

# Quasi-Chemical Model for Liquid Li-Cd Alloys

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Z. Naturforsch. **44a**, 529–532 (1989); received October 19, 1988

The quasi-chemical model based on pairwise interactions is used to study the concentration dependent thermodynamic properties of Li-Cd liquid alloys. Special attention is given to the concentration-concentration correlation function in the long wavelength limit [Scc(0)] and the chemical short-range order parameter (CSRO). The activity, free energy of mixing, Scc(0) and CSRO are computed as functions of temperature and concentration.

## Introduction

The quasi-chemical model [1] has widely been applied on binary liquid alloys (for recent reviews see Bhatia [2], Singh [3]). Singh et al. [4] have successfully used it to study the thermodynamic properties of Li-Mg liquid alloys. This has encouraged us to apply it to the Li-Cd system, which is a suitable candidate for the regular solution model of the quasi-chemical theory because the size effect is negligible and the free energy of mixing is almost symmetrical about the mole fraction  $C_{\text{Cd}} = \frac{1}{2}$ .

Li-Cd exhibits interesting concentration dependent physical properties [5, 6], and there is strong indication for deviations from ideal mixture behaviour. The  $^7\text{Li}$  knight shift has a distinct bend at  $C = \frac{1}{2}$ , while the electrical resistivity is maximum ( $\cong 80 \mu\Omega \text{ Cm}$ ) at  $C_{\text{Cd}} = 0.4$ . The volume contraction [7] is of the order of 13% whereas the heat of formation has been found [8] to be low ( $-16 \text{ kJ/mol}$ ) around the equiatomic composition. Recently Langen et al. [8] have measured the e.m.f. at three different temperatures. To the best of our knowledge no theoretical investigation has been carried out as yet. We propose, therefore to investigate the free energy of mixing, the concentration fluctuations in the long wavelength limit and the chemical short range order parameter as a function of concentration. All of these computed thermodynamic functions deviate significantly from the ideal solution values, and there is evidence of strong interaction among the constituent species in the melt.

## 1. Formulation

Let us consider a binary alloy consisting of  $N_{\text{A}}$  ( $=\text{NC}$ ) atoms of the element A ( $\equiv \text{Li}$ ) and  $N_{\text{B}}$  [ $=N(1-C)$ ] atoms of the element B ( $\equiv \text{Cd}$ ). If we restrict ourselves to pairwise interactions, the most fundamental relation of the quasi-chemical theory [1] is the relation between the number of unlike atom pairs ( $N_{\text{AB}}$ ), like atom pairs ( $N_{\text{AA}}$  and  $N_{\text{BB}}$ ) and the ordering energy ( $\omega$ ), i.e.

$$\frac{4 N_{\text{AA}} \cdot N_{\text{BB}}}{N_{\text{AB}}^2} = e^{2\omega/zk_{\text{B}}T}, \quad (1)$$

where  $z$  is the coordination number for the first shell.  $\omega$  is the ordering energy and is so defined that if  $\varepsilon_{\text{AB}}$ ,  $\varepsilon_{\text{AA}}$  and  $\varepsilon_{\text{BB}}$  are bond energies for AB, AA and BB pairs of atoms; then

$$\omega = z \left( \varepsilon_{\text{AB}} - \frac{\varepsilon_{\text{AA}} + \varepsilon_{\text{BB}}}{2} \right).$$

Thus,  $\omega = 0$  signifies that there is no preferential ordering of atoms in the alloy,  $\omega < 0$  indicates that unlike atoms are preferred as nearest neighbours, and  $\omega > 0$  that like atoms tend to pair. Expression (1) leads to an expression for the free energy of mixing [1], ( $G_{\text{M}}$ ), as

$$G_{\text{M}} = G_{\text{M}}^{\text{id}} + G_{\text{M}}^{\text{xs}}, \quad (2)$$

where

$$G_{\text{M}}^{\text{id}} = RT \sum_i C_i \ln C_i, \quad (3)$$

$$G_{\text{M}}^{\text{xs}} = RT [C \ln \gamma_{\text{A}} + (1-C) \ln \gamma_{\text{B}}]. \quad (4)$$

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$\gamma_B$  and  $\gamma_B$  are activity coefficients and are related to the activity,  $a$ , by the relations

$$a_A = C \gamma_A \quad \text{and} \quad a_B = (1 - C) \gamma_B, \quad (5)$$

$$\gamma_A = \left[ \frac{\beta - 1 + 2C}{C(1 + \beta)} \right]^{\frac{1}{2}z}, \quad (6)$$

$$\gamma_B = \left[ \frac{\beta + 1 - 2C}{(1 - C)(1 + \beta)} \right]^{\frac{1}{2}z} \quad (7)$$

with

$$\beta = [1 + 4C(1 - C)(\eta^2 - 1)]^{1/2},$$

$$\eta = \exp\left(\frac{\omega}{z k_B T}\right). \quad (8)$$

Equation (2) can also be used to obtain the concentration-concentration correlation function [9] at  $q = 0$  (long wavelength), i.e.

