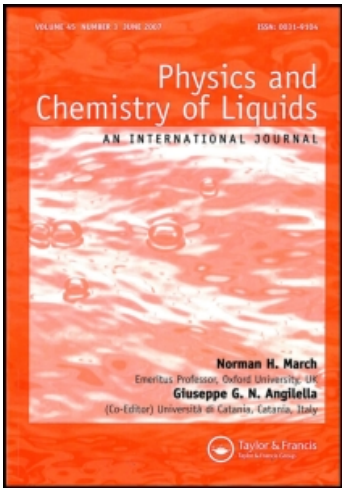

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Structural Study of Liquid Na-Pb Alloys by Hard-Sphere Model

S. Matsunaga[a]; S. Tamaki[b]; S. Takeda[c]
[a] Mitsuke High School, Niigata Prefecture, Japan [b] Department of Physics, Niigata University, Niigata, Japan [c] Department of Physics, Kyusyu University, Fukuoka, Japan

To cite this Article Matsunaga, S. , Tamaki, S. and Takeda, S.(1999) 'Structural Study of Liquid Na-Pb Alloys by Hard-Sphere Model', Physics and Chemistry of Liquids, 37: 4, 395 — 408
To link to this Article: DOI: 10.1080/00319109908031444
URL: http://dx.doi.org/10.1080/00319109908031444

Phys. Chem. Liq., 1999, Vol. 37, pp. 395–408
Reprints available directly from the publisher
Photocopying permitted by license only

STRUCTURAL STUDY OF LIQUID Na–Pb ALLOYS BY HARD-SPHERE MODEL

S. MATSUNAGA [a], S. TAMAKI [b,*] and S. TAKEDA [c]

[a] *Mitsuke High School, Niigata Prefecture, 954-01, Japan;*
[b] *Department of Physics, Niigata University, Niigata, 950-21, Japan;*
[c] *Department of Physics, Kyusyu University, Fukuoka, 812-81, Japan*

(Received 20 November 1997)

Faber–Ziman type partial structure factors in liquid Na–Pb alloys have been derived by using the so-called concentration independent method from the observed total structure factors. A ternary hard-sphere mixture model composed of atoms Na and Pb and Na_4Pb molecule is applied to this system.

It is shown that the estimated partial structure factors under the assumption of the mixture of hard spheres are in good agreement with the observed ones.

Keywords: Partial structure factor; ternary hard-sphere model

1. INTRODUCTION

In recent years, the so-called compound-forming liquid binary alloys or liquid semiconductors have extensively been studied [1]. The liquid alkali-polyvalent metal alloys such as the Na–Pb system are well known as typical examples. Observed thermodynamic quantities [2] and electronic properties such as resistivity [3, 4] and magnetic susceptibility [5] of Na–Pb alloys show an interesting behaviour suggesting the formation of a compound in their liquid states. Their concentration dependences have a maximum deviation from smoothed curves around the stoichiometric composition Na_4Pb.

Structural study of this system by neutron diffraction has been carried out by Takeda *et al.* [6]. In the Na-rich region, an additional

*Corresponding author.

small prepeak has been clearly observed in the low Q region at the left hand side of the main peak in the structure factors. This fact also seems to imply the formation of a local atomic association like a molecular cluster such as Na_4Pb in this alloy system [7]. The theoretical approach via the ternary hard-sphere mixture proposed by Hoshino [8] may be applicable to the present system.

The purpose of this paper is to derive the partial structure factors of liquid Na–Pb alloys by the concentration independent method from experimental total structure factors obtained by Takeda *et al.* [6].

And also the model of a ternary hard-sphere mixture is applied to this system in deriving the partial structure factors, the system being considered as a mixture of Na, Pb and Na_4Pb.

2. PARTIAL STRUCTURE FACTORS

Total structure factors $S(Q)$ experimentally obtained by Takeda *et al.*, are shown in Figure 1 together with that of pure Na, taken from the compilation of Waseda [9]. To begin with, we have re-examined the total pair distribution function $g(r)$, which can be written in the following equation:

$$g(r) = 1 + \frac{1}{2\Pi^2 r \rho_0} \int_0^\infty [S(Q) - 1] Q \sin(Qr) dQ \qquad (1)$$

where ρ_0 is the averaged number density of atoms, which is taken from the experimental data [12, 13].

