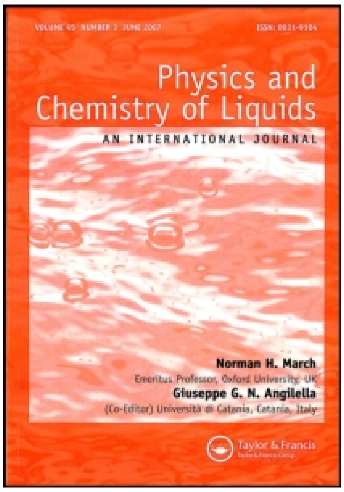

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A THEORETICAL STUDY OF STRUCTURE AND ORDERING IN Pb–Bi MOLTEN ALLOYS

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The solution of the Percus–Yevick (PY) equation for a binary mixture with a square well potential as a perturbation has been applied to the study of the Pb–Bi molten alloy system. The partial structure factors in the long wavelength limit is calculated and used to evaluate the long wavelength limit of the concentration–concentration fluctuations $S_{cc}(0)$. This has in turn been used to obtain the Warren–Cowley short range order parameter α_1 and the chemical diffusion D. The calculations indicate compound forming tendencies in Pb–Bi molten alloys with greater magnitude at low atomic fraction of Bismuth.

Keywords: Partial structure factors; liquid alloys

1 INTRODUCTION

Investigations [1–4] which have so far been carried out on the Pb–Bi system indicate that it is ‘anomalous’, partly because it manifests a positive excess volume and a negative enthalpy of mixing. It was further observed [2] that the system shows a small positive departure from linearity in the concentration dependence of liquid alloy volume.

Recently, Neuman *et al.* [4] suggested that the results of scattering investigation and thermodynamical measurements [1] can be explained by the assumption that atomic arrangements with a preference

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of unlike atomic pairs exist in the Pb–Bi molten alloy. The present work is an attempt to, firstly, obtain the partial structure factors for Pb–Bi from experimental total structure factors and secondly to investigate the nature of ordering in the system as deduced from structural information.

We note that Lead and Bismuth though adjacent to one another in the periodic table and with a low eutectic, have a significant disparity in structure. While molten Bismuth manifests a shoulder to the right of the principal peak of its structure factor, Lead in most cases exhibits structural features similar to those in a normal metal.

Theoretical studies of the structure of binary alloys require the accurate estimation of the three partial structure factors, $S_{11}(q)$, $S_{22}(q)$ and $S_{12}(q)$. Obtaining these partial structure factors from experiment is difficult since we require at least three independent measurements for evaluating these. Model calculations become inevitable, since it offers a way of determining the structure factors independent of experiment.

The perturbation treatment of the Percus–Yevick (PY) equations with a square wall attractive tail has been shown [5, 6] to explain the structural properties of liquid alloys satisfactorily. The result of the treatment is here applied to the Pb–Bi melt to obtain the Ashcroft Langreth partial structure factors $S_{ij}(q)$. The $S_{ij}(q)$'s are in turn used to compute the Bhatia–Thornton partial structure factors and these form the basis for calculations relating to ordering in the molten alloy being studied.

The layout of the present paper is thus as follows, in the next section, we summarize the necessary equations for our calculations. Section 3 deals with our discussion on the structure of the alloy while in section 4, we discuss the nature of ordering in the system. In section 5, we conclude with a summary of the important deductions made.

2 THEORETICAL FORMULATIONS

To obtain the partial structure factor $S_{ij}(q)$ of a system of liquid alloys, the Fourier transform of the direct correlation function is required. We define the direct correlation functions in the usual form appropriate for a hard sphere system with a wall [7, 8]:

$$C_{ij}(\mathrm{r}) = \begin{cases} C_{ij}^{hs}(r), & 0 \leqslant r < \sigma_{ij} \\ -\beta\varepsilon_{ij}, & \sigma_{ij} \leqslant r \leqslant A_{ij}\sigma_{ij} \\ 0, & r > A_{ij}\sigma_{ij} \end{cases} \tag{1}$$

where $\beta = \frac{1}{K_B T}$ and C_{ij}^{hs} is the Percus–Yevick [9] solution for the hard spheres. $\sigma_{ij}, \varepsilon_{ij}$ and A_{ij}, represent the hard sphere diameters, depth and breadth of the square well respectively.