$$\text{Scc}(0) = RT \left( \frac{\partial^2 G_M}{\partial C^2} \right)_{\text{TPN}}^{-1}. \quad (9)$$

Equations (2) and (9) yield

$$\text{Scc}(0) = C(1 - C) \left[ 1 + \frac{1}{2} z \left( \frac{1 - \beta}{\beta} \right) \right]^{-1}. \quad (10)$$

For an ideal alloy ( $\omega = 0$  and  $\beta = 1$ ).

$$\text{Scc}(0) = \text{Scc}^{\text{id}}(0) = C(1 - C). \quad (11)$$

Finally we record the expression for the Cowley-Warren [10, 11] short range order parameter ( $\alpha_1$ ) for the nearest neighbours, which is defined as

$$N_{AB} = N z C(1 - C)(1 - \alpha_1). \quad (12)$$

Equations (11) and (1) provide an expression for  $\alpha_1$ , i.e.

$$\alpha_1 = \frac{\beta - 1}{\beta + 1}, \quad (13)$$

where  $\beta$  is defined by (8). Obviously, if  $\omega > 0$ , then  $\text{Scc}(0) > \text{Scc}^{\text{id}}(0)$  and  $\alpha_1 > 0$ , i.e. there is a tendency of segregation (like atoms pairing as nearest neighbours), and if  $\omega < 0$ , then  $\text{Scc}(0) < \text{Scc}^{\text{id}}(0)$  and  $\alpha_1 < 0$ , and one has an ordered alloy (unlike atoms pairing as nearest neighbours).

Equations (10) and (13) further allow to express  $\alpha_1$  in terms of  $\text{Scc}(0)$ , i.e.

$$\alpha_1 = \frac{S - 1}{S(z - 1) + 1}, \quad S = \frac{\text{Scc}(0)}{\text{Scc}^{\text{id}}(0)}, \quad (14)$$

## 2. Results and Discussion

### 2.1. Activity

$\omega$  and  $z$  of (1) are basic inputs in the present theory. In liquid and amorphous state, the atoms are randomly distributed [12] in a nearly closed packed structure, and  $z$  for the nearest neighbour atoms is about 10. As to  $\omega$ , it is independent of concentration but may depend on temperature and pressure. In principle,  $\omega$  can be determined from first principles by using the pairwise interaction of the pseudopotential method [13, 14] but very little work has been done in this direction. Contrary to this,  $\omega$  can also be determined very easily from the observed activity data or from the free energy of mixing at any given concentration. For example, (4) at  $C = \frac{1}{2}$  reduces to

$$G_M^{\text{xs}} = RT \ln 2^{z/2} [1 + \exp(-\omega/z k_B T)]^{-\frac{z}{2}}. \quad (15)$$

Equation (15) determines  $\omega$ . For LiCd, we have obtained  $\omega = -5.7849 k_B T$  at 774 K. In order to compute the activity at different temperatures, we further assume that  $\omega$  and  $T$  are related through an expression

$$\omega = A + B/T. \quad (16)$$

The coefficients  $A$  and  $B$  are  $-2.3803 k_B T$  and  $-4.053 \times 10^6 k_B T^2$ .  $\omega$  as computed from (16) has been used in (5) to compute  $a_{\text{Li}}$  at  $T = 774$  K, 833 K and 905 K. The computed values are tabulated in Table 1 along with the experimental values of Langen et al. [8]. The two values are in reasonable agreement. Near  $C = \frac{1}{2}$  the disagreement between theory and experiment is within 3%.

Table 1. Theoretical and experimental values of  $a_{\text{Li}}$ .

