Concentration Fluctuations and Chemical Complexes in the Zn-Au Liquid Alloy

B. C. Anusionwu[a]

[a] Abdus Salam International Centre for Theoretical Physics, Trieste, Italy

PLEASE SCROLL DOWN FOR ARTICLE

CONCENTRATION FLUCTUATIONS AND CHEMICAL COMPLEXES IN THE ZN–AU LIQUID ALLOY

B. C. ANUSIONWU*

Abdus Salam International Centre for Theoretical Physics, Trieste, Italy

The concentration–concentration fluctuations in the long wavelength limit $S_{cc}(0)$ and the Warren–Cowley short range order parameters (SRO) α_1 have been calculated for the Zn–Au liquid alloy at 1173 K by applying the Quasi Chemical Approximation (QCA). The results of the calculations show that Zn–Au liquid alloy manifest hetero-coordination throughout its whole concentration range. There exist evidence for the presence of two complexes Zn_4Au_3 and Zn_4Au_6. The Zn_4Au_3 complex which manifests dominance in the thermodynamic properties of the liquid alloy yielded a minimum short range order value of about $\alpha_1^{min} \approx -0.26$ while Zn_4Au_6 has its minimum as $\alpha_1^{min} \approx -0.34$. Studies from the $S_{cc}(0)$ indicate that these complexes are weak and hence cannot encourage glass formation in the liquid alloy.

Keywords: Thermodynamic properties; chemical complexes

1. INTRODUCTION

Today more research efforts are being focused towards the under-standing of the dynamics of glass formation and structure of disordered matter [1–3]. Glasses have been reported to form in a variety of matter such as the CKN (a mixture of the anhydrous salts KNO_3 and $Ca(NO_3)_2$ in the molar proportions 3 : 2), biopolymers [4] and even metals [5]. Glasses formed from metallic alloys show properties which indicate that they are true glasses [5]. Many compound

---

*Address for correspondence: Department of Physics, Federal University of Technology, P. M. B. 1526 Owerri, Nigeria.

forming binary alloys such as MgZn and CuTi have been reported to be good glass formers [6].

Ramachandra Rao *et al.* [7] have utilized the knowledge of the concentration–concentration fluctuation at the long wavelength limit $S_{cc}(0)$ to explain the formation of glasses in compound forming binary liquid alloys. In the framework of their complex-formation model, the unassociated species (A and B atoms) of an A-B alloy and the complex ($A_\mu B_\nu$) may mix randomly. Such random mixing can presumably hinder nucleation and support glass formation. The existence of complexes in liquid compound forming alloys has been related to their glass forming tendencies. The nature and strength of the complexes are becoming of increasing interest. The knowledge of the $S_{cc}(0)$ for a liquid binary alloy can also be used successfully to assess the nature and strength of these chemical complexes ($A_\mu B_\nu$) where they exists.

The Quasi Chemical Approximation (QCA) [6] provides a means of determining the $S_{cc}(0)$ and hence the nature and strength of complex formed in a liquid binary alloy by using the measured thermodynamic data of the alloy. This approximation appears better than the widely used conformal solution model [8] which actually has been successful in reproducing the $S_{cc}(0)$ with the use of the interchange energy, but it ignores the extent of local ordering and hence provide no information on the short range order in the liquid alloy. The Quasi chemical approximation apart from successfully reproducing the measured $S_{cc}(0)$ for a given liquid alloy, provides information on the Warren–Cowley short range order parameter and predicts the actual nature of the complex in the alloy.

There are also the *ab-initio* methods [9, 10] which use the pseudopotential formalism to calculate thermodynamic quantities and predict $S_{cc}(0)$. This formalism has severe limitation in situation where there is formation of complexes. In this case the Car–Parinello [11] type of simulations can be used but this is computationally demanding. From the aforementioned, one is still of the opinion that the use of QCA in predicting the $S_{cc}(0)$ is still justified.

