Thermodynamic properties of liquid glass-forming Ca–Mg alloys

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Abstract

The complex formation model was used to investigate the thermodynamic properties of liquid Ca–Mg glassy alloys. Our expressions reproduce the thermodynamic functions such as free energy of mixing, enthalpy of mixing, entropy of mixing and activity ratio. The study of long wavelength concentration–concentration fluctuations ($S_{CC}(0)$) provides structural information about liquid glass-forming Ca–Mg alloys. Chemical short range order parameter (α_1) was obtained from $S_{CC}(0)$ to quantify the degree of order. The study reveals that the formation of more than one type of complex may be related to the process of glass formation. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Scientifically, glassy alloys have been the subject of wide interest [1]. The atomic arrangement of a glass is similar to that of the liquid having the same composition. Hence, glasses are referred to as super cooled liquids. The factor governing glass formation tendency and thermal stability [2–4] is to separate geometric packing consideration from the thermal excitations [5]. The correlation between glass formation and the formation of certain types of stoichiometric crystalline compounds is twofold [6]. X-Ray diffraction analysis of $Ca_{10}Mg_{90}$ throughout the full concentration range [7,8] shows that liquid Ca–Mg alloy is not entirely glassy. However, the phase diagram of CaMg [9] shows that there is a wide range of concentrations for which glassy alloys may be obtained by rapid quenching from the liquid state of this alloy. It has been reported by Sommer [10] that in the case of liquid Ca–Mg alloy, complete glass formation is available in the concentration range between 50 and 74 at.% Ca whereas partial glass formation lies in the concentration ranges 10–50 and 74–85 at.% Ca. Liquid Ca–Mg alloy has also been reported [2,11,12], a simple metal glass. Thermal analysis has been carried out by Vosskühler [13] for a certain range of concentrations and by Baar [14] through the whole

concentration range and at different temperatures. Agarwal et al. [15] have also measured the enthalpies of mixing for liquid Ca–Mg alloys for the concentration range $C_{Mg} = 0.522$–0.959 at 1023 K. They found that the phase diagram contains a congruently melting compound $CaMg_2$, which divides the phase diagram into two eutectic systems. The solubility of Mg is not well-defined and is apparently negligible [16].

The mixing behaviour of two metals forming a binary alloy reveals the energetics [17–19] and structural readjustment of the constituent atoms. The split second peak and pronounced asymmetry of the first peak in the partial structure factor of liquid Ca–Mg alloy from an elastic X-ray diffraction experiment [20] shows the well-known features characteristic of metallic glasses. The interatomic forces are promising in the structure of metallic glasses [21] and the potential energy mapping of Ca–Mg [22] is the best indicator of glass formation. A chemical short range order has been found in a series of metallic glasses, which have been investigated using diffraction techniques such as X-ray and neutron diffraction [23], and extended X-ray absorption fine structure analysis [24,25]. However, X-ray diffraction of Ca–Mg and its positive temperature coefficient of resistivity at low temperature are not very sensitive to the degree of chemical short range order.

There are a number of liquid binary alloys which are characterised by negative heats of mixing with an

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asymmetric compositional dependence. The minima in the enthalpy plots occur at stoichiometric compositions at which stable intermetallic compounds exist in the solid state or form in a metastable manner during rapid quenching from melt. Asymmetry in the free energy of mixing (G_M) and heat of mixing (H_M) is responsible for promoting complex formation in the alloy but these properties need not necessarily imply complex formation. In recent years, concentration–concentration fluctuations at long wavelength limit ($S_{CC}(0)$) and chemical short range order parameter (α_1) [26–30] have emerged as powerful microscopic functions to understand the phenomena of complex formation and phase segregation in the liquid alloys. Hence, use of $S_{CC}(0)$ is a better way [31] of evaluating the extent of association in the liquid compared to direct analysis of thermodynamic data and to analyse the factors responsible for the formation of metallic glasses.

The liquid Ca–Mg alloy is considered because it is a prototype of metallic glasses and has a simple phase diagram. G_M [9] and H_M [32] are negative and asymmetric about 50% composition, but the entropy of mixing (S_M) [33] is positive and has maximum values at two concentrations, 25 and 75 at.% Mg. Liquid Ca–Mg alloy with $G_M(\max)/RT = -1.08$ [9] is a weakly interacting system because those systems are strongly associated systems for which $G_M(\max)/RT \geq 3.0$ [34]. The complex formation model has been used to calculate the dependence of various thermodynamic properties such as G_M, H_M, S_M, thermodynamic activities and activity ratio, $S_{CC}(0)$ and α_1 of liquid Ca–Mg alloy.

