

Local order in Cd-based liquid alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 8457

(<http://iopscience.iop.org/0953-8984/2/42/022>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 06:56

Please note that [terms and conditions apply](#).

Local order in Cd-based liquid alloys

R N Singh, I K Mishra and V N Singh

Department of Physics, Bhagalpur University, Bhagalpur-812007, India

Received 16 May 1990, in final form 23 July 1990

Abstract. A simple approach based on a statistical mechanical model is used to discuss the nature of atomic ordering in Cd-based (Cd–Bi, Cd–Mg and Cd–Ga) liquid alloys in the framework of the chemical short-range order parameter, concentration fluctuation in the long-wavelength limit and the excess free energy of mixing. It has been observed that the nature of atomic order in binary liquid alloys could be understood with the help of their melting curves.

Recently Singh and Mishra (1988) have studied the thermodynamics of the alloying of binary liquid alloys based on a simple statistical mechanical model. The grand partition function has been used to obtain analytic expressions for the conditional probabilities enumerating the occupation of two neighbouring sites by the atoms of the constituent elements in terms of the ordering energy. Various other thermodynamic relations such as the chemical short-range order parameter, concentration fluctuations in the long-wavelength limit, free energy of mixing and activity follow readily. Such an approach has an added advantage (Young 1987) over the first-principles pseudopotential method (Umar *et al* 1974, Hafner 1977, Ashcroft and Stroud 1978, Singh 1980, Pandey *et al* 1988) owing to the restricted use of the latter.

We intend to discuss the nature of atomic ordering in Cd-based liquid alloys (Cd–Bi, Cd–Ga and Cd–Mg) in the light of the phase diagram. Our choice for these liquid alloys has been influenced by the following facts.

(i) Each of these alloys has a characteristic melting curve. The liquidus line of Cd–Bi is a simple eutectic; Cd–Ga is a monotectic and the liquidus line of Cd–Mg rises monotonically from Cd to Mg. The liquidus lines of these alloys are schematically represented in figure 1.

(ii) Cd is highly reactive and therefore it is difficult to perform diffraction experiments. A theoretical investigation giving structural information on such systems is highly desirable.

If we consider that a binary alloy consists of $N_A (=NC_A)$ atoms of the element A and $N_B (=NC_B)$ atoms of the element B so that there are $N (=N_A + N_B)$ atoms in total, then the grand partition function for the alloy can be written as

$$\Xi = \sum_E q_A^{N_A}(T) q_B^{N_B}(T) \exp\left(\frac{\mu_A N_A + \mu_B N_B - E}{k_B T}\right) \quad (1)$$

where $q_i(T)$ are the partition functions of atoms i ($\equiv A$ or B) associated with inner and

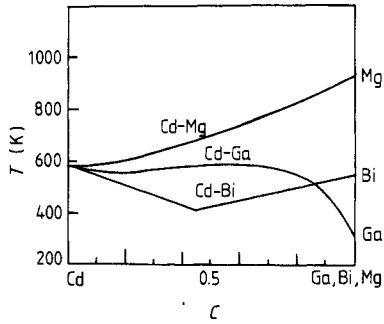


Figure 1. Schematic representation of liquidus lines for Cd-Bi, Cd-Mg and Cd-Ga alloys (from Hultgren *et al* (1973)).

vibrational degrees of freedom. It has been assumed that q_i remain the same whether the atom i is located in the pure state or in the alloy. μ_A and μ_B are the chemical potentials and E is the configurational energy. By considering (Singh 1987, Singh and Mishra 1988) the atomic clusters of different sizes, equation (1) can be utilized to obtain expressions for the conditional probability $P_{A/B}$, which denotes the probability of finding atom A as a nearest neighbour of a given atom B, i.e.

$$P_{A/B} = [1 + (C_B/C_A)\sigma^{-1} \exp(\omega/zk_B T)]^{-1} \quad (2)$$

and also

$$P_{B/A} = [1 + (C_A/C_B)\sigma \exp(\omega/zk_B T)]^{-1} \quad (3)$$

with

$$\sigma = (\beta + 2C - 1) \exp(-\omega/zk_B T)/2C \quad (4)$$

$$\beta = \{1 + 4C_A C_B [\exp(2\omega/zk_B T) - 1]\}^{1/2}. \quad (5)$$

ω is usually called the ordering energy of the alloy and it is very important to understand the alloying behaviour of binary alloys. $\omega = 0$ refers to ideal alloys, $\omega > 0$ suggests like atoms pairing as nearest neighbours whereas $\omega < 0$ occurs when there is a tendency to form unlike-atom pairs. Z is the coordination number. In the present work we have determined ω at a given concentration from the observed activity and treated it as concentration independent.

