (1897).
- 05Hio: A.H.Hio, Trans. Faraday Soc., 1, 179(1905).
- 07Jer: K. Jeriomin, Z. Anorg. Chem., 55, 412 (1907) in German.
- **07Por:** M.A. Portevin, *Rev. Metall.*, *4*, 1077 (1907) in French.
- **27Han:** D. Hansen and G.W. Ford, J. Inst. Met., 37, 169 (1927).
- **46Rau:** E. Raub and A. Engel, *Z. Metallkd.*, *37*, 76(1946) in German.
- **47Voc:** E. Voce and A.R.C. Hallowes, *J. Inst. Met.*, 73, 323 (1947).
- **52Kle:** O.J. Kleppa, *J. Amer. Chem. Soc.*, 74, 6074 (1952).
- **57Bas:** G.Bassi, *Z. Metallkd.*, 48, 394 (1957) in German.
- 57Tay: J.W. Taylor, Rev. Metall., 54, 960 (1957) in French.
- **61Oel:** W.Oelsen, E.Schurmann, and D. Buchholz, *Arch. Eisenhüttenwes.*, *32*, 39(1961) in German.
- 62Nat: M.W. Nathans and M. Leider, J. Phys. Chem., 66, 2012 (1962).
- 64Lom: A.L. Lomov and A.H. Krestovnikov, *Izv. V. U. Z. Tsvtn. Metall.*, *1*, 84(1964) in Russian.
- 67Aza: T. Azakami and A. Yazawa, J. Min. Metall. Inst. Jpn., 83, 666 (1967).
- 72Gra: D.E. Gray, Ed., American Institute of Physics Handbook, 3rd ed., McGraw–Hill, New York, 123 (1972).
- 73Hul: R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelley, Selected Values of the Thermodynamic Properties of Binary

Basic and Applied Research: Section I

alloys, American Society for Metals, Metals Park, OH, 28, 778 (1973).

- 73Pre: B. Predel and A. Emam, Z. Metallkd., 64, 496(1973) in German.
- **76Gom:** M. Gomez, L. Martin–Garin, H. Ebert, P. Bedon, and P. Desre, *Z. Metallkd.*, 67, 131 (1976) in German.
- 81Tas: P. Taskinen and J. Niemelä, Scand. J. Metall., 10, 195 (1981).
- 81Vas: M.V. Vasil'ev, Russ. J. Phys. Chem., 55(3), 338(1981).
- 84Cha: D.J. Chakrabarti and D.E. Laughlin, Bull. Alloy Phase Diagrams, 5, 148 (1984).
- **86Nie:** J.Niemelä, G.Effenberg, K.Jack, and P.J.Spencer, *Calphad*, *10*, 77 (1986).
- **90Meh:** H.Mehrer(ed.), *DiffusioninSolidMetalsandAlloys*, Landolt–Börnstein New Series, *Vol. III/26*, Springer-Verlag, Berlin, 142 (1990).
- **90Tep:** O. Teppo, J. Niemelä, and P. Taskinen, *Thermochim. Acta*, *173*, 137 (1990).
- 91Din: A.T. Dinsdale, CALPHAD, 15, 317 (1991).
- **92Bra:** E.A. Brandes and G.B. Brook, Ed., *Smithells Metals Reference Book*, 7th ed., Butterworth Heinemann, Oxford (1992).
- 92Sin: R.N. Singh and F. Sommer, Z. Metallkd., 83, 533 (1992).
- **94Som:** F. Sommer and R. N. Singh, Z. Metallkd., 85, 621 (1994).
- **95Li:** Q.–H.Li and L.–D. Zhang, *Acta Metall. Sin.*, *31*(3), 130(1995) in Chinese .