Section 2 deals with the formalism of different thermodynamic properties and results and discussion have been included in Section 3. Section 4 contains the conclusion.

2. Formalism

Let us suppose that a liquid binary alloy containing in all $N_A = C_1 N$ atoms of A and $N_B = C_2 N$ atoms of B consists of $n_1 N$ free atoms of A, $n_2 N$ free atoms of B and $n_3 N$ complexes $A\mu B\upsilon$ which also act as independent scattering centres in the alloy. From the conservation of atoms we can write

$$n_1 = C_1 - \mu n_3$$
$$n_2 = C_2 - \upsilon n_3 \tag{1}$$
$$n = n_1 + n_2 + n_3$$

Here C_1, C_2 are the concentrations of first and second species of the alloy.

2.1. Number of complexes and thermodynamic properties of mixing

The concentration dependence number of complexes n_3 is obtained through the condition.

$$(\partial G_M / \partial n_3)_{T,P,C} = 0 \tag{2}$$

where the Gibbs energy of mixing (G_M) is given by [35,36]

$$G_M = -n_3 g + RT \sum_{i=1}^{3} n_i \ln(n_i/n) + \sum\sum_{i<j} (n_i n_j/n) W_{ij} \tag{3}$$

Here g is the formation energy and $(-n_3 g)$ lowers the free energy of mixing of the alloy due to the formation of the complexes. W_{ij} ($i, j = 1, 2, 3$) are the interaction energies through which leftover Ca atoms, Mg atoms and CaMg$_2$ complex interact with one another. W_{ij} are independent of the concentration but may depend on temperature and pressure. R is the gas constant and T is the specified absolute temperature. Eqs. (2) and (3) yield

$$n_1^\mu n_2^\upsilon = n_3 \, n^{(\mu + \upsilon - 1)} \exp(-g/RT) \exp(Z) \tag{4}$$

where

$$\begin{aligned}
Z &= Z_1 + Z_2 + Z_3 \\
Z_1 &= [(\mu + \upsilon - 1) n_1 n_2/n - \mu n_2 - \upsilon n_1] (W_{12}/nRT) \\
Z_2 &= [(\mu + \upsilon - 1) n_1 n_3/n - \mu n_3 + n_1] (W_{13}/nRT) \\
Z_3 &= [(\mu + \upsilon - 1) n_2 n_3/n - \upsilon n_3 + n_2] (W_{23}/nRT)
\end{aligned} \tag{5}$$

The heat of formation (H_M) can be obtained through Eq. (3) and the relation

$$H_M = G_M - T (\partial G_M / \partial_T)_{P,C,N} \tag{6}$$

Eqs. (3) and (6) yield

$$\begin{aligned}
H_M = &-n_3(g - T(\partial g/\partial T)) \\
&+ \sum\sum_{i,j} (W_{ij} - T(\partial W_{ij}/\partial T))(n_i n_j/n)
\end{aligned} \tag{7}$$

The entropy of mixing (S_M) is given by

$$S_M = (H_M - G_M)/T \tag{8}$$

2.2. Activity ratio

The activity ratio (a) is given by

$$a = a_1/a_2 \tag{9}$$

a_1, a_2 are the activities of the first and second species of the alloy and are given by

$$\begin{aligned}
RT \ln a_i(i = 1, 2) &= (\partial G_M/\partial N_i)_{T,P,N} \\
&= G_M + (1 - C_i)(\partial G_M/\partial C_i)_{T,P,N}
\end{aligned} \tag{10}$$

On using Eqs. (1–3), Eq. (9) gives

$$\ln a_i = \ln(n_i/n) + (1/RT)\left[\sum_{r=1}^{3} (n_r/n)W_{ir} - \sum\sum_{r<s} (n_r n_s/n^2)W_{rs} \right] \tag{11}$$

Here

$W_{ir} = 0$ for $i = r$

From Eq. (11) we get

$$\ln a_1 = \ln (n_1/n)$$
$$+ (1/RT)\big[(n_2 W_{12} + n_3 W_{13})/n - (n_1 n_2 W_{12}$$
$$+ n_1 n_3 W_{13} + n_2 n_3 W_{23})/n^2\big] \qquad (12)$$

$$\ln a_2 = \ln (n_2/n)$$
$$+ (1/RT)\big[(n_1 W_{12} + n_3 W_{23})/n - (n_1 n_2 W_{12}$$
$$+ n_1 n_3 W_{13} + n_2 n_3 W_{23})/n^2\big] \qquad (13)$$