The conditional probabilities are also related to the Warren–Cowley (Warren 1969, Cowley 1950) chemical short-range order parameter α_1 for the first coordination shell, i.e.

$$P_{A/B} = C_A(1 - \alpha_1) \quad P_{B/A} = C_B(1 - \alpha_1). \quad (6)$$

Equations (2)–(6) allow us to express α_1 in terms of the ordering energy ω , i.e.

$$\alpha_1 / [(1 - \alpha_1)^2 C_A C_B] = \exp(2\omega/zk_B T) - 1. \quad (7)$$

It is interesting to observe that an expression for short-range order of the type (7) can also be obtained (Khvaya *et al* 1977) by following an entirely different approach from the pseudopotential method in second-order perturbation theory. The expressions used by Cowley (1950) and Clapp and Moss (1966, 1968a, b) for short-range order for the first shell also reduce to equations of the form (7).

Further we observe from equation (7) that, for $\omega = 0$, $\alpha_1 = 0$, which implies a random distribution of atoms in the alloy. If $\omega > 0$, α_1 is positive, i.e. there is segregation, and, if $\omega < 0$, α_1 is negative, which shows ordering in the alloy.

Table 1. Coordination number z and the ordering energy ω in binary liquid alloys.

Alloy	T (K)	z	ω (eV)
Cd-Bi	773	10	-0.0148
Cd-Mg	923	10	-0.1864
Cd-Ga	700	10	+0.1132

On the other hand, equation (4) can be used to obtain an analytic expression for the excess free energy G_M^{xs} of mixing (which equals $G_M - Nk_B T \sum_i C_i \ln C_i$) using the integral (Bhatia and Singh 1982)

$$\frac{G_M^{\text{xs}}}{Nk_B T} = \int_0^C \ln \sigma^z dC = C_A \ln \gamma_A + C_B \ln \gamma_B \quad (8)$$

where

$$\gamma_A = [(\beta - 1 + 2C_A)/C_A(1 + \beta)]^{z/2} \quad \gamma_B = [(\beta + 1 - 2C_A)/C_B(1 + \beta)]^{z/2}. \quad (9)$$

Therefore, the concentration fluctuation (Bhatia and Thornton 1970) in the long-wavelength limit becomes

$$\begin{aligned} S_{CC}(0) &= RT(\partial^2 G_M / \partial C^2)_{T,P,N}^{-1} \\ &= C_A C_B [1 + (z/2\beta)(1 - \beta)]^{-1}. \end{aligned} \quad (10)$$

$S_{CC}(0)$ can also be identified in terms of the excess stability function E^{xs} (Darken 1967), i.e.

$$E^{\text{xs}} = RT [1/S_{CC}(0) - 1/C_A C_B]. \quad (11)$$

By eliminating the ordering energy of equation (7) with the help of equation (10), one arrives at a relation between α_1 and $S_{CC}(0)$, i.e.

$$\alpha_1 = (S - 1)/[S(z - 1) + 1] \quad S = S_{CC}(0)/C_A C_B. \quad (12)$$

For ideal alloys ($\omega = 0$), one readily obtains $\alpha_1 = 0$, $G_M^{\text{xs}} = 0$, $S_{CC}(0) = C_A C_B$ and $E^{\text{xs}} = 0$.

The application of these relations to binary liquid alloys depends upon knowledge of the coordination number z and the ordering energy ω . In the liquid and amorphous states, the atoms are randomly distributed in a nearly close-packed structure and the coordination number of the nearest neighbour atoms is about 10. So far as ω is concerned, it can be determined from first principles by using the pairwise interaction of the pseudopotential method (Hayes *et al* 1968) but very little work has been done in this direction. On the other hand, ω can also be determined very easily from the observed activity data or from the free energy of mixing (Bhatia and Singh 1982). For example, the excess free energy of mixing (equation (8)) for the equiatomic composition ($C_A = C_B = \frac{1}{2}$) becomes

$$G_M^{\text{xs}}/Nk_B T = \ln 2^{z/2} [1 + \exp(-\omega/zk_B T)]^{-z/2}. \quad (13)$$

The observed values of G_M^{xs} at equiatomic composition can be used in equation (13) to obtain the ordering energy.

