

Thermodynamic Reevaluation of the Cu-Zn System

M. Kowalski and P.J. Spencer
 Lehrstuhl für Theoretische Hüttenkunde
 R.W.T.H. Aachen
 D-52074 Aachen, Germany

In the present reevaluation of the Cu-Zn system, the ordering in the β phase is described using a two sublattice model, whereas four sublattices are used to model the γ phase. A self-consistent set of coefficients has been obtained, allowing both the equilibrium phase diagram and the thermodynamic properties to be calculated in close agreement with experimental observations.

1. Introduction

Because of their major technological importance, Cu-Zn alloys have been widely investigated. The Cu-Zn phase diagram is generally well established [44Ray, 58Han, 86Mas], and only small uncertainties concerning the phase boundaries at lower temperatures remain. A large number of thermodynamic investigations of solid and liquid alloys also have been made. There is qualitative agreement between the different results, but the scatter is significant in some of the experimental data, particularly for liquid, β , and γ phase alloys.

In his book *Metallurgical Thermochemistry*, Kubaschewski [55Kub] already in 1955 presented evaluated data for the Cu-Zn system and used plots of the different thermodynamic properties to discuss the characteristic features of partial and integral thermodynamic functions in homogeneous and heterogeneous ranges of an alloy system, as well as the behavior of the functions at phase boundaries. This work represents one of the earliest detailed thermodynamic assessments in which

consistency between measured thermodynamic values and phase boundaries of an alloy system is taken into account fully. As such, it constitutes part of Kubaschewski's pioneering work in the area of thermodynamic evaluation of phase diagrams, a field which, due to the availability of the computer, now contributes significantly to the large-scale efforts devoted to constitution studies in complex systems of all types.

The present evaluation of the Cu-Zn system also makes use of computer methods to assist the reliable selection of thermodynamically self-consistent values from all available experimental data. An earlier study [86Spe], which used the simple substitutional model for all the solution phases, produced satisfactory agreement between experimental and calculated phase boundaries and thermodynamic properties. However, the thermodynamic data for pure Cu and Zn used in that work have subsequently been amended as part of a general revision of Gibbs energy values for the pure elements carried out by Dinsdale [89Din] at the instigation of the Scientific Group Thermodata Europe (SGTE). This necessitates up-dating of

Table 1 Experimental [86Mas] and Calculated Invariant Equilibria

Equilibrium	Temperature, K		Phase	Composition, at. % Zn	
	Experimental	Calculated		Experimental	Calculated
Peritectic					
(Cu) + L \leftrightarrow β	1176	1176	(Cu)	0.319	0.319
			β	0.361	0.353
			L	0.368	0.373
β + L \leftrightarrow γ	1108	1108	β	0.558	0.558
			γ	0.591	0.586
			L	0.591	0.592
γ + L \leftrightarrow δ	973	973	γ	0.692	0.678
			δ	0.724	0.719
			L	0.800	0.802
δ + L \leftrightarrow ϵ	871	873	δ	0.760	0.773
			ϵ	0.781	0.792
			L	0.880	0.882
ϵ + L \leftrightarrow (Zn).....	697	695	ϵ	0.872	0.875
			(Zn)	0.972	0.981
			L	0.983	0.983
Eutectoid					
δ \leftrightarrow γ + ϵ	831	832	γ	0.700	0.693
			δ	0.740	0.749
			ϵ	0.780	0.777

the previous evaluation, which at the same time provides an opportunity to use a physically more realistic model for the description of the structures of the different phases. Additional experimental information also has been incorporated in the present assessment.

Optimization of the excess Gibbs energy coefficients for the different solution phases was carried out using the program due to Lukas [77Luk], whereas the ordering parameter in the β phase was optimized using the program Thermo-Calc [85Sun]. The latter software also was used to produce the figures illustrating the results of the present assessment.