In this work therefore, we wish to apply the quasi-chemical approximation to the experimental thermodynamic data of Zn–Au liquid alloys, to determine the possible complexes formed in the alloys, the strength of the complexes, ordering in the liquid state and also predict its possible glass forming tendencies.

Studies on the Zn–Au alloy systems show that they are characterized by the existence of a phase β'-AuZn which has the ordered CsCl(B2) structure [12]. They are also found to exhibit a wide range of homogeneity on both sides of the equiatomic composition [13].

In the next section, we outline the basic theoretical concepts of the quasi-chemical approximation. In Section 3, the results of the calculations are presented and discussed. Section 4 outlines the conclusions of the work.

2. THEORETICAL CONCEPTS

The fundamental idea about the quasi chemical model is that the properties of a compound forming A-B alloy can be explained by treating the alloy as pseudo ternary mixture of A atoms, B atoms and $A_\mu B_\nu$ complexes. Details of the formulations are given in Ref. [6].

The excess free energy of mixing G_m^{xs} is related to the free energy G_m by the expression,

$$G_m^{xs} = G_m - RT\left[c \ln c + (1 - c)\ln(1 - c)\right] \qquad (1)$$

here, c is the concentration of atom A, and R is the universal gas constant. The quasi chemical expression for the excess free energy of mixing G_m^{xs} is given as:

$$\frac{G_m^{xs}}{RT} = z\int_0^c [\ln \sigma + (2kT)^{-1}(P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB})]dc + \psi \qquad (2)$$

where z is the co-ordination number, k, the Boltzman constant and $\ln \sigma$ is

$$\ln \sigma = \frac{1}{2}\ln\frac{(1 - c)(\beta + 2c - 1)}{c(\beta - 2c + 1)} \qquad (3)$$

with

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

and

$$\eta^2 = \exp\left(\frac{2w}{zk_BT}\right)\exp\left(\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{k_BT}\right) \quad (5)$$

w, $\Delta\varepsilon_{AB}$, $\Delta\varepsilon_{AA}$, $\Delta\varepsilon_{BB}$ are the interaction parameters with w denoting the interchange energy and $\Delta\varepsilon_{ij}$ being the change in the energy if the ij bond is in the complex $A_\mu B_\nu$. P_{ij} denotes the probability that the bond is part of the complex and the expressions are given as follows:

$$P_{AB} = c^{\mu-1}(1-c)^{\nu-1}[2 - c^{\mu-1}(1-c)^{\nu-1}] \quad (6)$$

$$P_{AA} = c^{\mu-2}(1-c)^\nu[2 - c^{\mu-2}(1-c)^\nu], \quad \mu \geq 2 \quad (7)$$

$$P_{BB} = c^\mu(1-c)^{\nu-2}[2 - c^\mu(1-c)^{\nu-2}], \quad \nu \geq 2 \quad (8)$$

The constant ψ is determined from the requirement that $G_m = 0$ at $c = 1$.

The activities of the metals are obtained by

$$a_m = c\gamma_m \quad (9)$$

where c is the concentration of the species and γ_m is its activity coefficient given by

$$\gamma_m = \left\{\frac{\beta - 1 + 2c}{c(1 + \beta)}\right\}^{(1/2)z} \quad (10)$$

where β is as defined in Eq. (4).

The concentration–concentration fluctuations in the long wavelength limit $S_{cc}(0)$ for highly interacting systems can be obtained from the thermodynamic expression

$$S_{cc}(0) = \frac{RT}{(\partial^2 G_m/\partial c^2)_{T,P,N}} \quad (11)$$

This can further be expressed as

$$S_{cc}(0) = c(1-c)\left\{1 + \frac{1}{2}z\left(\frac{1}{\beta} - 1\right) + \Omega\right\}^{-1} \quad (12)$$

where Ω is the expression given below:

$$\Omega = \frac{zc(1-c)}{2\beta kT}\Theta \tag{13}$$

and

$$\Theta = [2(1-2c)P'_{AB}\Delta\varepsilon_{AB} + (\beta - 1 + 2c)P'_{AA}\Delta\varepsilon_{AA}$$
$$- (\beta + 1 - 2c)P'_{BB}\Delta\varepsilon_{BB}] \tag{14}$$

where the prime on P denotes the first derivative with respect to c.