C	T = 774 K		T = 833 K		T = 905 K	
	theor.	exper.	theor.	exper.	theor.	exper.
0.1	0.0006	0.0004	0.0009	0.0007	0.0015	0.0013
0.2	0.0028	0.0019	0.0041	0.0031	0.0059	0.0050
0.3	0.0101	0.0084	0.0138	0.0122	0.0186	0.0176
0.4	0.0329	0.0319	0.0415	0.0412	0.0520	0.0525
0.5	0.0959	0.0959	0.1110	0.0111	0.1281	0.1282
0.6	0.2296	0.02230	0.2480	0.2388	0.2679	0.2551
0.7	0.4356	0.4158	0.4502	0.4231	0.4656	0.4276
0.8	0.6663	0.6528	0.6736	0.6450	0.6813	0.6281
0.9	0.8650	0.8923	0.8667	0.8658	0.8689	0.8257

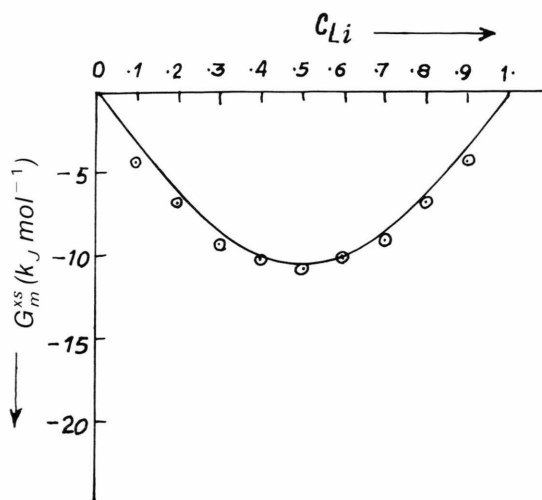


Fig. 1. Excess free energy of mixing,  $G_M^{xs}$ , of Li-Cd liquid alloys at 833 K. — Theory and  $\circ\circ\circ$  experimental points [8].

## 2.2. Excess Free Energy of Mixing

Equation (4) in conjunction with (16) has been used to compute  $G_M^{xs}$  at 860 K as a function  $C$ . The results are plotted in Fig. 1 along with the experimental values of Langen et al. [8]. The coincidence is satisfactory.

It may be noted that  $G_M^{xs}$  of Li-Cd deviates considerably from the ideal values but is symmetrical about  $C = \frac{1}{2}$ , like in Li-Mg.  $G_M^{xs}$  for Li-Cd ( $\cong -10$  kJ/mol) lies in between the values for Li-Mg [15] ( $\cong -4.6$  kJ/mol) and Li-Pb [16] ( $\cong -22$  kJ/mol). However, the excess free energy of mixing in Li-Pb is quite asymmetric around  $C_{Li} = 0.7$ , unlike Li-Cd and Li-Mg.

## 2.3. Concentration-Concentration Correlation Function in the Long Wavelength Limit

$S_{cc}(0)$  has been computed via (10) at 774 K, 833 K and 905 K. As usual,  $z$  has been taken equal to 10 and  $\omega$  has been determined from (16). The computed  $S_{cc}(0)$  vs.  $C$  is depicted in Figure 2.

It is well known that  $S_{cc}(0)$  can not be determined directly from the experiment, but can be evaluated from the observed activity through the relation

$$S_{cc}(0) = \frac{(1-C) a_A}{\left(\frac{\partial a_A}{\partial C}\right)_{TPN}} = \frac{C a_B}{\left(\frac{\partial a_B}{\partial (1-C)}\right)_{TPN}}. \quad (17)$$

Equation (17) has also been used to evaluate  $S_{cc}(0)$  directly from the observed activity data [8]. Both

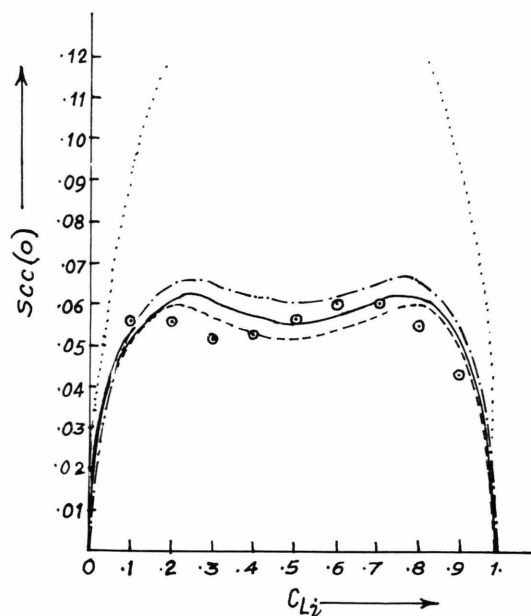


Fig. 2. Concentration fluctuations at  $q=0$ ,  $S_{cc}(0)$ , of liquid Li-Cd at different temperatures. — Theory at 833 K, --- theory at 774 K and ..... theory at 905 K.  $\circ\circ\circ$  refers to experimental values at 833 K, .....  $S_{cc}(0)$ .