The Fourier transform $C_{ij}(q)$ of the direct correlation function $C_{ij}(r)$ can be found in the literature [10, 11]. The partial structure factors are obtained from the $C_{ij}(q)$ [12] as

$$S_{11}(q) = [1 - \rho_{11}C_{11}(q) - \rho_{11}\rho_{22}C_{12}^2(q)/(1 - \rho_{22}C_{22}(q))]^{-1} \tag{2}$$

$$S_{22}(q) = [1 - \rho_{22}C_{22}(q) - \rho_{11}\rho_{22}C_{12}^2(q)/(1 - \rho_{11}C_{11}(q))]^{-1} \tag{3}$$

$$S_{12}(q) = \frac{(\rho_{11}\rho_{22})^{1/2}C_{12}(q)}{[(1 - \rho_{11}C_{11}(q))(1 - \rho_{22}C_{22}(q)) - \rho_{11}\rho_{22}C_{12}^2(q)]} \tag{4}$$

where the ρ_{ii} represent the number density of the ith component. The total structure factor $S(q)$ is related to the partial structure factors by the relation

$$S(q) = \sum_{j=1}^{2}\sum_{i=1}^{2}(c_i c_j)^{\frac{1}{2}}\frac{f_i(q) f_i(q)}{c_1 f_1(q) + c_2 f_2(q)} S_{ij}(q) \tag{5}$$

where $f_i(q)$ and $f_j(q)$ are the atomic scattering factors of the ith and jth component respectively. c_i and c_j are the atomic fractions of comp onents i and j respectively. The Bhatia–Thorntom partial structure factors are related to the $S_{ij}(q)$'s by the relationship [13]

$$S_{NN}(q) = c_1 S_{11}(q) + c_2 S_{22}(q) + 2\sqrt{c_1 c_2}S_{12}(q) \tag{6}$$

$$S_{CC}(q) = c_1 c_2[c_2 S_{11}(q) + c_1 S_{22}(q) - 2\sqrt{c_1 c_2}S_{12}(q)] \tag{7}$$

$$S_{NN}(q) = c_1 c_2\left[S_{11}(q) - S_{22}(q) + S_{12}(q)\frac{c_2 - c_1}{\sqrt{c_1 c_2}}\right] \tag{8}$$

where c_1 and c_2 are the atomic fractions of the components 1 and 2 respectively. An understanding of the nature of alloy formation in the molten state depends on the knowledge of the concentration–concentration fluctuation in the long wavelength limit $S_{CC}(0)$. This can be obtained via the long wavelength limit of the partial structure factors $S_{11}(0)$, $S_{22}(0)$ and $S_{12}(0)$, which in turn depends on the $q \to 0$ limit of the $S_{ij}(q)$'s, i.e.

$$S_{CC}(0) = c_1 c_2 [c_2 S_{11}(0) + c_1 S_{22}(0) - 2(c_1 c_2)^{\frac{1}{2}} S_{12}(0)] \tag{9}$$

The long wavelength limit of the direct correlation function, can be expressed [10, 11] as:

$$C_{ij}(0) = C_{ij}^{HS}(0) + C_{ij}^{w}(0) \tag{10}$$

where

$$C_{ij}^{HS}(0) = \frac{\pi}{3}[-4a_i \lambda_{ij}^3 + 6f_{ij}(\lambda_{ij}^2 - \sigma_{ij}^2) + 4a_{ij}(\lambda_{ij}^3 - \sigma_{ij}^3)$$

$$+ b_{ij}(\lambda_{ij}^4 - \sigma_{ij}^4) + 10d(\sigma_{ij}^6 - \lambda_{ij}^6)] \tag{11}$$

and

$$C_{ij}^{W}(0) = \frac{4\pi\varepsilon_{ij}\sigma_{ij}^3}{3K_B T}[1 - A_{ij}^3] \tag{12}$$

The constants $a_{ii}, f_{ii}, b_{ii}, d$ and their cross terms are complex functions of the packing density of the i and j components and they can be obtained from the literature [10, 11].

The Warren–Cowley short range order parameter (α_1) [14, 15] gives a measure of the tendency to compound formation or phase separation in molten alloys. It is also considered [16] as an important indicator of the degree of ordering in a binary alloy.

With the knowledge of $S_{CC}(0)$, α_1 can be easily evaluated from the expression by Singh *et al.* [17]:

$$\alpha_1 = \frac{(S-1)}{S(Z-1)+1}, \tag{13}$$

where

$$S = \frac{S_{CC}(0)}{c(1-c)}, \tag{14}$$

Z is the coordination number of the alloy, and c the atomic fractions of one of the components of the alloy.