The values of the ordering energy ω and the coordination number z used in the present investigation are listed in table 1. The computed values of α_1 for Cd-Bi, Cd-Mg

Table 2. Chemical short-range order parameter α_1 for Cd–Bi, Cd–Mg and Cd–Ga liquid alloys.

C_{Cd}	α_1		
	Cd–Bi (773 K)	Cd–Mg (923 K)	Cd–Ga (700 K)
0.1	–0.0029	–0.0424	0.032
0.2	–0.0069	–0.0664	0.062
0.3	–0.0112	–0.0936	0.081
0.4	–0.0146	–0.1130	0.091
0.5	–0.0150	–0.1135	0.095
0.6	–0.0120	–0.1135	0.091
0.7	–0.0046	–0.0950	0.080
0.8	–0.0003	–0.0679	0.074
0.9	–0.0008	–0.0353	0.038

and Cd–Ga are given in table 2. This indicates that the chemical short-range order parameters are negative for Cd–Bi and Cd–Mg but are positive for Cd–Ga. The negative values for Cd–Bi and Cd–Mg suggest heterocoordination (preference for unlike atoms pairing as nearest neighbours) in the molten state. Since the magnitude of α_1 for Cd–Mg is greater than for Cd–Bi, the heterocoordination in the earlier system is intense in comparison with the latter. Cd–Bi liquid alloy whose liquidus line is a simple and shallow eutectic is very close to the behaviour of an ideal alloy. Cd–Ga liquid alloy which is a monotectic system (see figure 1) behaves differently from Cd–Bi and Cd–Mg. The short-range order parameters for Cd–Ga are positive which indicates self-coordination or segregation (preference for like atoms pairing as nearest neighbours) in the liquid phase.

The computed values of α_1 could not be compared because of lack of experimental measurements. The only experimental result (Boos and Steeb 1977) for Cd-based liquid alloys is for $Mg_{75}Cd_{25}$. The experimental value of α_1 is equal to -0.13 which corresponds to $z = 7$ and $T = 823$ K. For comparison we have also computed α_1 for $Mg_{75}Cd_{25}$ and, taking $z = 7$, our value of $\alpha_1 = -0.113$ compares satisfactorily with the experimental value.

The excess free energy of mixing for Cd–Bi, Cd–Mg and Cd–Ga is plotted in figure 2. The computed values are in very good agreement with the experimental observations (Hultgren *et al* 1973). G_M^{xs} is positive for the segregating system Cd–Ga but is negative for the heterocoordinating systems Cd–Mg and Cd–Bi. The relative magnitudes of G_M^{xs} for the three systems should also be noted. The values of $S_{CC}(0)$, which are plotted in figure 3, depict the behaviour of the three systems more clearly than the other thermodynamic functions. This was expected because $S_{CC}(0)$ is obtained from the second derivative of G_M with respect to C . Thus $S_{CC}(0)$ is very sensitive to G_M – C variation. $S_{CC}(0)$ values for Cd–Ga are much larger than the values for Cd–Bi and Cd–Mg. In the dilute region, the curvature of the $S_{CC}(0)$ – C curve for Cd–Ga is also different from those for Cd–Bi and Cd–Mg.

$S_{CC}(0)$ can also be obtained directly from the measured activity data (Hultgren *et al* 1973), i.e.

$$S_{CC}(0) = C_B a_A (\partial a_A / \partial C_A)_{T,P,N}^{-1} = C_A a_B (\partial a_B / \partial C_B)_{T,P,N}^{-1} \quad (14)$$

where a_A and a_B are the thermodynamic activities of components A and B in the mixture.

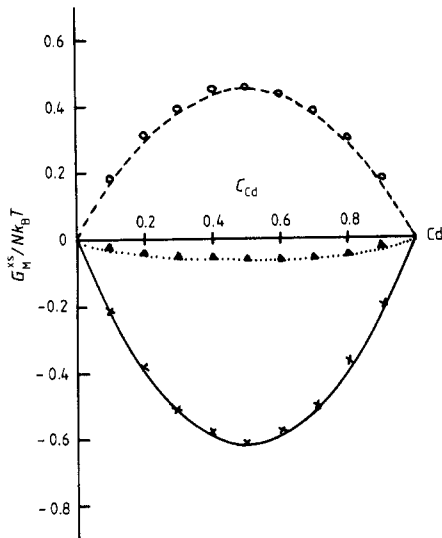


Figure 2. Excess free energy of mixing of Cd-Ga, Cd-Bi and Cd-Mg liquid alloys: ----, theory, Cd-Ga; O, experiment, Cd-Ga at 700 K; ····, theory, Cd-Bi; ▲, experiment, Cd-Bi at 773 K; —, theory, Cd-Mg; ×, experiment, Cd-Mg at 923 K.