2. Experimental Phase Diagram Information

Figure 1 presents the experimental phase diagram used as a basis for this assessment. It is essentially that proposed by Raynor [44Ray] from a review of the earlier experimental investigations and reproduced with minor modifications by Hansen [58Han] and later by Massalski [86Mas]. The temperatures and compositions of coexisting phases at invariant equilibria as reported by Massalski [86Mas] are presented in Table 1.

3. Experimental Thermodynamic Information

3.1 Liquid Alloys

The relative chemical potential of Zn in liquid Cu-Zn alloys (Fig. 2) has been determined by Schneider and Schmid [42Sch] (923 to 1123 K), Everett et al. [57Eve] (1069 to 1303 K), Downie [64Dow] (1200 K), Azakami and Yazawa [68Aza] (1073 to 1473 K), Solovev et al. [79Sol] (1373 K), and Sugino and Hagiwara [86Sug] (1323 to 1423 K) using a variety of va-

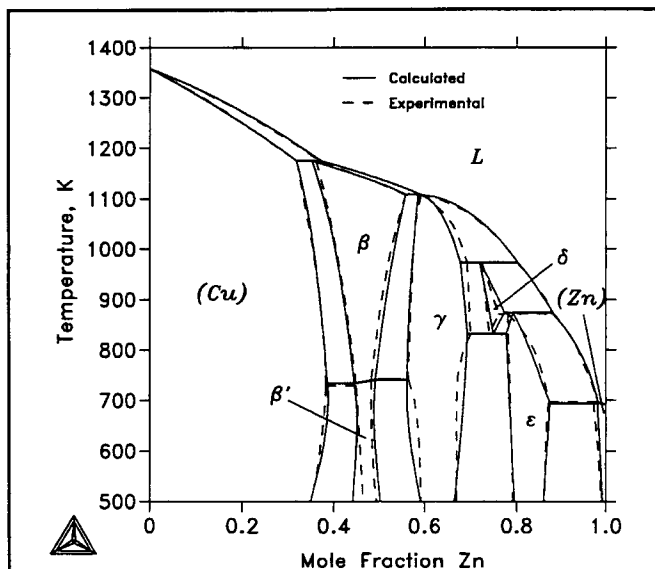


Fig. 1 Experimental Cu-Zn phase diagram reported by Massalski [86Mas] compared with the phase diagram calculated using evaluated data from this assessment.

por pressure techniques; by Leitgeb [31Lei] (1188 to 1773 K) and by Baker [70Bak] (1373 to 1473 K) using the boiling point method; and by Kleppa and Thalmayer [59Kle] (900 K) and Gerling and Predel [80Ger] (1073 to 1174 K) from emf investigations. There is a good general agreement between the different experimental values.

Enthalpies of mixing for the liquid phase (Fig. 3) have been determined calorimetrically by von Samson-Himmelstjerna [36Sam] (1273 K) and by Parameswaran and Healy [78Par] (1400 K). However, apart from values for copper-rich alloys, the results from the two investigations show large differences.

3.2 Solid Alloys

Most experimental investigations of solid Cu-Zn alloys (Fig. 4) have been confined to the fcc phase. Hargreaves [39Har] (800 to 1283 K), Seith and Krauss [38Sei] (1073 to 1123 K), Argent and Wakeman [58Arg] (1000 K), and Masson and Sheu [70Mas] (1063 K) all used vapor pressure methods in obtaining values of the chemical potential of Zn for fcc alloys. The fcc phase also has been investigated by Pemsler and Rappert [69Pem] (523 to 823 K) using an atomic absorption method.

The investigations by Hargreaves [39Har] and Seith and Krauss [38Sei] included measurements for the β phase, whereas Ölander [33Ola], using an emf method, obtained data for β , γ , δ , and ϵ phase alloys (685 to 899 K).

The results for the fcc (Cu) phase are rather scattered, the scatter between the different investigations increasing with increasing Zn concentration. For the β phase, chemical potentials of Zn determined by Ölander [33Ola] lie between the values obtained by Seith and Krauss [38Sei] and by Hargreaves [39Har], which show large differences (ignoring the temperature dependence of the data).