Then Warren–Cowley short range order parameter α_1 [14, 15] for the nearest neighbours is defined in terms of the probability that two neighbouring sites are occupied by A and B atoms. Essentially, it can be stated that given an atom A at a lattice site 1, say, let (B/A) denote the probability that a B atom exists at a site 2 which is the nearest neighbour to site 1, then

$$(B/A) = (1-c)(1-\alpha_1) \tag{15}$$

here $\alpha_1 = 0$ for a random alloy, since $(B/A) = (1-c)$, the mean concentration of B atoms. From simple probabilistic considerations, it follows that α_1 lies in the range

$$\frac{-c}{1-c} \leq \alpha_1 \leq 1, \quad c \leq \frac{1}{2} \tag{16}$$

$$\frac{-(1-c)}{c} \leq \alpha_1 \leq 1, \quad c \geq \frac{1}{2} \tag{17}$$

Using arguments based on probability, α_1 can be expressed as:

$$\alpha_1 = \frac{\beta - 1}{\beta + 1} \tag{18}$$

3. RESULTS AND DISCUSSIONS

The essential equations have been outlined in the preceding section. In applying the QCA, we assume the liquid alloy under consideration (in this case Zn–Au) to consist of a mixture of Zn atom, Au atom and the complexes $Zn_\mu Au_\nu$. Next, the interaction parameters

w, $\Delta\varepsilon_{AB}$, $\Delta\varepsilon_{AA}$ and $\Delta\varepsilon_{BB}$ have to be determined. Essentially what one does is to assume suitable values of μ and ν for the alloy under consideration. The values of μ and ν can be taken from conjectures or based on phase diagrams where available. Now Eq. (2) is solved and the interaction parameters are fine tuned such that they reproduce simultaneously to a reasonable extent the measured free energy of mixing and the activity. In this work the values of μ and ν were conjectured from phase studies [13].

Table I shows values of μ and ν and their corresponding interaction parameters which reproduced simultaneously to a resonable extent the measured free energy of mixing and activity for Zn–Au liquid alloy at 1173 K. A plot of the calculated and experimental G_m/RT for the two sets of values of μ and ν are given in Figure 1. The experimental data for the free energy of mixing and activity are taken from Ref. [12]. Figure 2 shows the plots of the experimental and calculated values of the activity of Zn in Zn–Au liquid alloy for the two sets of values of μ and ν. It is obvious from the figures that our complex parameters μ and ν and the interaction parameters reproduce fairly well the observed G_m/RT and activity. Due to the closeness of the fit for the two sets of complex parameters, we present in Table II their χ^2 values as a measure of the relative goodness of their fit. The plots using $\mu = 4$ and $\nu = 3$ showed a better fit reproducing more closely the location of symmetry for G_m/RT. The plot for $\mu = 4$ and $\nu = 6$ showed an underestimation of the activity above 0.35 at. frac. of Zn thereby resulting in a relatively large χ^2 value, while the plot for $\mu = 4$ and $\nu = 3$ shows an underestimation below 0.35 at. frac. of Zn.

Having reproduced simultaneously the measured G_m/RT and activity data with the two sets of complex parameters ($\mu = 4$, $\nu = 3$ and $\mu = 4$, $\nu = 6$) one can confidently infer the existence of the complexes Zn_4Au_3 and Zn_4Au_6 in the liquid Zn–Au alloy. This is not strange as three complex compositions (Ba_3Mg, Ba_3Mg_2 and $BaMg_2$) of BaMg melt have been reported to exist simultaneously [7].