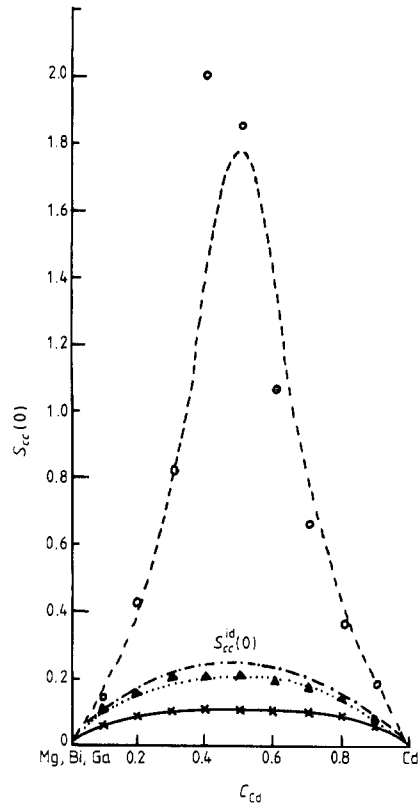


Figure 3. $S_{CC}(0)$ as a function of concentration: ----, theory, Cd-Ga; O, from activity, Cd-Ga; ····, theory Cd-Bi; ▲, from activity, Cd-Bi; —, theory, Cd-Mg; ×, from activity, Cd-Mg; ----, corresponds to $S_{CC}^{id}(0)$.

With a view to minimizing the uncertainty in the numerical differentiation, we have fitted the observed (Hultgren *et al* 1973) activity to a seventh-order polynomial in C and then we have computed $S_{CC}(0)$ following the last two equalities of equation (14). These are also shown in figure 3. The two values computed from the theoretical expression (10) and those from the measured activity are in good agreement. These values of $S_{CC}(0)$ can also be utilized in equation (11) to assess the relative stabilities of the Cd-based liquid alloys. The present study indicates that the stability is maximum in Cd-Mg followed by Cd-Bi and Cd-Ga.

References

- Ashcroft N W and Stroud D 1978 *Solid State Physics* vol 33 (New York: Academic) p 1
 Bhatia A B and Singh R N 1982 *Phys. Chem. Liq.* **11** 285
 Bhatia A B and Thornton D E 1970 *Phys. Rev. B* **2** 3004
 Boos A and Steeb S 1977 *Phys. Lett.* **63A** 333
 Cowley J M 1950 *Phys. Rev.* **77** 667

- Clapp P C and Moss S C 1966 *Phys. Rev.* **142** 418
— 1968a *Phys. Rev.* **171** 764
— 1968b *Phys. Rev.* **174** 754
Darken L S 1967 *Trans. Metall. Soc. AIME* **239** 80
Hafner J 1977 *Phys. Rev. A* **16** 351
Hayes T M, Brooks H and Bienenstoch A 1968 *Phys. Rev.* **175** 699
Hultgren R, Desai P D, Hawkins D T, Gleiser M and Kelley K K 1973 *Selected Values of the Thermodynamic Properties of Binary Alloys* (Metals Park, OH: American Society for Metals)
Khvaya F A, Katsnelson A A, Silonov V M and Khrushelov M M 1977 *Phys. Status Solidi* **826** 701
Pandey D K, Singh R N, Srivastava P L 1988 *Phys. Chem. Liq.* **18** 551
Singh R N 1987 *Can. J. Phys.* **65** 309
— 1980 *J. Phys. F: Met. Phys.* **10** 1411
Singh R N and Mishra I K 1988 *Phys. Chem. Liq.* **18** 303
Umar I H, Meyer A, Waseda M and Young W H 1974 *J. Phys. F: Met. Phys.* **4** 1091
Warren B E 1969 *X-ray Diffraction* (Reading, MA: Addison-Wesley)
Young W H 1987 *Can. J. Phys.* **65** 241