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## The segregation–order transformation in CdNa liquid alloy

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**Abstract.** The large asymmetry observed in the properties of mixing of CdNa liquid alloys is discussed on the basis of a simple theory based on the complex formation model. The results for long wavelength concentration–concentration fluctuations,  $S_{cc}(0)$ , number–number fluctuations,  $S_{NN}(0)$  and number–concentration fluctuations,  $S_{Nc}(0)$  are presented as a function of concentration. This has been further used to obtain a chemical short-range order parameter ( $\alpha_1$ ).  $S_{cc}(0)$  and  $\alpha_1$  suggest that the segregation–order transformation occurs in the CdNa melt at around 60 at. % of Cd.

The concentration dependent properties of CdNa liquid alloys (Hultgren *et al* 1973, Hoshino and Endo 1982, Harada *et al* 1988) are interesting in many ways. The excess free energy of mixing ( $G_M^{xs}$ ), heat of mixing ( $\Delta H$ ), entropy of mixing ( $\Delta S_M$ ) and volume of mixing ( $\Delta V_M$ ) are quite asymmetrical around the equi-atomic composition. So much so that the  $G_M^{xs}-c$  curve is S shaped (it is negative in the region  $0.35 \leq c_{Cd} \leq 1.0$  and becomes positive for  $0 \leq c_{Cd} \leq 0.35$ ). The concentration fluctuations at the long wavelength [ $S_{cc}(0)$ ] computed directly from the observed activity data are greater than the ideal value [ $S_{cc}^{id}(0) = c_A c_B$ ] in the region  $0.53 \geq c_{Cd} \geq 0$  whereas  $S_{cc}(0) < S_{cc}^{id}(0)$  in the region  $1.0 \geq c_{Cd} \geq 0.53$ . The chemical short-range order parameter ( $\alpha_1$ ) thus obtained is positive towards the Na-rich end and negative towards the Cd-rich end, which seems to indicate that segregation (preference for like-atoms pairs as nearest neighbours) to order (preference for unlike-atoms pairs as nearest neighbours) transformation occurs in the vicinity of 60 at. % of Cd. The size factor ( $\Omega_{Na}/\Omega_{Cd} = 1.77$ ,  $\Omega$  is the atomic volume) and the electronegativity difference are small to account for anomalous behaviour. Also, the phase diagram indicates a wavy liquidus line with a small hump around the stoichiometric composition  $Cd_2Na$  (melting point 657 °K).

Therefore, in the present work, a simple theory based on the complex formation model (for recent review see Singh 1987) has been considered to explain the concentration dependent segregation–order transformation in CdNa liquid alloys. The concentration variation of activity,  $G_M^{xs}$  and  $\Delta V_M$  have been investigated. In order to examine the stability of alloys, the long-wavelength limit of the three correlation functions, namely concentration–concentration functions,  $S_{cc}(0)$ ; the number–number correlation functions,  $S_{NN}(0)$ , and the number–concentration correlation functions,  $S_{Nc}(0)$ , have been studied as a function of concentration.  $S_{cc}(0)$ , in turn, is used to compute the Warren–Cowley short-range order parameter.

In the solid state the alloy forms two intermediate phases namely  $\gamma(\text{Cd}_2\text{Na})$  and  $\beta(\text{Cd}_{11}\text{Na}_2)$ . Since the  $\gamma$ -phase has a higher melting temperature, we assume that the chemical complexes,  $\text{Cd}_2\text{Na}$  ( $2\text{Cd} + \text{Na} \rightleftharpoons \text{Cd}_2\text{Na}$ ) exist in the liquid state close to the melting point temperature. Thus, the molten alloys consist of a mixture of Cd atoms, Na atoms, and a number of chemical complexes  $\text{Cd}_2\text{Na}$  all in chemical equilibrium with one another. If a binary alloy contains in all  $c$  gm atoms of Cd and  $(1 - c)$  gm atoms of Na then in the framework of the complex formation model (Bhatia and Hargrove 1974, McAlister and Crozier 1974, Hoshino and Young 1980, Gerling *et al* 1983, Jha *et al* 1990), the binary alloy can be assumed to consist of  $n_1$  gm atoms of Cd,  $n_2$  gm atoms of Na and  $n_3$  gm moles of the complexes  $\text{Cd}_2\text{Na}$ . From the conservation of atoms, therefore, one may write