TABLE I   Interaction parameters for the Zn–Au liquid alloy

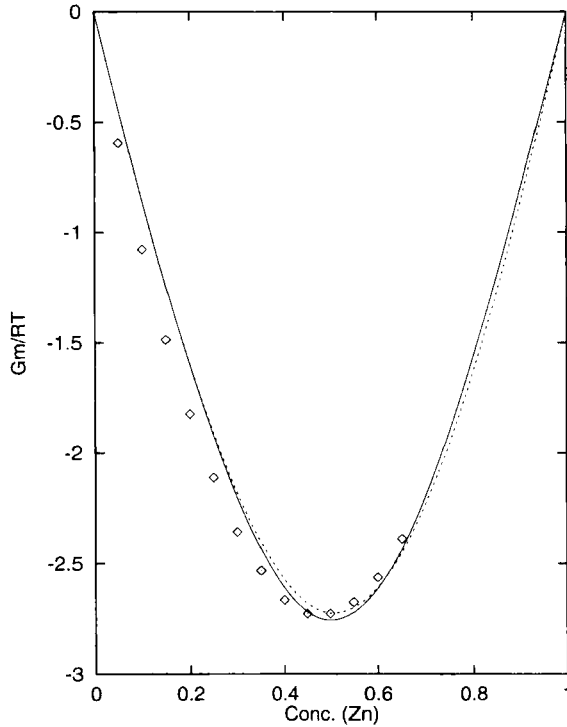| μ	ν	w/kT	$\Delta\varepsilon_{AB}/kT$	$\Delta\varepsilon_{AA}/kT$	$\Delta\varepsilon_{BB}/kT$
4	3	-8.78	-0.94	-4.50	-5.12
4	6	-9.20	3.40	-11.50	5.12

FIGURE 1 G_m/RT vs. atomic fraction of Zn. Solid lines rep. calculated values for $\mu = 4$ and $\nu = 3$ (Zn_4Au_3). Dashes rep. calculated values for $\mu = 4$ and $\nu = 6$ (Zn_4Au_6). Points rep. experimental values.

To investigate the phenomenon of ordering in this liquid binary alloy and hence assess the strengths of the complexes formed, the parameter of foremost interest is the concentration–concentration fluctuation at the long wavelength limit $S_{cc}(0)$. This quantity is of great interest because any deviation from the ideal value $S_{cc}^{id}(0) = c(1 - c)$ is significant in describing the nature of ordering in an alloy melt. Put in another form, $S_{cc}(0) < S_{cc}^{id}(0)$ shows a tendency to hetero-coordination or compound formation and $S_{cc}(0) > S_{cc}^{id}(0)$ indicates nearness to homocoordination or phase seperation.

The $S_{cc}(0)$ can be calculated using the QCA from Eq. (11). In this equation, the values of the the complex parameters (μ, ν) and the interaction parameters (w, $\Delta\varepsilon_{AB}$, $\Delta\varepsilon_{AA}$ and $\Delta\varepsilon_{BB}$) which reproduced
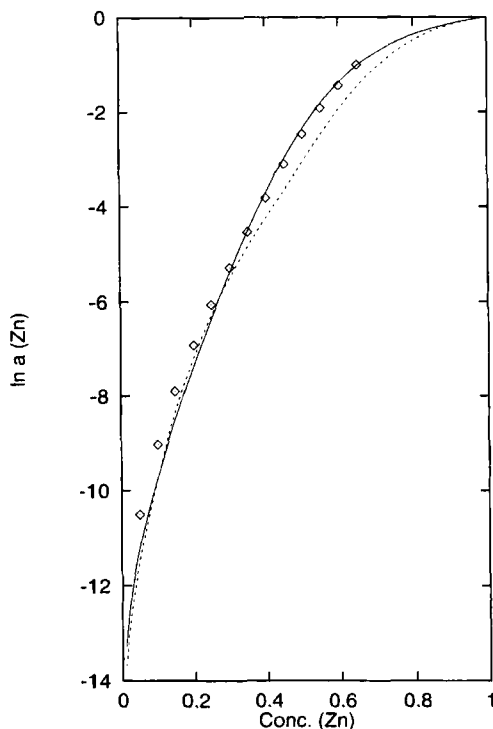
FIGURE 2 $\ln a_{Zn}$ vs. atomic fraction of Zn. Solid lines rep. calculated values for $\mu = 4$ and $\nu = 3$ (Zn_4Au_3). Dashes rep. calculated values for $\mu = 4$ and $\nu = 6$ (Zn_4Au_6). Points rep. experimental values.