As shown in Figure 2, the obtained $g(r)$'s are in good agreement with previous results [6]. Their structural profiles are similar to that of pure Pb, although some fine structures can be seen.

In order to facilitate the understanding of the particular structural behaviour, the usual concentration technique as the so-called Halder–Wagner's scheme [10] was used to derive the Faber–Ziman (F–Z) type [11] partial functions $a_{ij}(Q)$ and the partial pair distribution function $g_{ij}(r)$ to characterize a mixing effect.

The F–Z type partial structure factors $a_{ij}(Q)$ are related to the total weighting structure factor, $S(Q)$, as follows;

$$S(Q) = w_{11} a_{11}(Q) + 2w_{12} a_{12}(Q) + w_{22} a_{22}(Q) \qquad (2)$$

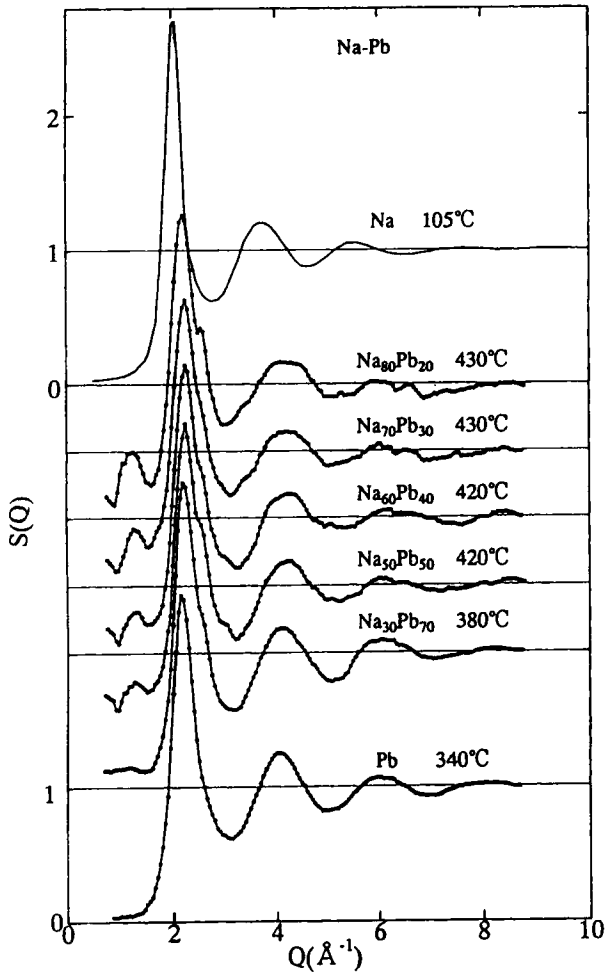

FIGURE 1 Structure factors of liquid Na–Pb alloys due to Takede *et al.* (1987), together with that of pure Na taken from Waseda (1980).

where $w_{ij} = c_i c_j b_i b_j / \langle b \rangle^2$ and $\langle b \rangle^2 = (\Sigma c_i b_i)^2$; c_i and b_i are the concentration and neutron coherent amplitude of atomic species i, respectively. The F–Z type partial structure factor is given by a generalized equation as follows;

$$a_{ij}(Q) = 1 + \rho_0 \int_0^\infty 4\Pi r^2 \left[g_{ij}(r) - 1 \right] \frac{\sin(Qr)}{Qr} \, dr \qquad (3)$$