2.3. Long wavelength concentration correlation function ($S_{CC}(0)$) and short range order parameter (α_1)

The long wavelength limit of the three correlation functions, namely the concentration–concentration correlation function ($S_{CC}(0)$), the number–number correlation function ($S_{NN}(0)$) and number–concentration correlation function ($S_{NC}(0)$) have been widely used to understand the stability [28–30,37] of the binary mixture. $S_{CC}(0)$ may be obtained theoretically as

$$S_{CC}(0) = RT \, (\partial^2 G_M/\partial C_1)_{T,P,N} \qquad (14)$$

Differentiating Eq. (3) twice with respect to C_1 and using Eqs. (1) and (4), one may derive after some algebra

$$S_{CC}(0) = S_{CC}/(1 + D S_{CC}) \qquad (15)$$

$$S_{CC}^{-1} = \sum_{i=1}^{3} \big[(n_i')^2/n_i - (n')^2/n\big] \qquad (16)$$

$$D = (2n/RT) \sum\sum_{i<j} (n_i/n)'(n_j/n)' W_{ij} \qquad (17)$$

where

$$(n_i/n)' = (n_i' n - n' n_i)/n^2 \qquad (18)$$

and a prime denotes differentiation with respect to C_1

$$n' = n_1' + n_2' + n_3'$$
$$n_1' = 1 - \mu n_3'$$
$$n_2' = -1 - \upsilon n_3' \qquad (19)$$
$$n_3' = A/B$$

$$A = \mu/n_1$$
$$- \upsilon/n_2 - (\mu + \upsilon - 1)\big[(n_2 - n_1)W_{12} + n_3(W_{13}$$
$$- W_{23})\big] (1/n^2 RT) - \big[(\mu - \upsilon)W_{12} + W_{13}$$
$$- W_{23}\big] (1/nRT) \qquad (20)$$

$$B = \mu^2/n_1 + \upsilon^2/n_2 + 1/n_3$$
$$+ \big[(\mu + \upsilon - 1)Z + \mu\upsilon W_{12} - \mu W_{13} - \upsilon W_{23}\big] (2/nRT)$$
$$- (\mu + \upsilon - 1)^2/n \qquad (21)$$

The Warren–Cowley [38,39] short range order parame-

ter (α_1) is computed to quantify the degree of order. α_1 can be determined experimentally from $S_{CC}(q)$ and $S_{NN}(q)$. However, the determination of these two parameters is difficult for all types of binary alloys [28,40–42]. But α_1 can be computed theoretically [28–30]

$$\alpha_1 = (S - 1)/(S(Z - 1) + 1) \qquad (22)$$

$$S = S_{CC}(0)/S_{CC}(0)id \qquad (23)$$

Z is the co-ordination number and $S_{CC}(0)id = C_1 C_2$. Z is taken as 10 in the case of liquid Ca–Mg alloy.

3. Results and discussion

It is clear from Section 1 that the likely complex to be formed in liquid Ca–Mg alloy is $CaMg_2$. The expressions derived in Section 2 were used to compute n_3 (Eq. (4)), G_M (Eq. (3)), H_M (Eq. (6)), S_M (Eq. (7)), $\ln a$ (Eq. (9)), $S_{CC}(0)$ (Eq. (14)) and α_1 (Eq. (22)) as a function of concentration for liquid Ca–Mg alloys. The basic inputs for computation of the above functions are the interaction energy parameters. A reasonable choice of the interaction energy parameters and number of complexes is made from the experimental results for G_M [9] at a couple of concentrations for liquid Ca–Mg alloys. The energy parameters evaluated for Ca–Mg are