TABLE II χ^2 values of the fits for the complexes[†]

Complex	χ^2 (G_m/RT)	χ^2 $(\ln a_{Zn})$	χ^2 $(S_{cc}(0))$
Zn_4Au_3	0.1884	0.2122	0.0078
Zn_4Au_6	0.1954	1.0428	0.0076

[†]All χ^2 values are acceptable at 0.005 level of significance.

the measured G_m/RT and activity were used. However, from the experimental point of view, the experimental $S_{cc}(0)$ can be computed from measured data by using the thermodynamic relationship

$$S_{cc}(0) = \frac{RT}{(\partial^2 G_m/\partial c)} \qquad (19)$$

this is further simplified as

$$S_{cc}(0) = \frac{c(1-c)}{c(\partial \ln \gamma_m/\partial c) + 1} \tag{20}$$

where γ_m is the measured activity coefficient for the alloy component.

Figure 3 illustrates a comparison of the experimental and calculated values of $S_{cc}(0)$ of the Zn–Au molten alloy for the cases of the complexes Zn_4Au_3 and Zn_4Au_6. The ideal values are also plotted in order to distinguish between phase separation and compound formation in the alloy. The interaction parameters were able to obtain a qualitative trend for $S_{cc}(0)$ though interestingly enough calculated $S_{cc}(0)$ for the Zn_4Au_3 complex gave a very good and closer
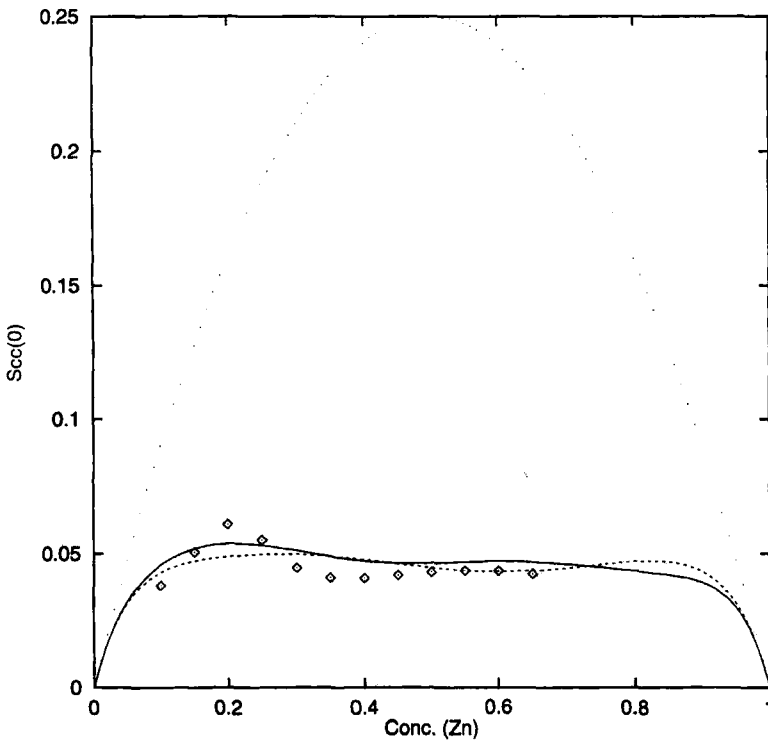