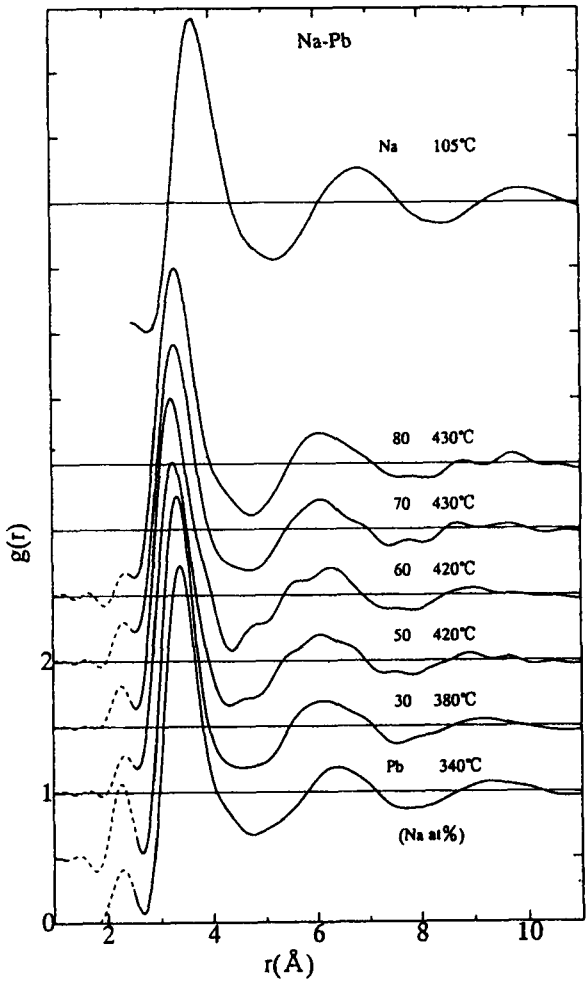

FIGURE 2 Pair distribution functions of liquid Na–Pb alloys.

The partial structure factors, in principle, depend on the alloy composition. However, the change of the total structure factors of liquid alloys is frequently gradual and monotonic in a certain composition range.

In such a case, the concentration dependence of the partial structure factors seems to be small and thus the above assumption could be acceptable as a first approximation. The alloys with 50, 60 and 70 at.%

Na might represent this situation. Assuming that the partial structure factors are independent of alloy composition, the weighting factor in Eq. (2) can be varied by only changing the concentration c. So we can immediately get three partial structure factors.

As mentioned previously [6], the maximum error in the total structure factor was suggested to be less than 2.0% and then the possible uncertainty of the present three partial structure factor is estimated to be of the order of 5%.

The partial structure factors thus obtained are given in Figure 3. The partial pair distribution functions $g_{ij}(r)$ are calculated by Fourier transformation in the manner of Eq. (3) and results are shown in Figure 4. The structural functions of liquid Na and Pb are also illustrated in Figures 3 and 4 for comparison.

As shown in Figure 3, the basic profile of the partial structure factor of $a_{\mathrm{PbPb}}(Q)$ is close to that of pure Pb.

However, peaks of $a_{\mathrm{NaNa}}(Q)$ are located at larger Q position than those of pure Na. As shown in Figure 4, the basic profile of the partial pair distribution function of $g_{\mathrm{PbPb}}(r)$ is very similar to that of pure Pb.

On the other hand, the peaks of $g_{\mathrm{NaNa}}(r)$ are obserbed at smaller r position than those of pure Na. In addition, the first peak position of $g_{\mathrm{NaPb}}(r)$ is located at a distance about 2.9 Å, that is, its position is smaller than those of $g_{\mathrm{NaNa}}(r)$ and $g_{\mathrm{PbPb}}(r)$, of which are located at about 3.3 Å and 3.4 Å, respectively.

3. ANALYSIS BASED ON THE TERNARY HARD-SPHERE MIXTURE MODEL

The results of the observed thermodynamic and electronic properties of this system strongly suggest a certain chemical short-range order at the composition of Na_4Pb [2–5]. Assuming that liquid Na–Pb alloys are a ternary mixture composed of the atomic association of Na_4Pb and its dissociated atoms of Na and Pb, Takeda *et al.* [6] have obtained a preliminary result for the concentration dependence of the structure factors of this sytem by using the hard-sphere mixture model provided by Hoshino [8]. The total structure factors they obtained qualitatively agree with the experimental results. In this paper we have carried out calculations of the partial structure factors of Na–Pb alloys in detail