For equiatomic composition ($c=\frac{1}{2}$), one has $-1 \leqslant \alpha_1 \leqslant 1$. The minimum possible value of α_1 i.e. $\alpha_1^{min} = -1$ represents the complete ordering of pairs of nearest neighbour atoms in the A–B configuration whereas $\alpha_1^{max} = +1$ suggests segregation leading to the formation of A–A pairs or B–B pairs in the alloy. $\alpha_1 = 0$ corresponds to a random distribution.

Finally, it is possible to investigate the nature of chemical diffusion in liquid alloys with the knowledge of the $S_{CC}(0)$ recently suggested by Singh and Sommer [18]. From the Darken's thermodynamic equation for diffusion [16, 19, 20], we obtain

$$D = \frac{D_m}{D_s} = \frac{c(1-c)}{S_{CC}(0)} \tag{15}$$

where D_m is the mutual diffusion coefficient and D_s is given by

$$D_s = cD_i + (1-c)D_j \tag{16}$$

where D_i and D_j are the self-diffusion coefficients of the ith and jth components.

3 DISCUSSION ON STRUCTURE OF Pb-Bi ALLOYS

The calculations for the Pb–Bi melt have been carried out for six different concentrations. Figure 1 shows a comparison of fitted and experimental data (from Ref. 4) for the total structure factors for three different concentrations. The figure indicates good agreement with

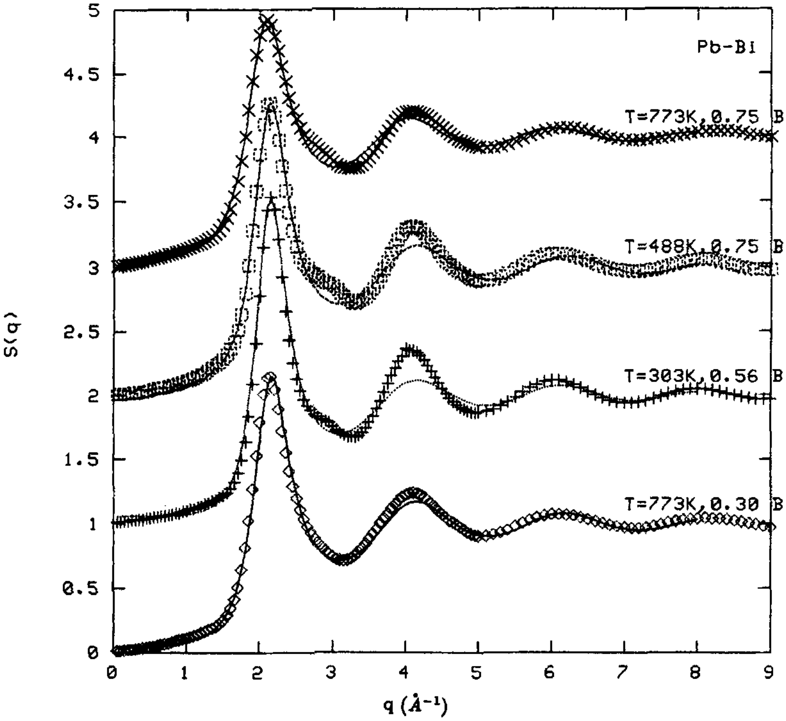

FIGURE 1 Fitted and experimental values of $S(q)$ vs. $q(\text{Å}^{-1})$ for Pb–Bi at concentrations and temperatures indicated on the graphs.

experiment for most concentrations. At concentrations close to equiatomic composition, a kink is observed in the experimental $S(q)$, this feature is however, not reproducible by our calculations. This seems to signal that the underlying theory used here is more suitable for alloys of simple metals. Bismuth, we note is not a simple metal and experimentally it exhibits a small hump in the main peak of its structure factor [21].

The parameters used to fit the potentials are given in Table I. Here, the slight variations in the potential parameters is suggestive of compound formation albeit of a low degree when compared with the situation for Cu–Bi [5] melts where almost all potential parameters are concentration dependent.