FIGURE 3 $S_{cc}(0)$ *vs.* atomic fraction of Zn. Solid lines rep. calculated values for $\mu = 4$ and $\nu = 3$ (Zn_4Au_3). Dashes rep. calculated values for $\mu = 4$ and $\nu = 6$ (Zn_4Au_6). Dots rep. ideal values of $S_{cc}(0)$. Points rep. experimental values.

reproduction of the trend of the experimental values. The calculated $S_{cc}(0)$ for Zn_4Au_6 complex shows a greater under estimation of the measured $S_{cc}(0)$ below 0.4 atomic fraction of Zn. The χ^2 values for $S_{cc}(0)$ in both cases strengthen the earlier prediction of the simultaneous existence of these two complexes Zn_4Au_3 and Zn_4Au_6. However, despite the higher χ^2 values of the complex Zn_4Au_6 for the $\ln a_{Zn}$ and G_m/RT fits, it has a lower value of χ^2 for the $S_{cc}(0)$ fit. Since the complex Zn_4Au_3 produced a curve that mimics better the shape of the experimental $S_{cc}(0)$, it can be inferred that the thermodynamic properties of the Zn–Au liquid alloy are influenced more by the presence of this complex. The complex Zn_4Au_3 can be said to be more dominant though it may be mixed randomly with the complex Zn_4Au_6.

The $S_{cc}(0)$ of the Zn–Au melt, show that the liquid alloy is a compound former over the whole concentration–concentration range. To measure quantitatively the degree of ordering and the extent of compound formation the Warren–Cowley short range order parameter for the nearest neighbour shell α_1 was calculated using the quasi chemical expression of Eq. (16). The results of the calculations are is shown in Figure 4. The presence of the Zn_4Au_6 complex leads to a more ordered system and hence higher tendency to compound formation with $\alpha_1^{min} \approx -0.34$ while the complex Zn_4Au_3 leads to a less ordered state with $\alpha_1^{min} \approx -0.26$.

The strength of the complexes can be inferred from the $S_{cc}(0)$. The position of the dip in the $S_{cc}(0)$ $vs.$ c curve yields information on the nature of the complex and its depth signifies strength [6]. The position of the dips in Figure 3 can suggest that with the formation of Zn_4Au_3 complex, the glass forming composition range for the liquid alloy will be between 0.04 and 0.24 at. frac. Zn and between 0.24 and 0.36 for Zn_4Au_6 complex. However, at these composition ranges, the departure of the $S_{cc}(0)$ values from the ideal values are very wide thereby reducing the possibility of glass formation, since for glass forming systems, $S_{cc}(0)$ within the glass forming composition range tends to the ideal values [7]. The complex Zn_4Au_3 though may be more prevalent in the Zn–Au melt, is very weak as the dip in its $S_{cc}(0)$ is very shallow. The complex Zn_4Au_6 with reference to the dip in its $S_{cc}(0)$ is yet weaker and its presence in the melt will have low impact on the glass forming tendencies of the liquid alloy.
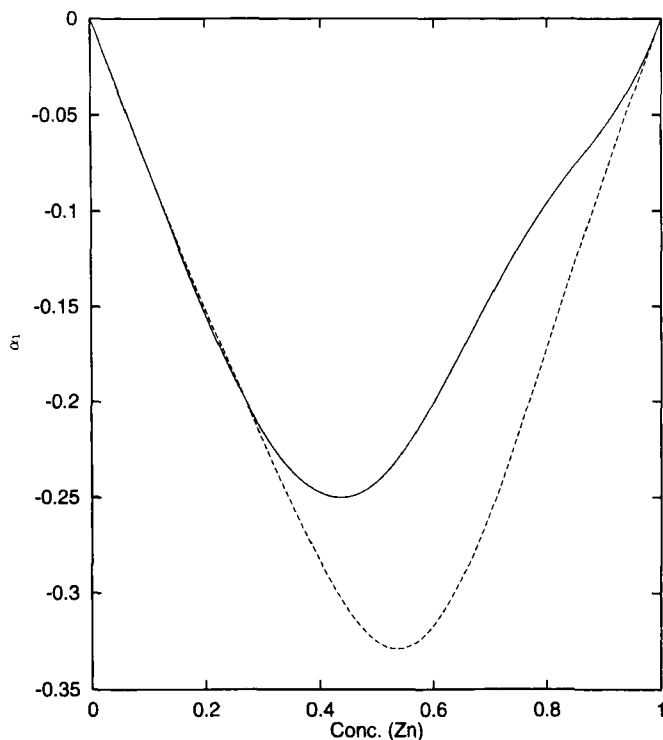
FIGURE 4 Warren–Cowley short range order value (α_1) *vs.* atomic fraction of Zn. Solid lines rep. calculated values for $\mu = 4$ and $\nu = 3$ (Zn_4Au_3). Dashes rep. calculated values for $\mu = 4$ and $\nu = 6$ (Zn_4Au_6).