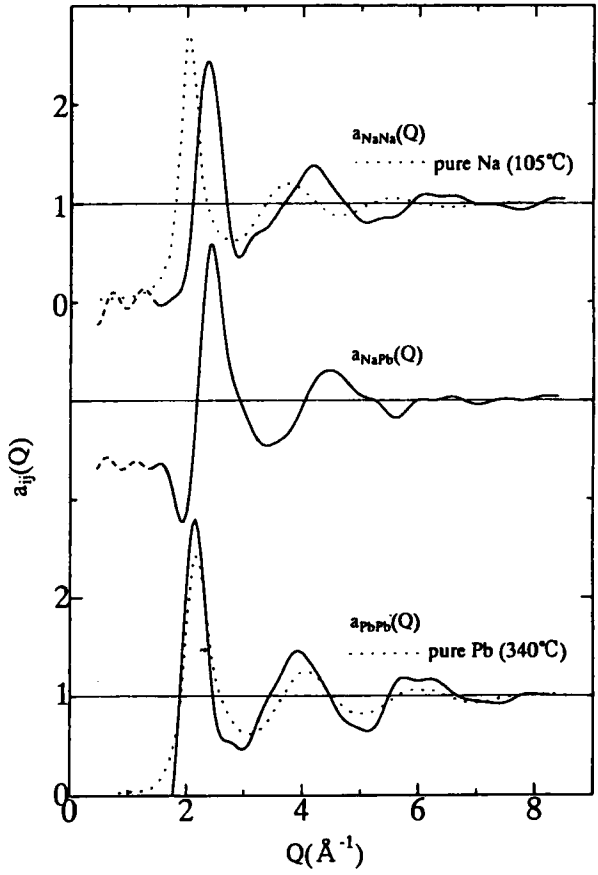

FIGURE 3 F–Z type partial structure factors of liquid Na–Pb alloys. Experimental results (full line); Total structure factors of pure Na and Pb (dotted line).

and have re-estimated them by using the ternary hard-sphere mixture model.

According to the ternary hard-sphere mixture model, the total structure factor can be expressed by the following equation;

$$\begin{aligned} S(Q) = [\, & x_1 b_1^2 S_{11}(Q) + x_2 b_2^2 S_{22}(Q) \\ & + x_3[\langle b_3 \rangle^2 (S_{33}(Q) - 1) + \langle b_3(Q)^2 \rangle] \\ & + 2\sqrt{x_1 x_2}\, b_1 b_2 S_{12}(Q) + 2\sqrt{x_1 x_3}\, b_1 \langle b_3(Q) \rangle S_{13}(Q) \\ & + 2\sqrt{x_2 x_3}\, b_2 \langle b_3(Q) \rangle S_{23}(Q)] / \langle b^2 \rangle \end{aligned} \tag{4}$$

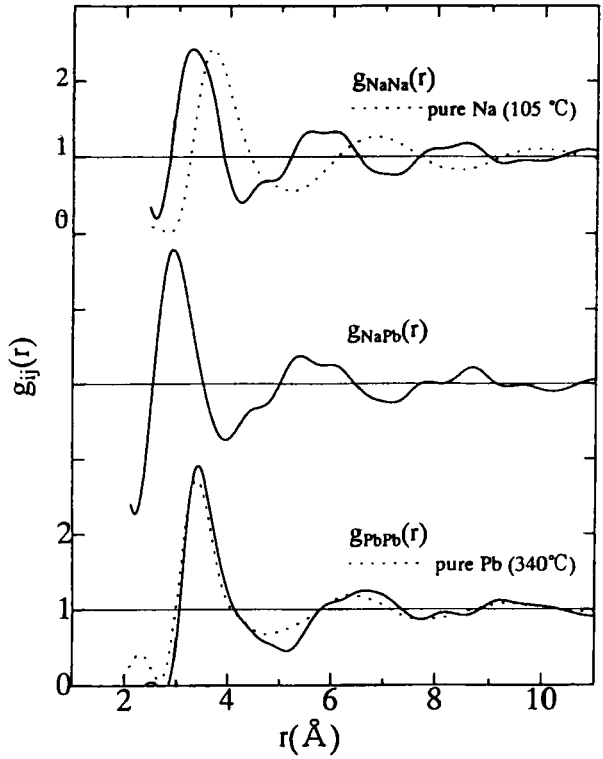

FIGURE 4 F–Z type partial pair distribution functions of liquid Na–Pb alloys. Experimental results (full line); Total distribution functions of pure Na and Pb (dotted line).