$$n_1 = c - 2n_3 \quad n_2 = (1 - c) - n_3 \quad (1)$$

and  $n = n_1 + n_2 + n_3$ . The free energy of mixing,  $G_M$ , of the binary alloy may be written as

$$G_M = -n_3g + G' \quad (2)$$

where  $g$  is the formation energy of the complex and thus the first term ( $-n_3g$ ) represents the lowering of the free energy due to the formation of the complexes in the alloy.  $G'$  represents the free energy of mixing of the ternary mixture of Cd, Na and  $\text{Cd}_2\text{Na}$ . Recently Bhatia and Singh (1984) formulated an expression for  $G'$  on the basis of quasilattice theory for the ternary mixture which can be expressed as

$$G' = RT[n_1 \ln n_1 + n_2 \ln n_2 + n_3 \ln 3n_3] + \sum_{i < j} \sum n_i n_j \nu_{ij} \quad (3)$$

where  $\nu_{ij}$  ( $i, j = 1, 2, 3$ ) are the interchange energies. The values of  $n_3$ , and hence  $n_1$  and  $n_2$ , at any given temperature, pressure and concentration of the mixture are determined from the equilibrium condition,

$$\left( \frac{\partial G_M}{\partial n_3} \right)_{T,P,c} = 0. \quad (4)$$

Using equations (2) and (3) in (4), the equilibrium value of  $n_3$  is given by

$$n_1^2 n_2 = 0.406 n_3 e^{-g/RT} e^Y \quad (5)$$

where

$$Y = (n_1 - 2n_3) \frac{\nu_{13}}{RT} + (n_2 - n_3) \frac{\nu_{23}}{RT} - (2n_2 + n_1) \frac{\nu_{12}}{RT}. \quad (6)$$

Equations (2) and (3) for the free energy of mixing can also be used to obtain an expression for activity  $a_{\text{Cd}}$  namely

$$RT \ln a_{\text{Cd}} = G_M + (1 - c) \left( \frac{\partial G_M}{\partial c} \right)_{T,P,N} \quad (7)$$

which yields,

$$\ln a_{\text{Cd}} = (1 - n) + \ln n + \ln \frac{n_1}{n_2} + n_2 \frac{\nu_{12}}{RT} + n_3 \frac{\nu_{13}}{RT} - \sum_{i < j} \sum n_i n_j \frac{\nu_{ij}}{RT}. \quad (8)$$

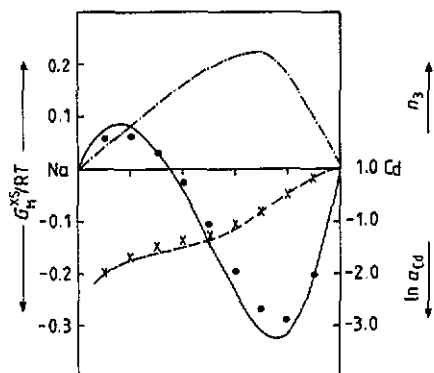


Figure 1. Activity,  $\ln a_{Cd}$ , excess free energy of mixing,  $G_M^{xs}/RT$ , and the chemical complexes,  $n_3(\text{gm mol}^{-1})$  for cadmium–sodium liquid alloys at 673 °K. ---, theory;  $\times \times \times$ , experiment;  $(\ln a_{Cd})$ ; —, theory;  $\bullet \bullet \bullet$ , experiment;  $(G_M^{xs}/RT)$ ; - · - · - ,  $(n_3)$ .

Equation (5) can be solved numerically to obtain the equilibrium value of  $n_3$  provided that the energy parameters  $g$  and  $\nu_{ij}$  are obtained. These parameters may depend on temperature and pressure but are independent of concentration in the present formalism. If  $g$  and  $\nu_{ij}$  are made concentration dependent then the very structure of the complex formation model weakens.  $g$  and  $\nu_{ij}$  are determined here following the procedure prescribed by Bhatia and Hargrove (1974). For CdNa liquid alloys at 673 °K the energy parameters are:

$$\frac{g}{RT} = +1.661 \quad \frac{\nu_{12}}{RT} = 2.10 \quad \frac{\nu_{23}}{RT} = 2.25 \quad \frac{\nu_{13}}{RT} = 0. \quad (9)$$

These are now used in equation (5) to determine  $n_3$  and hence

$$G_M^{xs} \left( G_M^{xs} = G_M - RT \sum_{i=1}^2 c_i \ln c_i \right)$$

via equations (2) and (3) which are plotted in figure 1 along with the experimental values (Hultgren *et al* 1973) of  $G_M^{xs}$ . The same values of energy parameters are again used in equation (8) to compute the activity ( $a_{Cd}$ ) as a function of concentration. These are also plotted in figure 1. This shows that the computed values of the activity are in good agreement with experimental observation (Hultgren *et al* 1973).