$$g/RT = 1.90, \ W_{12}/RT = -1.05, \ W_{13}/RT = 2.60,$$
$$W_{23}/RT = -0.70$$

The low value of complex formation energy (g/RT) reveals that Ca–Mg is a weakly interacting system [29,37,43] like Al–Ca, Al–Mg, Hg–Sn, Ag–Al, Cu–Sn and Mg–Zn liquid binary alloys. The evaluated values of interaction energies W_{12}, W_{13} and W_{23} suggest that Ca atoms and Mg atoms, Mg atoms and the complex $CaMg_2$ are attractive whereas Ca atoms and $CaMg_2$ are repulsive in nature in liquid Ca–Mg alloy. Eq. (4) was used to obtain equilibrium values of n_3 and hence G_M via Eq. (3). The computed values of n_3 and G_M versus concentration are shown for Ca–Mg liquid alloy in the upper and lower parts of Fig. 1, respectively. The experimental values of G_M [9] are also shown in Fig. 1. It can be seen from Fig. 1 that the values of G_M are negative at all concentrations, being minimum around the stoichiometric composition. The computed values are in close agreement with experiment. Fig. 1 shows that n_3 is maximum at $C_{Mg} = 0.75$.

The values of H_M are found to be in poor agreement with the experimental observation if energy parameters are taken independent of temperatures. Therefore the enthalpy of mixing and entropy of mixing of liquid Ca–Mg alloy were computed by considering the variation of energy parameters with temperature. The temperature-dependent energies at $T = 1150$ K are
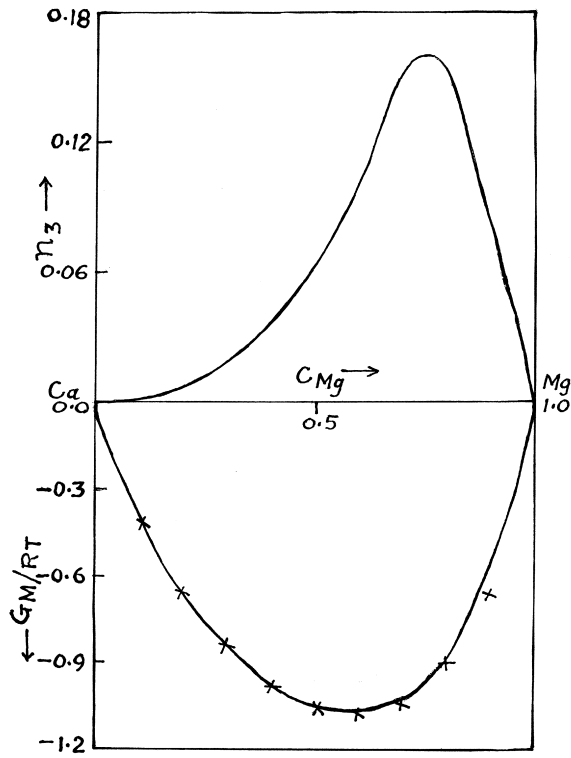
Fig. 1. Upper part: Number of complexes (n_3) of liquid Ca–Mg alloy versus concentration of Mg (C_{Mg}); ———, present value. Lower part: Energy of mixing (G_M) of liquid Ca–Mg alloy versus concentration of Mg (C_{Mg}); ———, present value; × × ×, expt. value [9] at $T = 1200$ K.

$$\partial g / \partial T = -2.69R, \quad \partial W_{12} / \partial T = 0,$$
$$\partial W_{13} / \partial T = -19.55R, \quad \partial W_{23} / RT = 0.8R$$

It is revealed that W_{12}, through which the interaction between left over Ca and Mg atoms is expressed, is independent of temperature. The computed values of H_M and S_M versus concentration are shown for Ca–Mg liquid alloys, respectively, in the lower and upper part of Fig. 2 together with the experimental values [15,32,33]. The computed values of H_M are in close agreement with experiment [32] whereas an appreciable difference is found with the experimental values by Agarwal et al. [15]. It is to be noted here that the experimental values [15] are at $T = 1023$ K and the difference between the theoretical and experimental values [15] may be minimized by considering the values of energy parameters at $T = 1023$ K in place of $T = 1150$ K since these parameters are temperature-dependent. A reasonable agreement is found between the computed and experimental [33] values of entropy of mixing. The values of H_M are negative and those of S_M are positive throughout the whole composition range. The values of S_M are maximum around two compositions and we are successful in reproducing the nature of the curve. The difference in the experimental and theoretical values of S_M may be related to the fact that the theoretical computations were carried out at $T = 1200$ K whereas the experimental values are at $T = 1010$ K. However, a close agreement
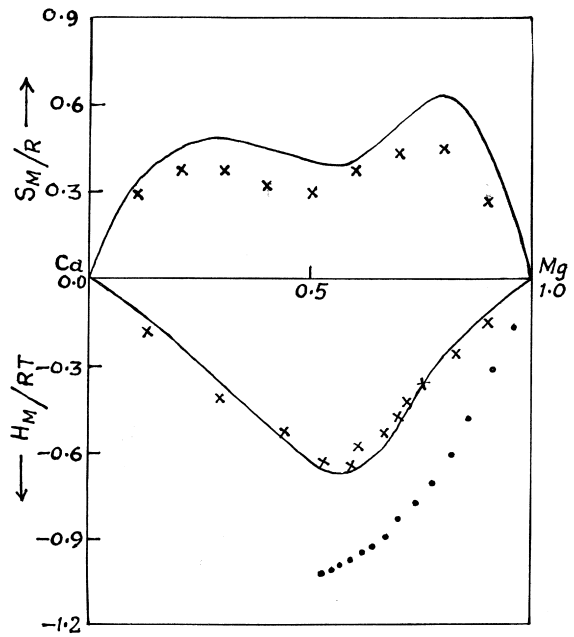