where $S_{ij}(Q)$ ($i, j = 1$, 2 and 3) are the so-called Ashcroft–Langreth (A–L) type [14] partial structure factors (1; Na, 2; Pb and 3; Na_4Pb) defined as follows;

$$S_{ij}(Q) = \delta_{ij} + (c_i c_j)^{1/2} \rho_0 \int [g_{ij}(r) - 1] \exp(-i\vec{Q} \cdot \vec{r})\, d\vec{r} \qquad (5)$$

and;

$$\langle b_3(Q) \rangle = \left\langle b_1 \sum_{j=1}^{4} \exp(i\vec{Q} \cdot \vec{l}_j) + b_2 \right\rangle = 4b_1 \frac{\sin(Ql_0)}{Ql_0} + b_2 \qquad (6)$$

$$\langle b_3(Q)^2 \rangle = \left\langle \left| b_1 \sum_{j=1}^{4} \exp(i\vec{Q} \cdot \vec{l}_j) + b_2 \right|^2 \right\rangle$$
$$= b_1^2 \left(4 + 12 \frac{\sin(Ql_1)}{Ql_1}\right) + b_2^2 + 8b_1 b_2 \frac{\sin(Ql_0)}{Ql_0} \quad (7)$$

and l_0 and l_1 are the distance between Na and Pb, and that between Na and Na in the 'molecule' respectively, where $l_1 = \sqrt{8/3}\, l_0$ for a geometry of the tetrahedral unit structure. The angular bracket $\langle\,\rangle$ indicates the angle average and $\langle b^2 \rangle$ is equal to the following formula;

$$\langle b^2 \rangle \equiv x_1 b_1^2 + x_2 b_2^2 + x_3 (4b_1^2 + b_2^2)$$
$$= (c_1 b_1^2 + c_2 b_2^2)/n \quad (8)$$

$$x_i = n_i/n \quad (9)$$

Here, the relations of $n_1 = c_1 - 4n_3$, $n_2 = c_2 - n_3$, and $n = 1 - 4n_3$ are used, where c_1, c_2 are the nominal concentration of Na and Pb, respectively. The orientational correlation among Na_4Pb, Na and Pb are neglected in this model, since the molecule of Na_4Pb is assumed to be a hard sphere with an effective size of Na_4Pb, σ_{Na_4Pb}.

Each fraction of Na, Pb and Na_4Pb were determined from the thermodynamical analysis of this liquid system [2]. The hard-sphere diameters were chosen so as to reproduce the first and second peak of the experimentally obtained total structure factors and F–Z type partial structure factors. A slightly large value of the packing fraction in alloys, compared to the usual value of 0.45, was employed here and it is rather realistic with respect to a considerable volume contraction in liquid Na–Pb alloys [12, 13]. These hard sphere diameters, the packing fractions and each fraction employed here are listed in Table I, where we have made a slightly change for the parameters in comparison with those in the previous work in order to reproduce the F–Z type partial structure factors.

The conversion from A–L type to F–Z type partial structure factors is straightforward using following relations [9];

$$a_{11}(Q) = [S_{11}(Q) - c_2]/c_1 \quad (10)$$

TABLE I Several parameters of hard sphere diameters, σ_i's, packing fractions, η_i's, and each fractions, x_i's, in liquid Na–Pb alloys

	σ_{Na}	σ_{Pb}	σ_{Na_4Pb}	η	X_{Na}	X_{Pb}	X_{Na_4Pb}
$Na_{80}Pb_{20}$	3.1	3.26	5.25	0.508	0.762	0.190	0.048
$Na_{70}Pb_{30}$	3.03	3.19	5.2	0.511	0.645	0.309	0.046
$Na_{60}Pb_{40}$	3.0	3.17	5.2	0.521	0.526	0.428	0.046
$Na_{50}Pb_{50}$	3.0	3.17	5.15	0.520	0.44	0.530	0.030
$Na_{30}Pb_{70}$	2.98	3.17	5.15	0.498	0.255	0.729	0.016

$$a_{22}(Q) = [S_{22}(Q) - c_1]/c_2 \tag{11}$$

$$a_{12}(Q) = S_{12}(Q)(c_1 c_2)^{1/2} + 1 \tag{12}$$

Figures 5 and 6 show the comparison of the calculated total and F–Z type partial structure factors with the observed ones, respectively.

4. RESULTS AND DISCUSSION

The overall agreement between calculation and experiment in the structure factors in the first and second peak region can be recognized as shown in Figures 5 and 6. The oscillating profiles of $S(Q)$ in the large Q region are also in phase with the observed ones, although the prepeak, which may be a kind of characteristic feature for compound formation [7], is not reproduced. The simple hard-sphere mixture model is, however, basically adequate for this system, although fine differences can be seen.