The partial structure factor $S_{11}(q)$ are shown in Figure 2. At 0.95 atomic fraction of Bi, the principal peak height which is low is characterized by a shoulder to the left of the peaks. This shoulder reduces due to the

TABLE I Input Parameters used in the evaluation of the partial structure factors for Pb–Bi liquid alloys

TEMP (*K*)	*CONC.* %*Bi*	σ_{11} Å	σ_{22} Å	ε_{11}/K_B (*K*)	ε_{22}/K_B (*K*)	A_{11}	A_{12}
503	0.30	2.74	3.12	40.65	43.15	2.22	2.29
773	0.30	2.74	3.12	40.65	43.15	2.22	2.29
303	0.56	2.66	3.22	40.65	43.15	2.22	2.29
773	0.56	2.45	3.49	40.65	43.15	2.22	2.29
488	0.75	2.76	3.08	40.65	43.15	2.22	2.29
773	0.75	2.64	3.18	30.65	33.15	2.22	2.29

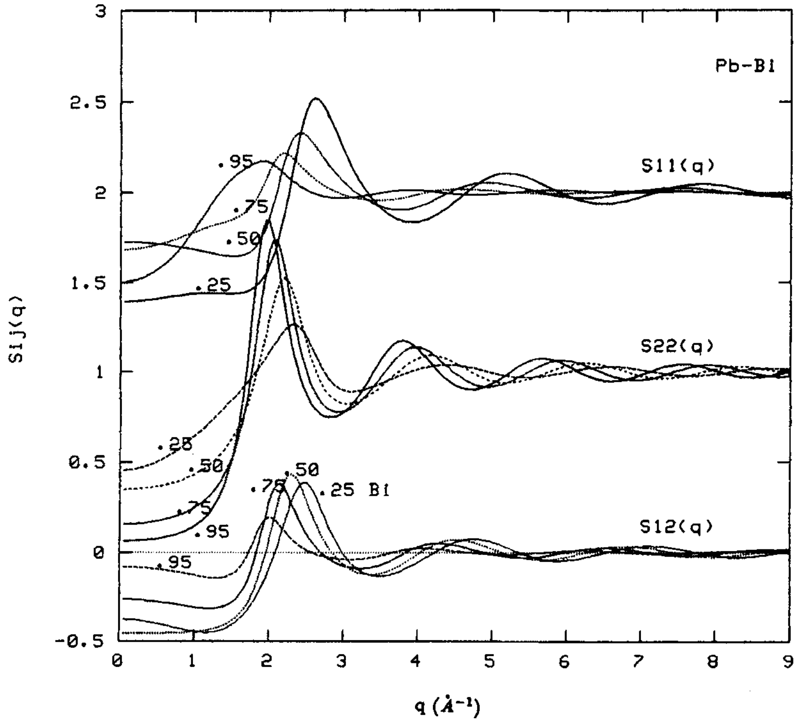

FIGURE 2 Ashcroft- Langreth partial structure factors $S_{ij}(q)$ vs. q(Å^{-1}) for Pb–Bi alloy at Bi concentrations indicated on graphs.

precipitation of a small pre-peak at low atomic fraction of Bi. This indicates some form of ordering at low concentrations of Bi. One is of the opinion that the presence of the Bi affects the Pb in the molten alloys giving rise to a pre-peak.

For $S_{22}(q)$, the principal peak increases with increase in the concentration of the bismuth atoms. At low Bi concentrations, there is a marked departure from a symmetric nature in the principal peaks. At higher concentrations of Bi, the molten alloy tends to exhibit properties which can be associated with a regular alloy. In the case of $S_{12}(q)$, the maximum peak occurs at the equiatomic composition. This noticeable effect is more pronounced in Mg–Bi [7] and Cu–Bi [5] systems. The authors of these papers attribute the behaviour to the segregating nature of bismuth. However, since, the elements Pb and Bi are chemically inert, segregation to either Bi–Bi or Pb–Pb atoms are not very likely. Neumann *et al.* [4] suggested that the assumption of an A–B form of ordering for Pb–Bi systems could be used to explain the observations.

The $S_{NN}(q)$ curves is shown in Figure 3. At high concentrations of Bi (0.95 at. frac. Bi), a large shoulder prior to the peak was observed as in Cu–Bi [5]. It is also observed that $S_{CC}(q)$ lies between zero and c_1c_2. $S_{NC}(q)$ tends to zero at large q. In addition, there is a non uniform behaviour of $S_{NC}(q)$ at low q and a broadening of peaks and sharper negative peaks are observed for high atomic concentration of Bi.