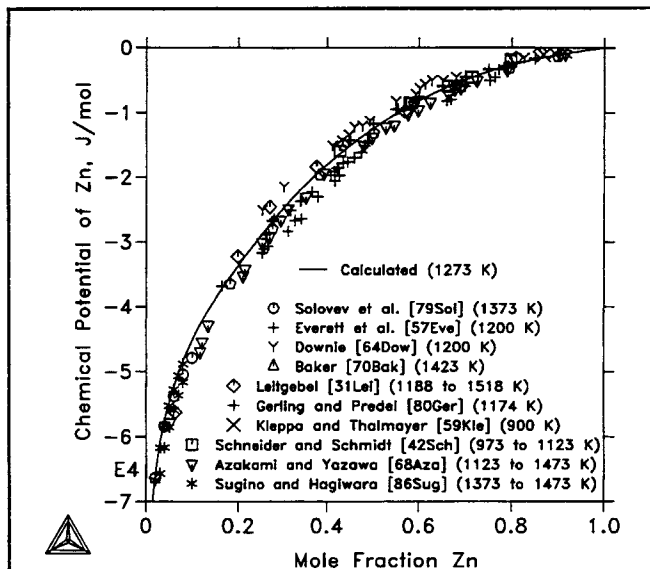
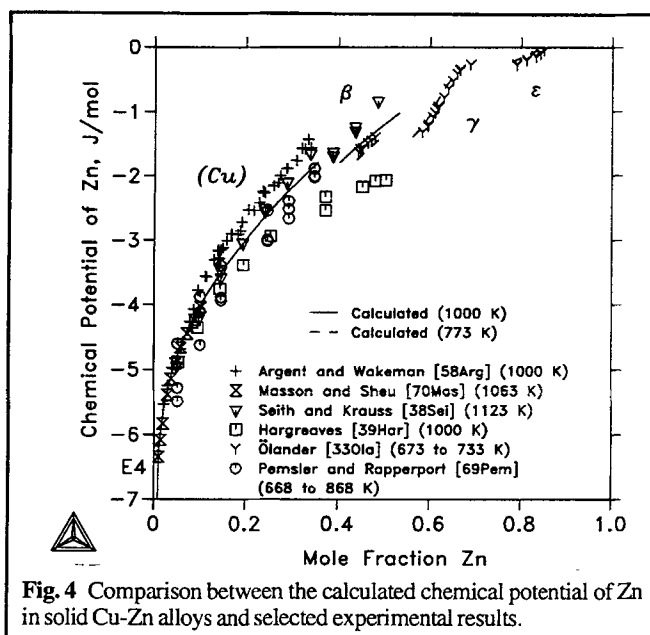
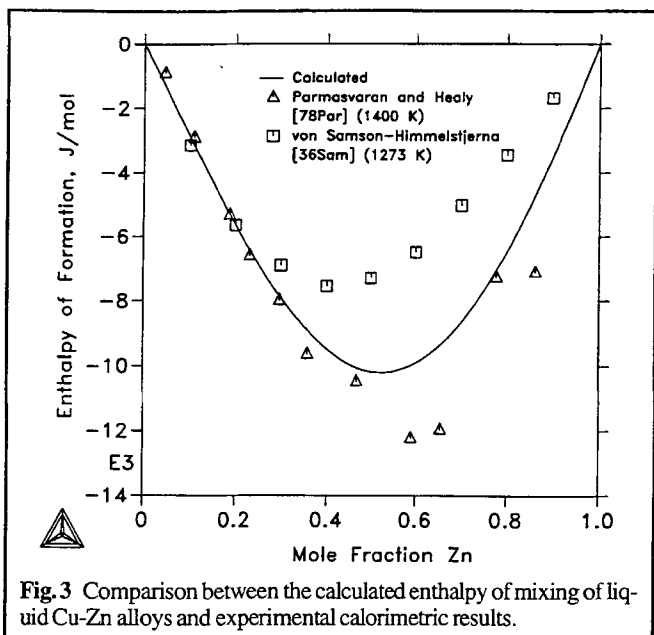


Fig. 2 Comparison between the calculated chemical potential of Zn in liquid Cu-Zn alloys and selected experimental results.