Concentration variation of the estimated hard-sphere diameters of Na and Pb are also shown in Figure 7. The hard sphere diameter of Na atom in the alloys is smaller than that of Pb atom in the entire concentration range. This concentration dependence of hard sphere diameters in the Na rich region may be caused by a volume contraction. This tendency is in good agreement with the concentration dependence of the radii of Wigner–Seitz spheres of Na and Pb in this system [15].

The measured structure factors of liquid Na–Pb alloys have the prepeak around $Q = 1.25\,\text{Å}^{-1}$ for all alloy compositions. Misawa [16]

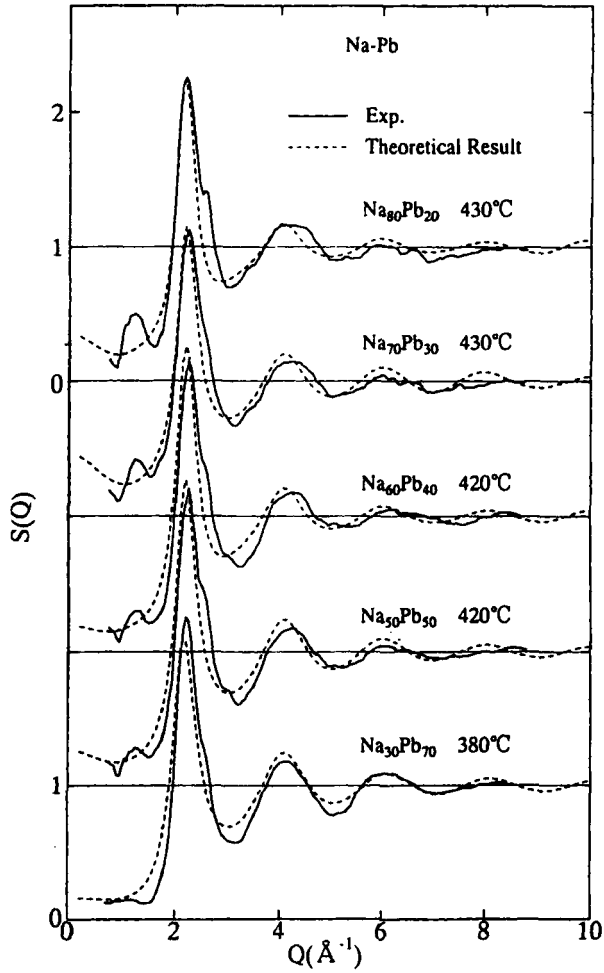

FIGURE 5 Several structure factors $S(Q)$. Experimental results (full lines); Theoretical results (broken lines).

has shown that the growth of small prepeak at the low Q region appears if the ratio of the intermolecular atomic spacing to the intramolecular atomic spacing becomes larger in forming tetrahedral and diatomic clusters or molecules. Now we assume that there exists a tetrahedral 'cluster' in alloys and try to estimate the ratio of the intertetrahedral spacing to the intratetrahedral spacing. Contribution