One observes that the structure factors of Pb–Bi are significantly temperature dependent. Temperature changes do not affect their general structure but have considerable effect on the magnitude. The partial structure factors taken at temperatures of 500, 700 and 900 K show the typical feature of decrease in the magnitude of the peak with increase in temperature.

4 ORDERING IN Pb-Bi ALLOYS

From discussions given in the section above, it is apparent that there is a need to investigate using some techniques, the nature of ordering in the molten Pb–Bi alloys. This is the main subject in this part of the paper.

The procedure and equations for determining $S_{CC}(0)$ from the total structure factors have been enumerated in section 3. Figure 5 shows a comparison of computed $S_{CC}(0)$ and the ideal values. To interprete this graph, we note that ordering in liquid alloys can be measured from the departure of $S_{CC}(0)$ from the ideal value given by $S_{CC}^{id}(0) = c(1-c)$.

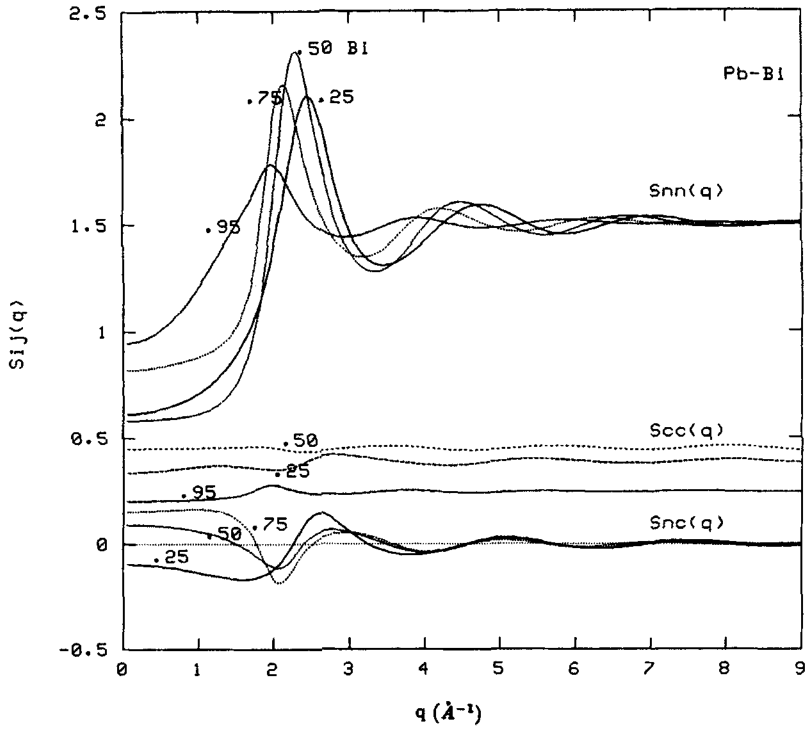

FIGURE 3 Bhatia- Thornton partial structure factors vs. q (Å^{-1}) for Pb–Bi molten alloy. $S_{CC}(q)$ is pushed up by 0.2 units and $S_{NN}(q)$ by 0.5, all on $S_{ij}(q)$ axis.

Basically $S_{CC}(0) < S_{CC}^{id}(0)$ is an indication of heterocoordination (preference of unlike atoms to pair as nearest neighbours) while $S_{CC}(0) > S_{CC}^{id}(0)$ implies a tendency for homocoordination (preference for like atoms to pair as nearest neighbours) also called phase separation. The position of the $S_{CC}(0)$ versus c curve yields information on the nature of the complex while its depth signifies strength.

Experimental values of $S_{CC}(0)$ are not available to guide our deductions, so our discussions here would be based on calculations. On comparing $S_{CC}(0)$ for Pb–Bi with experiment, it is obvious that the Pb–Bi system exhibits compound forming tendencies. In order to give some quantitative discussion on the magnitude of compound formation we have computed the Warren–Cowley short range order parameter α_1. This is shown in Figure 5. The computed values of α_1 are quite illuminating, its negative throughout the concentration curve