Fig. 2. Upper part: Entropy of mixing (S_M) of liquid Ca–Mg alloy versus concentration of Mg (C_{Mg}); ———, present value; × × ×, expt. value [33] at $T = 1010$ K; Lower part: Heat of mixing (H_M) of liquid Ca–Mg alloy versus concentration of Mg (C_{Mg}); ———, present value; × × ×, expt. value [32] at $T = 1150$ K; · · ·, expt. values [15] at 1023 K.

between experimental and theoretical values is found if the experimental values of S_M are estimated [29] from experimental G_M [9] and H_M [32] values. These estimated experimental values along with computed theoretical values and experimental values [33] have been given in Table 1.

The computed values of thermodynamic activities a_{Ca} and a_{Mg} are given in Table 2 and those of ln a versus concentration are shown in Fig. 3 together with experimental values [9] for Ca–Mg liquid binary alloys. Table 2 and Fig. 3 show that the theoretical and experimental values are in close agreement except for the Mg-rich end where a difference is found.

The theoretical values of $S_{CC}(0)$ for Ca–Mg are com-

Table 1
Entropy of mixing (S_M/R) of liquid Ca–Mg glassy alloy

C_{Mg}	Entropy of mixing (S_M/R)		
	Present value (1200 K)	Estimated expt. value from expt. G_M [9] and H_M [28] (1200 K)	Expt. (1010 K)
0.1	0.314	0.294	0.288
0.2	0.447	0.372	0.372
0.3	0.479	0.443	0.360
0.4	0.449	0.438	0.313
0.5	0.404	0.424	0.288
0.6	0.405	0.449	0.361
0.7	0.523	0.545	0.421
0.8	0.629	0.600	0.433
0.9	0.434	0.496	0.265

Table 2
Thermodynamic activities of Ca and Mg in liquid Ca–Mg glassy alloy at 1200 K

C_{Ca}	a_{Ca}		a_{Mg}	
	Present	Expt.	Present	Expt.
0.1	0.007	0.022	0.866	0.730
0.2	0.065	0.096	0.642	0.572
0.3	0.226	0.212	0.429	0.442
0.4	0.339	0.331	0.342	0.348
0.5	0.449	0.437	0.278	0.278
0.6	0.551	0.551	0.216	0.209
0.7	0.660	0.671	0.155	0.145
0.8	0.775	0.786	0.095	0.089
0.9	0.891	0.896	0.041	0.041

puted through Eq. (14). Values of $S_{CC}(0)$ obtained directly from observed activity data [9] are usually termed as experimental values. The computed and experimental [31] values of $S_{CC}(0)$ versus concentration are shown in the upper part of Fig. 4 along with $S_{CC}(0)id$ for Ca–Mg liquid alloys. From $S_{CC}(0) < S_{CC}(0)id$, the existence of chemical ordering leading to complex formation is expected. Fig. 4 shows that $S_{CC}(0)$ is minimum around $C_{Mg} = 0.75$. The minimum in $S_{CC}(0)$ occurs around the composition where the fraction of chemical complexes (n_3) and entropy of mixing (S_M) are found maximum.