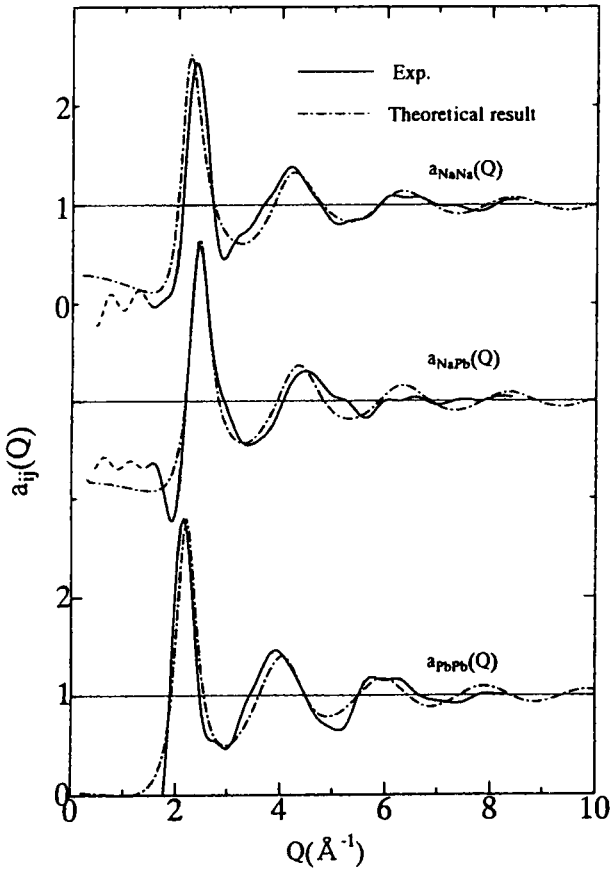

FIGURE 6 F-Z type partial structure factors. Experimental results (full lines); Theoretical results (dotted broken lines).

of prepeak of $S(Q)$ estimated from the result of Fourier transform at the low Q region to the total $g(r)$ at 80 at.% Na is shown in Figure 8. The first peak can be seen at about $r = 4.37$ Å. That is considered due to the intermolecular spacing. Schematic figure of the tetrahedral configuration is shown in Figure 9. If we assume the intramolecular spacing $l = 3.1$, the ratio ζ of the intermolecular spacing L to the intramolecular spacing l is 1.41.

Alblas *et al.* [7] have pointed out that in liquid Na-Sn alloys, intemediate correlation between Sn atoms' clusters is responsible for

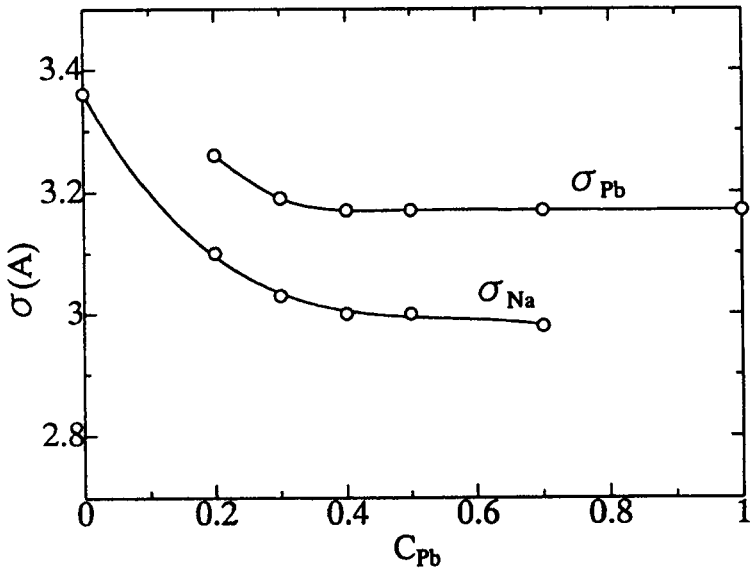

FIGURE 7 Concentration variations in the hard sphere diameter of Na and Pb.

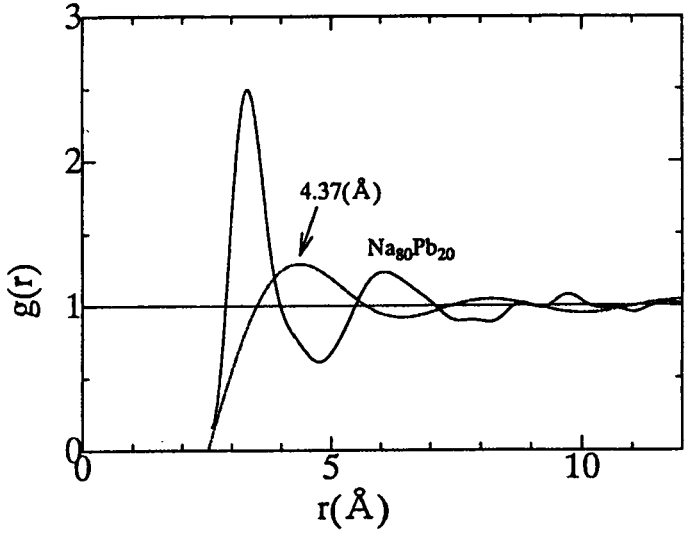

FIGURE 8 Contribution of prepeak of $S(Q)$ at low Q region to total $g(r)$ at 80 at.% Na.