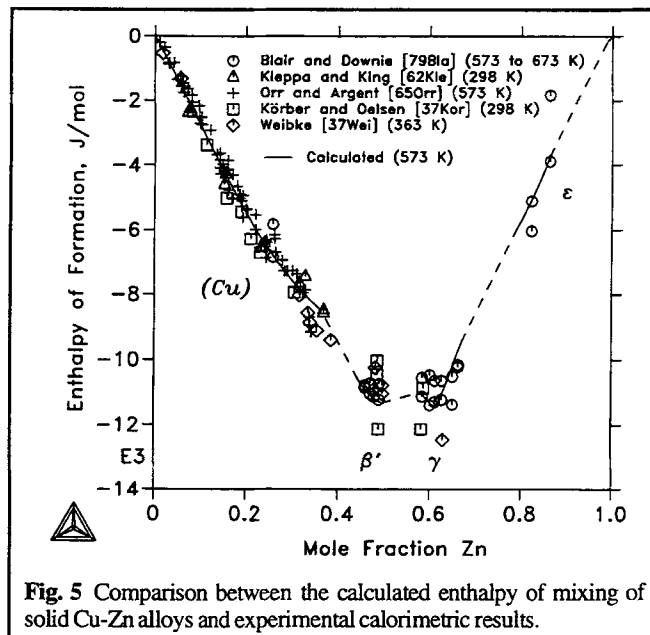
The only available results for γ , δ , and ϵ phase alloys are those obtained by Ölander [33Ola].

Enthalpies of formation of fcc alloys (Fig. 5) have been determined from calorimetric measurements made by von Samson-Himmelstjerna [36Sam] (293 K), Körber and Oelsen [37Kor] (298 K), Weibke [37Wei] (363 K), Kleppa and King [62Kle] (298 K), Orr and Argent [65Orr] (573 K), and Blair and Downie [79Blai] (573 to 673 K). Several of these authors also have made measurements for the β , γ , and ϵ phases of the system. Since it is difficult to establish equilibrium in the alloy specimens used for calorimetric measurements near room temperature, there must be some doubt as to whether the experimental values for ordered β and γ phase alloys are associated with homogeneous, single-phase specimens. This applies particularly to the investigations made by [36Sam], [37Kor], and [37Wei].

4. Method of Evaluation

This reevaluation of the Cu-Zn system was mainly carried out using the optimization program written by Lukas et al. [77Luk]. The excess coefficients (Redlich-Kister description) reported by Spencer [86Spe] were used as starting values, and the experimental data files used in conjunction with the earlier evaluation were supplemented by additional measurements [79Sol, 86Sug].

In the present work, the substitutional solution model has been applied to the liquid, (Cu), β (also δ), ϵ , and (Zn) phases. In contrast to the earlier assessment [86Spe], modelling based on the Wagner-Schottky theory [30Wag] has been used in describing the thermodynamic properties of the γ phase. An explicit description of the ordering in the β phase was achieved using the Thermo-Calc program [85Sun], whereby the only experimental information used was the temperature of the order-disorder transformation at the stoichiometric composition.



The assessed coefficient sets for the β and γ phases have been represented in equivalent sublattice form.

Gibbs energy values for pure Cu and Zn in all phases, expressed in conventional SGTE form, have been taken from the recent compilation due to Dinsdale [89Din].

5. Results and Discussion

All parameters assessed in this work are collected with the data for the pure elements in Table 2 (expressed in the form of a Thermo-Calc file).