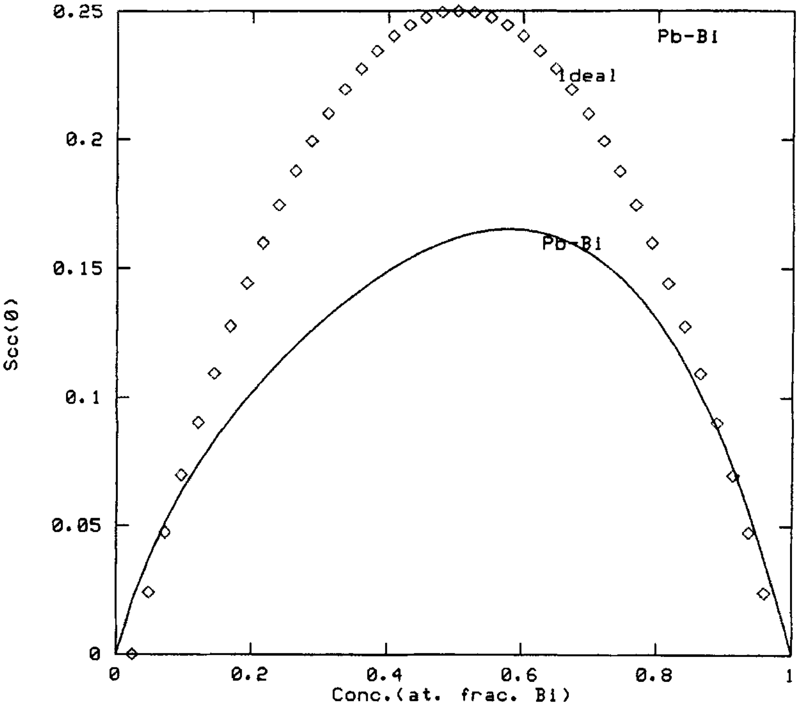

FIGURE 4 $S_{CC}(0)$ vs. concentration for Pb–Bi alloy.

but quite low $|\alpha_1^{min}| \approx 0.05$. This value is far from -1 which is the minimum value that could suggest strong compound formation. However, the value is close to zero which is the value of α_1 for a random distribution of constituents of the alloy. These values of α_1 suggests that the Pb–Bi molten alloy manifests very low compound forming tendencies. It could be inferred from the calculation that Pb–Bi molten alloy is close to an ideal alloy.

For the calculation of α_1 there is a relatively unknown quantity, the coordination number for which we have used the value $Z = 12$. The ratio of the mutual and self diffusion coefficients D also yield information similar to that of α_1 but without the uncertainty in Z. Essentially, one can show [16] that for ideal mixing $D \rightarrow 1$, for compound formation $D > 1$ and $D < 1$ corresponds to segregation. Features exhibited in the calculated values of D in Figure 5 are similar to those for α_1 thus, we feel in a better position to make some remarks.

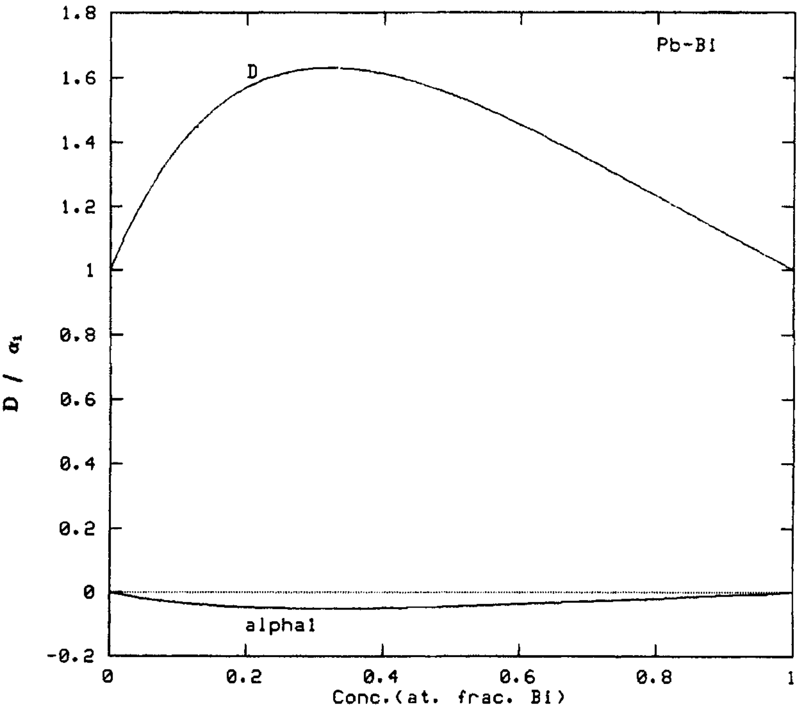

FIGURE 5 α_1 and the diffusion coefficient D against concentration for Pb–Bi molten alloy.