4. CONCLUSION

The manifestation of the complexes Zn_4Au_3 and Zn_4Au_6 in the Zn–Au melt is a pointer to the possibility of glass formation in the alloy. The presence of complexes in a liquid alloy has been suggested to hinder nucleation and encourage glass formation [7]. This inference can be misleading as the phenomenon of glass formation in molten alloys is very involved and may depend on many other factors. Nevertheless, many good compound forming alloys which have manifested the existence of complexes in their melts have been noted to be good glass formers.

In the case of Zn−Au melt, our calculations predicts the presence of complexes as already indicated in the discussions. However, when the deviation of the $S_{cc}(0)$ from the ideal values and the strength of these complexes are considered, one is of the opinion that complexes of such weak nature may not hinder nucleation and lead to glass formation. It can then be concluded that though Zn−Au alloy is strong compound former and manifest the presence of complexes, it may not be a good glass former due to the low strength of its complexes.

Acknowledgments

References

[1] Cardenas, M., Franz, S. and Parisi, G. (1999). *J. Chem. Phys.*, **110**(3), 1397.
[2] Franz, S. and Parisi, G. (1997). *Phys. Rev. Lett.*, **79**, 2486.
[3] Mezard, M. and Parisi, G. (1996). *J. Phys. A*, **29**, 6516.
[4] Angel, C. A. (1995). *Science*, **267**, 1924.
[5] Greer, A. L. (1995). *Science*, **267**, 1947.
[6] Singh, R. N. (1987). *Can. J. Phys.*, **65**, 309.
[7] Ramachandra Rao, P., Singh, R. N. and Lele, S. (1984). *J. Non-Cryst. Solids*, **64**, 387.
[8] Longuet-Higgins, H. C. (1951). *Proc. R. Soc. London*, **A205**, 247.
[9] Lai, S. K., Matsuura, M. and Wang, S. (1983). *J. Phys.*, **F13**, 2033.
[10] Hafner, J. and Jank, W. (1988). *J. Phys.*, **F18**, 333.
[11] Car, R. and Parrinello, M. (1985). *Phys. Rev. Lett.*, **55**, 2471.
[12] Ipser, H., Krachler, R. and Komarek, K. L. (1988). *Z. Metallkde.*, **79**, 725.
[13] Moffatt, W. G. (1980). *The Handbook of Binary Phase Diagrams*, General Electric Company, Schenectady, NY.
[14] Warren, B. E. (1969). *X-Ray Diffraction*, Addison Wesley, Reading: MA.
[15] Cowley, J. M. (1950). *Phys. Rev.*, **77**, 669.