Figures 1 to 6 and the comparison of temperatures and compositions of invariant equilibria presented in Table 1 summarize

Table 2 Assessed Parameters for the Cu-Zn System

Liquid

(Cu,Zn)₁

$${}^0G_{Cu}^{Liquid} - H_{Cu}^{SER} = 12\,964.84 - 9.510243 \times T - 5.839 \times 10^{-21} \times T^7 + GH_{Cu}^{SER}$$

for 298.14 < T < 1358.01

$$13\,495.4 - 9.920463 \times T - 3.646 \times 10^{29} \times T^{-9} + GH_{Cu}^{SER}$$

for 1358.01 < T < 2000.00

$${}^0G_{Zn}^{Liquid} - H_{Zn}^{SER} = 7157.27 - 10.292343 \times T - 3.5865 \times 10^{-19} \times T^7 + GH_{Zn}^{SER}$$

for 298.14 < T < 692.73

$$7450.123 - 10.736234 \times T - 4.7066 \times 10^{26} \times T^{-9} + GH_{Zn}^{SER}$$

for 692.73 < T < 2000.00

$${}^0L_{Cu,Zn}^{Liquid} = -40\,695.54 + 12.65269 \times T$$

$${}^1L_{Cu,Zn}^{Liquid} = 4402.72 - 6.55425 \times T$$

$${}^2L_{Cu,Zn}^{Liquid} = 7818.10 - 3.25416 \times T$$

fcc-(Cu)

(Cu,Zn)₁

$${}^0G_{Cu}^{fcc} - H_{Cu}^{SER} = GH_{Cu}^{SER}$$

$${}^0G_{Zn}^{fcc} - H_{Zn}^{SER} = 2969.82 - 1.56968 \times T + GH_{Zn}^{SER}$$

$${}^0L_{Cu,Zn}^{fcc} = -42\,803.75 + 10.02258 \times T$$

$${}^1L_{Cu,Zn}^{fcc} = 2936.39 - 3.05323 \times T$$

$${}^2L_{Cu,Zn}^{fcc} = 9034.20 - 5.39314 \times T$$

bcc-β, β', δ

(Cu,Zn)₁(Cu,Zn)₁

$${}^0G_{Cu:Cu}^{bcc} - H_{Cu}^{SER} = G_{Cu}^{bcc}$$

$${}^0G_{Zn:Zn}^{bcc} - H_{Zn}^{SER} = G_{Zn}^{bcc}$$

$${}^0G_{Cu:Zn}^{bcc} - 0.5 \times H_{Cu}^{SER} - 0.5 \times H_{Zn}^{SER} = 0.25 \times L_0 + 0.5 \times G_{Cu}^{bcc} + 0.5 \times G_{Zn}^{bcc} - P$$

$${}^0G_{Zn:Cu}^{bcc} - 0.5 \times H_{Zn}^{SER} - 0.5 \times H_{Cu}^{SER} = 0.25 \times L_0 + 0.5 \times G_{Cu}^{bcc} + 0.5 \times G_{Zn}^{bcc} - P$$

$${}^0L_{Cu,Zn:Cu}^{bcc} = {}^0L_{Cu,Zn:Zn}^{bcc} = {}^0L_{Cu:Cu,Zn}^{bcc} = {}^0L_{Zn:Cu,Zn}^{bcc} = 0.25 \times L_0 + 0.375 \times L_1 + 0.1875 \times L_2 + P$$

$${}^1L_{Cu,Zn:Cu}^{bcc} = {}^1L_{Cu,Zn:Zn}^{bcc} = {}^1L_{Cu:Cu,Zn}^{bcc} = {}^1L_{Zn:Cu,Zn}^{bcc} = 0.125 \times L_1 + 0.25 \times L_2$$

$${}^2L_{Cu,Zn:Cu}^{bcc} = {}^2L_{Cu,Zn:Zn}^{bcc} = {}^2L_{Cu:Cu,Zn}^{bcc} = {}^2L_{Zn:Cu,Zn}^{bcc} = 0.0625 \times L_2$$