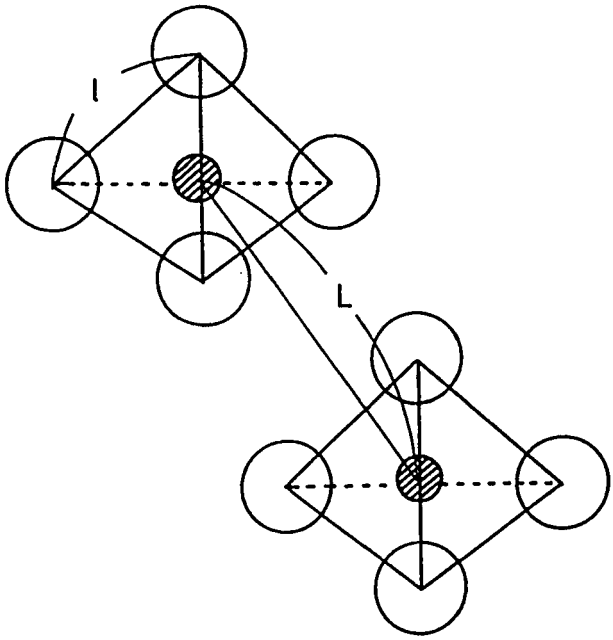

FIGURE 9 Schematic figure of the tetrahedral configuration. The ratio ζ of the intermolecular spacing L to the intramolecular spacing l are 1.41 for Na_4Pb.

prepeak in $S(Q)$ and have reproduce the position of the prepeak in the $S(Q)$ using the hard sphere model. In liquid Na–Pb system, this analysis may be useful, although we don't want to go into detail, because the structural information is still not enough to analyze further.

In conclusion, the partial structure factors of liquid Na–Pb alloys have been obtained by Halder–Wagner's scheme from the measured total structure factors. The theory based on the ternary mixture model, where Na, Pb, Na_4Pb are approximated by hard spheres, appears to reproduce the characteristic features of the experimental total and partial structure factors.

Acknowledgement

One of the authors (S. Matsunaga) would like to thank Mr. T. Koisi for useful discussions.

References

[1] See for example, Enderby, J. E. and Barnes, A. C. (1990). *Rep. Prog. Phys.*, **53**, 85.
[2] Matsunaga, S., Ishiguro, T. and Tamaki, S. (1983). *J. Phys. F (Met. Phys.)*, **13**, 587.
[3] van der Marel, C., van Oosten, A. B., Greertsma, W. and van der Lugt, W. (1982). *J. Phys. F (Met. Phys.)*, **12**, 2349.
[4] Matsunaga, S. and Tamaki, S. (1983). *J. Phys. Soc. Jpn.*, **52**,1725.
[5] Matsunaga, S., Takeda, S. and Tamaki, S. (1984). *J. Phys. Soc. Jpn.*, **53**, 4362.
[6] Takeda, S., Harada, S., Tamaki, S., Matsubara, E. and Waseda, Y. (1987). *J. Phys. Soc. Jpn.*, **56**, 3934.
[7] Alblas, B. P., van der Lugt, W., Dijkstra, J., Geertsma, W. and van Dijk, C. (1983). *J. Phys. F (Met. Phys.)*, **13**, 2465.
[8] Hoshino, K. (1983). *J. Phys. F (Met. Phys.)*, **13**, 1981.
[9] Waseda, Y., The Structure of Non-Crystalline Materials (McGraw-Hill, New York, 1980).
[10] Halder, N. C. and Wagner, C. N. (1967). *J. Chem. Phys.*, **47**, 4385.
[11] Faber, T. E. and Ziman, J. M. (1965). *Phil. Mag.*, **11**, 153.
[12] Hesson, J. C., Shimotake, H. and Tralmer, J. M. (1968). *J. Metals*, **20**, 6.
[13] McAlister, S. P. (1972). *Philos. Mag.*, **26**, 853.
[14] Ashcroft, N. W. and Langreth, D. C. (1967). *Phys. Rev.*, **159**, 500.
[15] Takeda, S. and Tamaki, S. (1986). *J. Phys. F (Met. Phys.)*, **16**, 285.
[16] Misawa, M. (1990). *J. Chem. Phys.*, **93**, 6774.