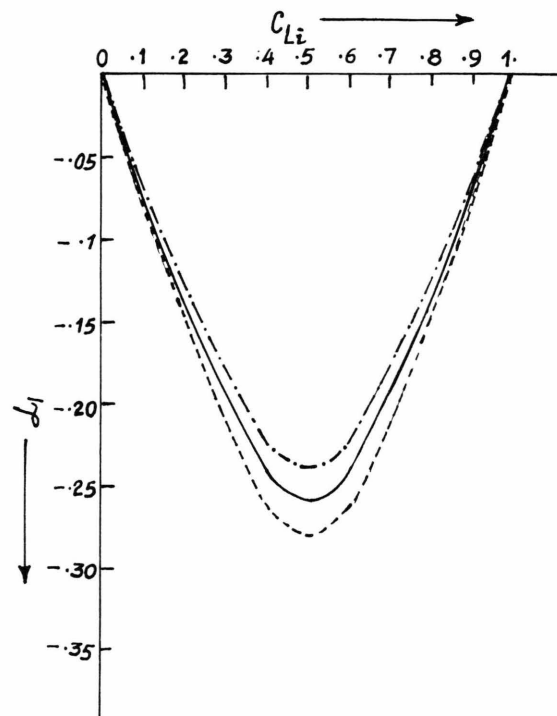


Fig. 3. Short range order parameter,  $\alpha_1$ , of Li-Cd liquid alloys at different temperatures. — Theory at 833 K, --- theory at 774 K and ..... theory at 905 K.

$\text{Sc}(0)$  as computed from (10) and (17) exhibit a dip with a bump on either side (see Figure 2). The positions of the dip, however, differ.  $\text{Sc}(0)$  computed directly from the activity via (17) is minimum around  $C_{\text{Li}} = 0.35$ , whereas according to (10) it is around  $C_{\text{Li}} = 0.5$ . We have also tried a model [17, 18] based on the assumption of the formation of chemical complexes such as  $\text{Li}_2\text{Cd}$  as anticipated by Langen et al. [8], but we have failed to reproduce the nature of  $\text{Sc}(0)$  as obtained from (17).

$\text{Sc}(0)$  for Li-Cd deviates largely from the ideal solution value  $\text{Sc}^{\text{id}}(0)$  (see Figure 2). A dip at  $C = \frac{1}{2}$  with a bump on either side is not exhibited in Li-Mg liquid alloys [4].  $\text{Sc}(0)$  of Li-Pb is very asymmetric around  $C_{\text{Li}} \cong 0.8$ .

The temperature dependence of  $\text{Sc}(0)$  also presents an interesting feature. With rise in temperature, the magnitude of  $\text{Sc}(0)$  increases. The dip of  $\text{Sc}(0)$  tends to disappear at higher temperatures and the bumps reduce.

#### 2.4. Chemical Short Range Order Parameter

$\alpha_1$  of Li-Cd computed at 774 K, 833 K and 905 K from (13) is displayed in Figure 3.  $\omega$  and  $z$  used in the computation are the same as earlier. We observe that  $\alpha_1$  is symmetrical and negative at all concentrations. It is as low as  $-0.2814$  at 774 K. In this context we may

recall that for complete ordering  $\alpha_1$  must attain a minimum value of  $-1$ . Though the ordering in molten LiCd is much larger than in the Li-Mg system [19] ( $\alpha_1 = -0.04$  for  $\text{Li}_{0.7}\text{Mg}_{0.3}$ ), but it is comparable to the value of the order parameter of Li-Pb alloys [20] ( $\alpha_1 = -0.23$  for  $\text{Li}_{0.5}\text{Pb}_{0.5}$ ). It may be pointed out that  $G_{\text{M}}^{\text{xs}}$  and  $\text{Sc}(0)$  of Li-Cd and Li-Pb differ markedly but  $\alpha_1$  for the first coordination shell in the two cases is very much alike. This is not unexpected because the first two properties furnish an averaged effect.

The rise in temperature adversely affects the extent of local ordering.  $\alpha_1$  increases with increasing temperature. When the temperature is increased by 131 K, then the local ordering has been found to be reduced by 15%.

### 3. Conclusion

The quasi-chemical theory successfully explains the observed values of activity and excess free energy of mixing of Li-Cd liquid alloys. The large negative value of the ordering energy ( $\omega = -0.3857$  eV) indicates strong heterocoordination in the melt. The concentration-concentration correlation function at  $q = 0$  has a dip around  $C = \frac{1}{2}$  with a bump on either side. The chemical short range order parameter for Li-Cd in the first coordination shell is much smaller than in Li-Mg liquid alloys but is comparable to that of Li-Pb.

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