$${}^0L_{Cu,Zn:Cu,Zn}^{bcc} = -1.5 \times L_2$$

γ-phase

(Cu,Zn)₈(Cu,Zn)₈Cu₁₂Zn₂₄

$${}^0G_{Cu:Cu:Cu:Zn}^{\gamma} - 0.53847 \times H_{Cu}^{SER} - 0.46154 \times H_{Zn}^{SER} = K_4 + 0.15385 \times K_5 + 0.53846 \times GH_{Cu}^{SER} + 0.46154 \times GH_{Zn}^{SER}$$

$${}^0G_{Zn:Cu:Cu:Zn}^{\gamma} - 0.38462 \times H_{Cu}^{SER} - 0.61539 \times H_{Zn}^{SER} = K_4 + 0.15385 \times K_5 + 0.15385 \times K_6 + 0.38462 \times GH_{Cu}^{SER} + 0.61539 \times GH_{Zn}^{SER}$$

$${}^0G_{Cu:Zn:Cu:Zn}^{\gamma} - 0.38462 \times H_{Cu}^{SER} - 0.61539 \times H_{Zn}^{SER} = K_4 + 0.38462 \times GH_{Cu}^{SER} + 0.61539 \times GH_{Zn}^{SER}$$

$${}^0G_{Zn:Zn:Cu:Zn}^{\gamma} - 0.23077 \times H_{Cu}^{SER} - 0.76924 \times H_{Zn}^{SER} = K_4 + 0.15385 \times K_6 + 0.23077 \times GH_{Cu}^{SER} + 0.76924 \times GH_{Zn}^{SER}$$

ε-phase

(Cu,Zn)₁

$${}^0G_{Cu}^{\epsilon} - H_{Cu}^{SER} = 1 + GH_{Cu}^{SER}$$

$${}^0G_{Zn}^{\epsilon} - H_{Zn}^{SER} = 2969.82 - 1.56968 \times T + GH_{Zn}^{SER}$$

$${}^0L_{Cu,Zn}^{\epsilon} = -35\,433.3 + 5.24516 \times T$$

$${}^1L_{Cu,Zn}^{\epsilon} = 25\,276.81 - 9.96989 \times T$$

(Zn)

(Cu,Zn)₁

$${}^0G_{Cu}^{cph} - H_{Cu}^{SER} = 600 - 0.2 \times T + GH_{Cu}^{SER}$$

$${}^0G_{Zn}^{cph} - H_{Zn}^{SER} = GH_{Zn}^{SER}$$

$${}^0L_{Cu,Zn}^{cph} = -14\,432.17 - 10.7814 \times T$$

Functions

$$GH_{Cu}^{SER} = -7770.458 + 130.485403 \times T - 24.112392 \times T \times \ln T - 0.00265684 \times T^2 + 1.29223 \times 10^{-7} \times T^3 + 52.478/T$$

for 298.14 < T < 1358.01

$$-13\,542.33 + 183.804197 \times T - 31.38 \times T \times \ln T + 3.64643 \times 10^{29} \times T^{-9}$$

for 1358.01 < T < 2000.00

$$GH_{Zn}^{SER} = -7285.787 + 118.469269 \times T - 23.701314 \times T \times \ln T(T) - 0.001712034 \times T^2 - 1.264963 \times 10^{-6} \times T^3$$

for 298.14 < T < 692.73

$$-11\,070.597 + 172.344911 \times T - 31.38 \times T \times \ln T + 4.70657 \times 10^{26} \times T^{-9}$$

for 692.73 < T < 2000.00

$$G_{Cu}^{bcc} = GH_{Cu}^{SER} + 4017 - 1.255 \times T \quad G_{Zn}^{bcc} = GH_{Zn}^{SER} + 2886.96 - 2.5104 \times T$$

$$L_0 = -51\,595.87 + 13.06392 \times T \quad K_4 = -11\,552.71 - 1.67824 \times T$$

$$L_1 = 7562.13 - 6.45432 \times T \quad K_5 = 15\,732.30 - 10.26575 \times T$$

$$L_2 = 30\,743.74 - 29.91503 \times T \quad K_6 = 37\,289.20 - 13.05259 \times T$$

$$P = 3085$$

Note: In J/mol.

and illustrate the results obtained from the present assessment. There is excellent agreement between calculated and experimental values across the entire system. In particular, by appli-

cation of physically more realistic modeling to the β and γ phases as compared to the previous evaluation [86Spe], a much improved description of phase boundaries and thermo-

Section I: Basic and Applied Research

dynamic properties at lower temperatures as well as in Zn-rich alloys has been achieved. Because various models have been used in conjunction with the different phases, the particular problems associated with each are discussed separately below.