α_1 provides immediate insight into the local arrangements of atoms in the mixture. $\alpha_1 < 0$ refers to unlike atoms pairing, $\alpha_1 > 0$ corresponds to like atoms pairing as nearest neighbours and $\alpha_1 = 0$ indicates a random distribution of atoms. The computed values of α_1 are shown in the lower part of Fig. 4. The values of α_1 remain negative throughout the whole concentration range being minimum at two concentrations. Before the minimum value of α_1 at 80 at.% of Mg, there is a flat minimum around 20 at.% of Mg. Fig. 4 shows that liquid Ca–Mg alloy is more ordered towards the Mg-rich end.
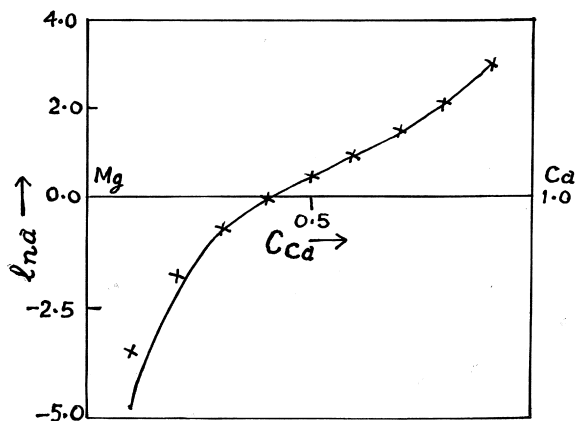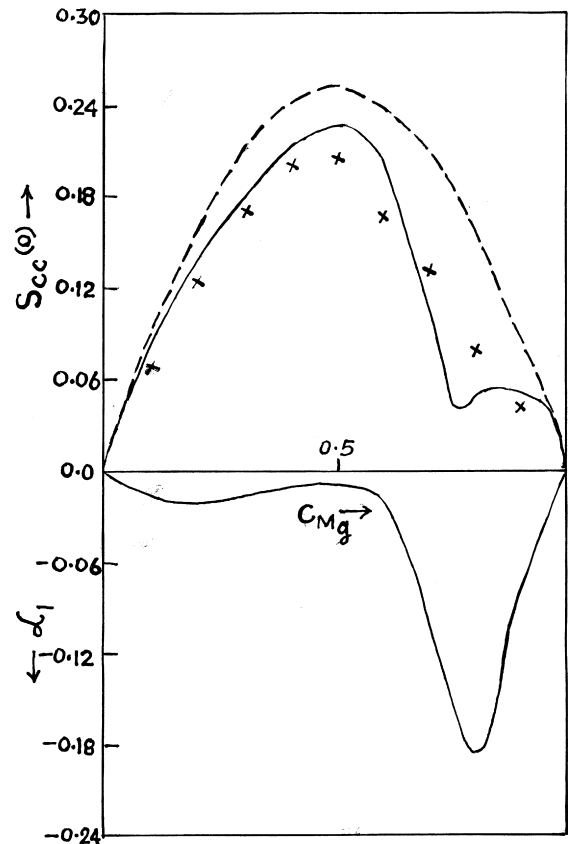

Fig. 4. Upper part: $S_{CC}(0)$ of liquid Ca–Mg alloy versus concentration of Mg (C_{Mg}) at $T = 1200$ K; ———, present value; $\times \times \times$, expt. value [31] calculated from the activity data [9]; — — —, ideal value ($S_{CC}(0)id$); Lower part: CSRO (α_1) of Ca–Mg liquid alloy versus concentration of Mg (C_{Mg}) at $T = 1200$ K; ———, present value.

4. Conclusion

Large negative values of G_M, H_M are sufficient to indicate the presence of intermetallic compounds $CaMg_2$ in Ca–Mg system. The negative values of chemical short range order parameter indicate the presence of chemical order essential for complex formation. The complex formation may not be directly related to glass formation. $S_{CC}(0) > S_{CC}(0)id$ leads to glass formation [31,44]. However, this may not be a sufficient condition. Other factors like solid–liquid interfacial energy, temperature, and diffusivity may also play an important role. It is well-known that the presence of associates in the alloy system is also a condition for easy glass formation. Sommer et al. [32] originally proposed that complexes of the composition $CaMg_2$ form in Ca–Mg system but Sommer [10] maintained that only CaMg complexes form. Thus in Mg–Ca system, associates with the composition MgCa are present, while the crystalline equilibrium phase has the composition Mg_2Ca. Thus it appears that the formation of more than one type of complex may be related to the process of glass formation in the Ca–Mg system.

Fig. 3. Thermodynamic activity ratio (ln a) versus concentration of Ca (C_{Ca}) in liquid Ca–Mg alloy; ———, present value; $\times \times \times$, expt. value [9] at $T = 1200$ K.

Acknowledgements

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