A linearity in the dependence of α_1 on concentration is observed between 0.62 and 1.00 atomic. frac. of Bi. It is perhaps coincidental that Sharrah and Petz [2] observed a decrease in coordination number of Pb–Bi liquid alloy near 0.6 at.frac. of Bi, from its value of 12 at other concentrations, in addition to their suggestion of a minimum viscosity near the composition. The above suggestion may be attributed to the level of compound forming tendency around these composition. The observations on the other hand suggests a high sensitivity of properties of Pb–Bi alloys to small changes in chemical compositions.

Significantly also, the maximum departure from linearity in the concentration dependence of liquid alloy volumes were observed [2] to occur between 0.2 and 0.3 at. frac. Bi. It may be inferred that some relatively higher level of ordering and compound formation occur in this region of concentration. These activities may be partially responsible for the anomalies previously observed in the aforementioned region.

5. CONCLUSIONS

The solutions of the Percus-Yevick equation with a square well attractive tail have been used to study the structure of Pb–Bi systems. The calculated results are in good agreement with experiment.

The calculated partial structure factors in the long wavelength limit were used to determine $S_{CC}(0)$, this was in turn used to study the nature of ordering in the molten Pb–Bi alloys. We note that though the concentration–concentration fluctuations in the long wavelength limit $S_{CC}(0)$ are lower than the ideal values at all concentrations, it does not exhibit a distinctive minimum at any stoichometric composition, this indicates that the formation of any complex in the alloy if it exists is of a weak nature in the liquid phase. $S_{CC}(0) < S^{id}_{CC}(0)$ throughout indicates that heterocoordination persists at all concentrations.

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References

[1] Kleppa, O. J., Kaplan, M. and Thalmayer, C. E. (1961). *J. Phys. Chem.*, **65**, 843.
[2] Sharrah, P. C. and Petz, J. T. (1960). *J. Chem. Phys.*, **32**, 241.
[3] Kubaschewski, O. and Cathedral, J. A. (1956). *Metal Physics and Physical Metallurgy*, **3**, 124 Pergamon Press, London.
[4] Neumann, H., Huiz, W. and Hoyer, W. (1995). *Phys. Chem. Liq.*, **29**, 211.
[5] Gopala Rao, R. V. and Satpathy, A. (1990). *Phys. Rev.*, **41**, 995.
[6] Gopala Rao, R. V. and Murty, A. K. K. (1975). *Z. Naturfosch*, **30A**, 383.
[7] Gopala Rao, R. V. and Das, R. (1987). *Phys. Rev.*, **36**, 6325.
[8] Silbert, M. and Young, W. H. (1976). *Phys. Lett.*, **58A**, 469.
[9] Hiroike, K. (1969). *J. Phys. Soc. Japan*, **27**, 1415.
[10] Gopala Rao, R. V. and Gupta, B. D. (1985). *Phys. Rev.*, **32**, 6429.
[11] Saadeddine, S., Wax, F., Grosdidier, B., Gasser, J. G., Regnaut, C. and Dubois, J. M. (1994). *Phys. Chem. Liq.*, **28**, 221.
[12] Kirkwood, J. G. and Buff, P. (1951). *J. Chem. Phys.*, **19**, 774.
[13] Bhatia, A. B. and Thornton, D. E. (1970). *Phys. Rev.*, **B2**, 3004.
[14] Warren, B. E. (1969). *X-Ray Diffraction, Addison Wesley, Reading: MA.*
[15] Cowley, J. M. (1950). *Phys. Rev.*, **77**, 669.

[16] Akinlade, O. and Bardikhan, Z. (1994). *Physica*, **B203**, 1.
[17] Singh, R. N., Panday, D. K., Sinha, S., Mitra, N. R. and Srivastava, P. L. (1987). *Physica*, **B145**, 358.
[18] Singh, R. N. and Sommer, F. (1992). *J. Phys. Cond. Matt.*, **4**, 5345.
[19] Singh, R. N. and Sommer, F. (1992). *Z. Metalkd*, **83**, 533.
[20] Darken, L. S. (1948). *Trans. Metall. Soc.*, AIME, **175**, 184.
[21] Lida, T. and Cuthrie, R. I. L. (1993). *The Physical Properties of Liquid metals*, Oxford: U. K.