5.1 Liquid Alloys

Liquid Cu-Zn alloys are described using the substitutional solution model. Excellent agreement with the experimental liquidus boundary is obtained across the entire system (Fig. 1). Calculated values of the relative chemical potential of Zn (Fig. 2) also reproduce the experimental results very well. Calculated enthalpies of mixing of liquid alloys (Fig. 3) are similar to those presented earlier [86Spe] and tend to support the calorimetric results obtained by Parameswaran and Healy [78Par]. The coefficients describing the excess properties of the liquid phase differ only slightly from the previous values [86Spe].

5.2 Solid Alloys

5.2.1 fcc Phase (Cu)

The copper-based fcc phase is also described using the substitutional solution model. Again, good agreement with experimental chemical potential and enthalpy measurements (Fig. 4 and 5), as well as good reproduction of phase boundaries involving the fcc phase (Fig. 1), has been achieved.

5.2.2 bcc Phases (β , δ)

The two bcc phases, β and δ , are both of the same W structure-type. (All structural information used in this evaluation is taken from Massalski [86Mas] and Villars and Calvert [85Vil]). As in the earlier assessment of the system [86Spe], the phases are described with the same coefficient set using the

substitutional solution model. The evaluated coefficients enable phase boundaries involving the β phase to be reproduced to within ~ 1.5 mol% and the δ phase to within ~ 2 mol% (Fig. 1). The calculated chemical potential of Zn in the β phase (Fig. 4) is in excellent accord with the experimental data of Ölander [33Ola].

5.2.3 Hexagonal Phases (ϵ , (Zn))

Two solution phases having the cph Mg-type structure, ϵ and (Zn), are present in the Zn-rich region of the Cu-Zn system. Because of the large difference in c/a ratio for the (Zn) and ϵ phases (1.856 and 1.556, respectively) and the rather small change in c/a across the homogeneity range of ϵ , the two phases have been treated separately. If a single treatment of ϵ and (Zn) is used, with solid immiscibility between the two, application of higher order interaction terms is found to be necessary. These lead to rather unrealistic numerical values of the interaction coefficients. Similar difficulties still arise when the phases are treated as two different cph phases, i.e. with two different sets of interaction coefficients. Consequently, because the value of the c/a ratio for the ϵ phase lies closer to the c/a ratio of the ideal closest packed structure (1.633), the well-established value of the lattice stability for pure Zn in the fcc structure was used in the thermodynamic description of ϵ .