The values of the complexes ( $n_3$ ) are quite asymmetric at the concentration  $c = 1/2$ . The maximum value of  $n_3$  ( $=0.2234$ ) occurs at  $c_{Cd} = 0.67$ , a slightly higher concentration than the complex-forming concentration,  $c_c = c_{Cd} = 0.66$ . We may recall from equation (5) that the maximum permissible value of  $n_3$  (for  $g \rightarrow +\infty$ , refers to the situation where there is a very strong tendency to form the chemical complexes) is about 0.33. The contents of  $n_3$  are high towards Cd-rich end. The concentration dependence of  $G_M^{xs}$  of CdNa is more interesting and is usually not found in binary liquid alloys. It is positive in the region  $0 \leq c_{Cd} \leq 0.35$  and is negative in the concentration range  $0.35 \leq c_{Cd} \leq 1.0$ . Thus, the observed S-shaped behaviour of  $G_M^{xs}$ - $c$  can be explained on the basis of the complex formation model where the energy parameters are considered concentration independent. The minimum in  $G_M^{xs}$  ( $= -0.33 RT$ ) occurs at  $c_{Cd} = 0.75$ . It may be pointed out that though  $G_M^{xs}$  for NaCd does not have a large negative value, the asymmetry in  $n_3$  and  $G_M^{xs}$  is pronounced.

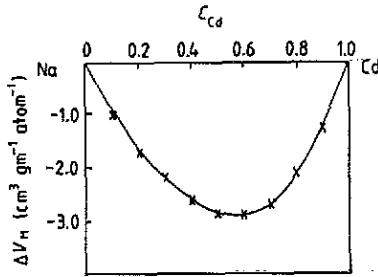


Figure 2. Volume of mixing,  $\Delta V_M$ , of CdNa alloys at 673 °K. —, theory and  $\times \times \times$ , experiment.

Hoshino and Endo (1982) have measured experimentally the volume of mixing ( $\Delta V_M$ ) of NaCd liquid alloys and found a large volume contraction around the concentration corresponding to  $\text{Cd}_2\text{Na}$ . We have therefore used equation (2) to obtain the concentration dependence of  $\Delta V_M$ , i.e.

$$\Delta V_M = V - cV_{\text{Cd}}^{(0)} - (1-c)V_{\text{Na}}^{(0)} = \left(\frac{\partial G_M}{\partial P}\right)_{T,c} = \left(\frac{\partial G_M}{\partial P}\right)_{T,c,n_3} \quad (10)$$

The last equality follows from the use of equation (4). Thus we get

$$\Delta V_M = -n_3 \left(\frac{\partial g}{\partial P}\right) + \sum_{i < j} \sum n_i n_j \left(\frac{\partial \nu_{ij}}{\partial P}\right) \quad (11)$$

With the previous knowledge of  $n_1$ ,  $n_2$  and  $n_3$ , the pressure derivatives of the interaction energies are treated as parameters. The computed values of  $\Delta V_M$  as a function of concentration are plotted in figure 2 and are compared with the experimental observation (Hoshino and Endo 1982). The figure indicates that the variation of  $\Delta V_M$  as a function of concentration can be explained provided that the energy parameters ( $g$  and  $\nu_{ij}$ ) are made pressure dependent. The minimum in  $\Delta V_M$  occurs around  $c_{\text{Cd}} = 0.6$ . It is interesting to observe that though CdNa alloy is not a very strong interacting system ( $G_M^E/RT \approx -0.33$ ), the molar volume undergoes a large volume contraction, likewise strong interacting alloys, e.g. HgNa (Ishiguro *et al* 1984) and LiPb (Ruppertsberg and Speicher 1976).