5.2.4 γ -Phase

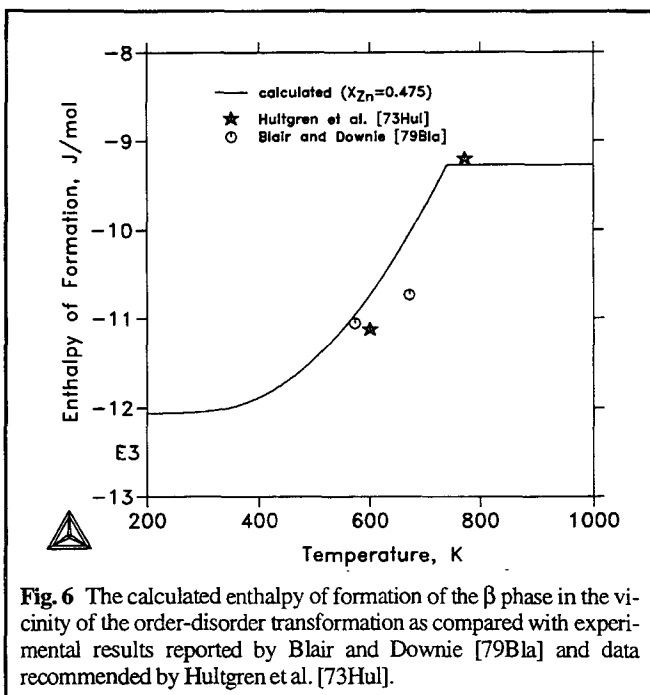
The γ phase, with the Cu_5Zn_8 prototype structure, is stable over a relatively wide composition range. The elementary cell contains 52 atoms occupying four site sets denoted by 8c, 12e, 8c, and 24g (Wyckoff notation). The distribution of the Cu and Zn atoms over all sites was investigated by von Heidenstam et al. [68Hei] using neutron diffraction. The three possible distribution models proposed lead to a four-lattice model and are shown in Table 3. Mixing on all four sublattices gives rather poor agreement with diffraction data and therefore has been eliminated [68Hei].

The first manner of distribution (A) can be applied only for strict stoichiometric phases and has been rejected in this assessment. Two further possible site occupations (B,C) also have been verified. The distribution denoted B, i.e. mixing of Cu and Zn sites 8c, has been accepted in this work as leading to greater defect density (site fraction of Zn on sublattice I and vice versa) at the stoichiometric composition than the distribution C.

Table 3 Atomic Distribution Models for the Stoichiometric γ Phase According to [68Hei]

Model	Site/sublattice occupation			
	8c/I	8c/II	12e/III	24g/IV
A	Cu	Zn	Cu	Zn
B	Cu,Zn	Cu,Zn	Cu	Zn
C	Cu	Zn	Cu,Zn	Cu,Zn

Note: The symbol Cu,Zn denotes a random distribution over all sites so designated.



The agreement between calculated and experimental thermodynamic values for γ phase alloys is very good, as illustrated in Fig. 4 and 5.

5.2.5 β' Phase

The bcc β' phase is an ordered modification of the β phase with the CsCl structure. The ordering is composition dependent and occurs in the temperature range from 730 to 740 K. A two sublattice model proposed by Saunders [89Sau] has been used to describe the order-disorder transformation. This description is based on an assessment of ordering in the Al-Li-Zr system.

The β phase contains two atoms (sublattices) in the elementary cell. In the disordered state, the site fractions of the same element on the two sublattices are identical and equal to the phase composition. The energy terms in the two sublattice model for the disordered bcc phase have been derived from the excess terms of the substitutional solution model for this phase. Consequently, the calculated excess Gibbs energy is identical in the two cases. In order to stimulate the distribution of Cu and Zn between the two sublattices, a supplementary energy term has been introduced to decrease the interaction energy between Cu and Zn atoms on different sublattices and to increase the interactions on the same sublattice (Table 1). This term was evaluated using Thermo-Calc [85Sun]. Because of uncertainties in the phase boundary information, only the temperature of the order-disorder transformation was used in the assessment.

The calculated boundaries of the ordered β phase and the thermodynamic properties of mixing (Fig. 6) show good agreement with available experimental information. At Zn concentrations corresponding to the homogeneity range of the δ phase ($X_{Zn} = 0.75$) the temperature of the order-disorder transformation reaches ~ 600 K and is thus significantly lower than the lower stability limit of the δ phase.

6. Summary

A reevaluation of the Cu-Zn system has been carried out; it incorporates an explicit description of the ordering in the β phase, a four sublattice model applied to the γ phase, and new lattice stability data for the pure elements. The resulting assessment provides a physically more realistic treatment of the phases in the system and results in a set of coefficients that allow all experimental phase diagram and thermodynamic data to be reproduced within narrow limits. A reliable basis for evaluation of higher-order systems containing the phases of the Cu-Zn system thus has been established.

Acknowledgment

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