Equation (2) has been further utilised to obtain long-wavelength correlation fluctuations (Bhatia and Thornton 1970) namely the concentration–concentration correlation functions,  $S_{cc}(0)$ , the number–number correlation functions,  $S_{NN}(0)$  and the number–concentration correlation functions,  $S_{Nc}(0)$ . These functions are widely used (Bhatia 1977, Singh 1987) in the understanding of the stability and atomic nature of order in binary alloys. These are readily derivable from the thermodynamic functions,

$$S_{cc}(0) = RT \left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}^{-1} = (1-c)a_A \left(\frac{\partial a_A}{\partial c}\right)_{T,P,N}^{-1} = ca_B \left(\frac{\partial a_B}{\partial(1-c)}\right)_{T,P,N}^{-1} \quad (12)$$

$$S_{NN}(0) = \rho k_B T \chi_T + \theta^2 S_{cc}(0) \quad (13)$$

$$S_{Nc}(0) = -\theta S_{cc}(0) \quad (14)$$

$$\theta = \frac{1}{V} \left(\frac{\partial V}{\partial c}\right)_{T,P,N} \quad (15)$$

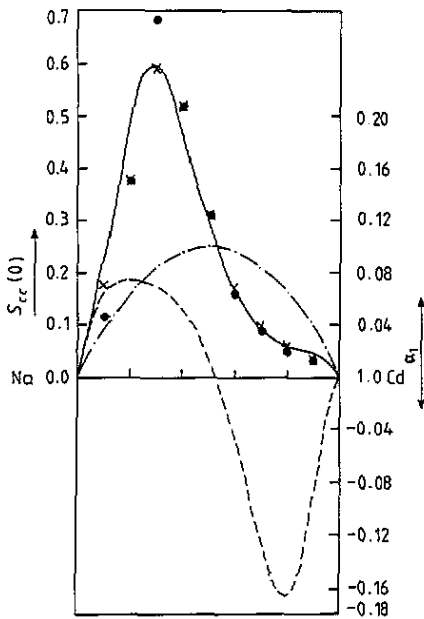


Figure 3. Concentration fluctuations,  $S_{cc}(0)$ , and chemical short-range order parameter,  $\alpha_1$  of CdNa alloys at 673 °K. —, theory and  $\times \times \times$ , computed directly from activity for  $S_{cc}(0)$ ; ---,  $\alpha_1$ ; — · — · —,  $S_{cc}^{id}(0)$ ; ● ● ●, corresponding to Harada *et al* (1988) values.

where  $a_A$  and  $a_B$  are activities of the component element,  $V$  is the molar volume,  $\rho$  is the number density, and  $\chi_T$  stands for the isothermal compressibility. Obviously  $S_{cc}(0)$  is the basic function and can be obtained theoretically by substituting equation (2) into the first equality of equation (12), i.e.

$$S_{cc}(0) = \left[ \sum_{i=1}^3 \frac{(n'_i)^2}{n_i} + \frac{2}{RT} \sum_{i < j} n'_i n'_j \nu_{ij} \right]^{-1} \tag{16}$$

where a prime denotes differentiation with respect to  $c$ .  $n'_i$  can easily be evaluated by taking a straightforward differentiation of equations (1) and (5). It may be pointed out that the theoretical expression (16) for  $S_{cc}(0)$  does not involve any other adjustable parameters. All the quantities, i.e.  $n_i$ ,  $g$  and  $\nu_{ij}$  have already been determined earlier.  $S_{cc}(0)$  values computed for CdNa liquid alloys via equation (16) are displayed in figure 3. These are compared with the values obtained directly from the observed activity data (Hultgren *et al* 1973) using the last two identities of equation (12). The latter is usually known as the experimental values of  $S_{cc}(0)$ . Recently Harada *et al* (1988) have measured the EMF in liquid Na–Cd alloys over a wide range of concentrations and hence obtained  $S_{cc}(0)$ . These are also plotted in figure 3.

The two sets of data for  $S_{cc}(0)$  are in good agreement with one another and are quite asymmetric as a function of concentration. They exhibit only a weak deepening around the concentration  $Cd_2Na$ . It may be mentioned that sometimes, like in NaCs, the size effect (Bhatia and March 1975, Singh and Bhatia 1984) is also responsible for producing asymmetry in the properties of mixing and  $S_{cc}(0)$ . We have thus also tried this method on CdNa alloys but found that the observed asymmetry could not be explained just by considering the size effect.

The  $S_{cc}(0)$ – $c$  curve is of great significance in understanding the nature of atomic order (Singh 1987, Singh *et al* 1990) in binary alloys. We recall that the deviation of  $S_{cc}(0)$  from

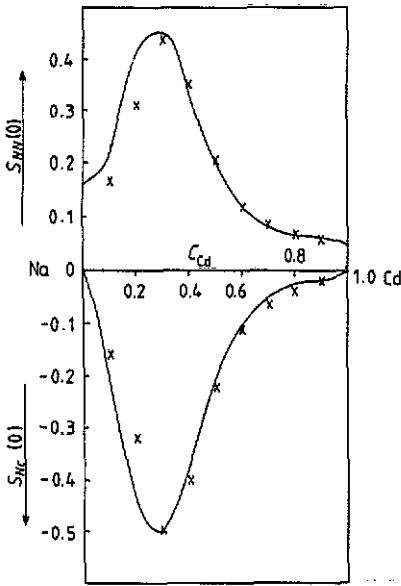


Figure 4. Number-number correlation function,  $S_{NN}(0)$  and number-concentration correlation function  $S_{Nc}(0)$  of NaCd alloys 673 °K. —, theoretical  $S_{cc}(0)$  and  $\times \times \times$ ,  $S_{cc}(0)$  obtained directly from activity.

the ideal value,  $S_{cc}^{id}(0) [=c(1-c)]$ , is used to visualize the nature of interaction in the alloy. If, at a given composition,  $S_{cc}(0) \geq S_{cc}^{id}(0)$ , then there is a tendency for segregation,  $S_{cc}(0) \leq S_{cc}^{id}(0)$  is an indication of the order in the alloy.

The  $S_{cc}(0)$  of CdNa liquid alloys plotted in figure 3 clearly indicates that in the concentration range,  $0 \leq c_{Cd} \leq 0.53$ , the like, i.e. Cd-Cd or Na-Na atoms are pairing as nearest neighbours whereas in the concentration range  $0.53 \leq c_{Cd} \leq 1.0$ , the unlike Cd-Na, atoms are pairing as nearest neighbours. With a view to strengthening the observation, we have also computed the Warren-Cowley (Warren 1969, Cowley 1950) chemical short-range order parameter  $\alpha_1$  for the first coordination shell following the relation (Singh *et al* 1987),

$$\alpha_1 = \frac{S - 1}{S(z - 1) + 1} \quad S = \frac{S_{cc}(0)}{S_{cc}^{id}(0)} \quad (17)$$

Though relation (17) is the approximate version of an (exact) sum rule between  $S_{cc}(0)$  and  $\alpha_1$  (Ruppersberg and Egger 1975, March *et al* 1976) it can safely be used for the first coordination shell. The computed values of  $\alpha_1$  are plotted in figure 3. This indicates that  $\alpha_1$  is positive in the region  $0 \leq c_{Cd} \leq 0.53$  and becomes negative for  $0.53 \leq c_{Cd} \leq 1.0$ . The maximum in  $\alpha_1$  ( $=0.074$ ) occurs near the composition of solid  $\beta$  phase. The minimum in  $\alpha_1$  ( $= -0.164$ ) has been observed around the concentration  $c_{Cd} = 0.8$ . Both  $S_{cc}(0)$  and  $\alpha_1$  suggest that the segregation-order transformation occurs around 60 at. % of Cd.

The  $S_{cc}(0)$  as computed from equation (16) have been used to obtain  $S_{NN}(0)$  and  $S_{Nc}(0)$ . To estimate the latter quantities one needs data on the variation of  $V$  and  $\chi_T$  with concentration.  $V$ - $c$  values have been taken from Hoshino and Endo (1982) and  $\chi_T$  have been estimated by using the pure metal values

$$\chi_T = c\chi_T^{Cd} + (1-c)\chi_T^{Na} \quad (18)$$

because compressibility measurements have not been made for NaCd alloys. The computed values of  $S_{NN}(0)$  are plotted in figure 4. As  $S_{cc}(0)$  has been used to interpret the

chemical short-range order,  $S_{NN}(0)$  can be used (Wagner 1985) to discuss the topological short-range order in structurally disordered systems. Similarly the  $S_{Nc}(0)$  signifies the coupling between the chemical and the topological order.

Figure 4 indicates that  $S_{NN}(0)$  and  $S_{Nc}(0)$  depend strongly on concentration and are quite asymmetric around the equi-atomic composition. The magnitudes of both the fluctuations are maximum towards the Na-rich end and exhibit a distinct peak around  $c_{Na} = 0.7$ . The Cd-rich end, however, reveals comparatively small fluctuations in  $S_{NN}(0)$  and  $S_{Nc}(0)$ . We also observe that in the vicinity of concentration, where segregation-order transformation is likely to occur, both  $S_{NN}(0)$  and  $S_{Nc}(0)$  fall to a small value.

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