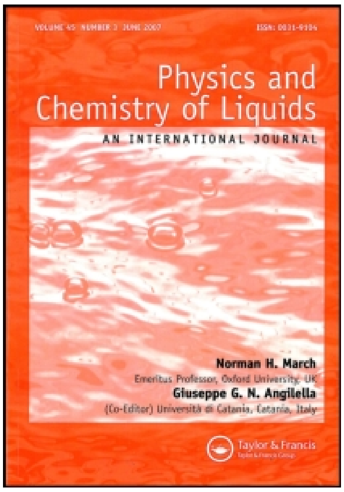

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Structure of Liquid Pb-Bi Alloys by X-ray Diffraction

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X-ray diffraction measurements were made at temperatures about 50°C above liquidus in the Pb-Bi system. Three partial structure factors $S_{ij}(Q)$ were evaluated from the observed X-ray intensities assuming that each $S_{ij}(Q)$ is independent on the relative abundance of the constituent elements in the alloys. The partial reduced distribution functions $G_{ij}(r)$ were also calculated. The functions $S_{ij}(Q)$ and $G_{ij}(r)$ have maxima which lie between those of the pure elements. The radii of the first coordination sphere show a linear dependence on the concentration as expected from random distribution of the atoms in liquid Pb-Bi alloys. A comparison was made between the partial and total structure factors obtained in this work and those calculated from the hard sphere model. Adequate agreement was obtained on the first peak, but good agreement of the damping behaviour and phase was not necessarily found.

1. INTRODUCTION

Studies of X-ray or neutron diffraction from liquid metals directly lead to information about atomic distribution by Fourier analysis. In the recent progress of the theory of liquid binary alloys, for example the theoretical consideration of the electron-transport properties, the importance of three partial distribution functions (i-i, j-j and i-j) of atoms has been emphasized.

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Some of the liquid binary systems[1-4] were investigated mainly from the point of view of interpreting their electron-transport properties.

In order to understand more detailed arrangements of atoms in liquid binary alloys, X-ray diffraction patterns of liquid Pb-Bi alloys with 20, 36, 56 and 80 at % Bi were measured at temperatures about 50°C above liquidus. The first reason for the choice of this alloy system was that the two components have similar scattering factors for X-rays. This is an important factor for the normalization of the X-ray scattering intensities observed. The second reason was to examine the contribution of the difference of crystal structures to the atomic arrangement for a liquid binary alloy. Furthermore Pb has a closed-packed (face centered cubic) structure whereas Bi has more loosely packed (rhombohedral) structure in the solid state and their atomic weight, atomic size and electronegativity are almost identical.

In addition, a comparison is made between the structure factors obtained from diffraction data and those calculated by the hard sphere model[5-7]. The results are discussed below.

2. EXPERIMENTAL PROCEDURES

The experimental arrangement used for the measurement of the scattered X-ray intensities from liquid metals is identical to the one described in our previous paper.[8] A few additional details are given below. The radiation was obtained from a Philips sealed-off molybdenum X-ray tube at 60 kV and 20 mA. Measurements were taken at intervals of 15′ over the angular range between 4° and 20° and at intervals of 30′ between 20° and 45°. This angular range corresponds to a range from Q_{min}=1.30 Å^{-1} to Q_{max}=12.0 Å^{-1}. The data reported here correspond to an average of three runs at each measurement.

The samples of the Pb-Bi alloys were prepared by melting appropriate amounts of Pb and Bi, both 99.9999 % purity, in an Ar-10% H_2 atomosphere in the high temperature apparatus. The liquid samples were held in a boron nitride (BN) crucible (30 x 20 mm^2) at 300°C above liquidus temperature for about 2 hours and then rapidly cooled to room temperature. The surface of solid samples was cleaned with emery paper and mirror finished on a metallographic polishing wheel. Such samples were re-melted to measure the scattered X-ray intensities. The sample temperature was measured by a Pt-Pt, Rh thermocouple with 0.3 mm diameter, which was inserted into the side hole of the BN crucible.

In order to convert the observed counts into electron units, the Krogh-Moe method[9], modified for an alloy, was used with the dispersion corrected scattering factors of Cromer.[10]

3. ANALYSIS OF INTENSITY PATTERNS

Using the method of Wagner and Halder[11], the total structure factor S(Q) can be defined in terms of the coherently scattered intensity $S_{eu}^{coh}(Q)$ per atom in electron units as follows;

$$S(Q) = [\, S_{eu}^{coh}(Q) - \langle f^2\rangle + \langle f\rangle^2 \,] \,/\, \langle f\rangle^2, \tag{1}$$

and

$$S_{eu}^{coh}(Q) = \langle f^2\rangle + \langle f\rangle^2 \int_0^\infty 4\pi r^2 \, [\rho(r) - \rho_0\,] \frac{\sin(Qr)}{Q\,r}\, dr, \tag{2}$$

where $\langle f^2\rangle = \sum_{i=1}^{2} c_i f_i^2$, $\langle f\rangle^2 = \sum_{i=1}^{2} (c_i f_i)^2$, ρ_0 is the average density of atoms, $\rho(r)$ is the radial density function, c_i and f_i are the atomic concentration and atomic scattering factor of the i-kind of atoms respectively and $Q=4\pi \sin\theta/\lambda$, where $2\,\theta$ is the angle between the incident and diffracted X-ray beams and λ is the wavelength.

The total reduced distribution function G(r) is obtained by the following Fourier transformation of the total structure factor S(Q);

$$G(r) = 4\pi r\, [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q\,[S(Q) - 1]\, \sin(Qr)\, dQ\,. \tag{3}$$

On the other hand, for a binary alloy the total structure factor S(Q) directly obtained by experiments is connected to three partial structure factors, $S_{11}(Q)$, $S_{22}(Q)$ and $S_{12}(Q)$ as follows;

$$S(Q) = \frac{c_1^2 f_1^2}{\langle f\rangle^2} S_{11}(Q) + \frac{c_2^2 f_2^2}{\langle f\rangle^2} S_{22}(Q) + \frac{2 c_1 c_2 f_1 f_2}{\langle f\rangle^2} S_{12}(Q)\,. \tag{4}$$

Here, the partial structure factor $S_{ij}(Q)$ can be written as;

$$S_{ij}(Q) = 1 + \int_0^\infty 4\pi r^2 \left[\frac{\rho_{ij}(r)}{c_j}\right] - \rho_0 \, \frac{\sin(Qr)}{Q\,r}\, dr\,, \tag{5}$$

where $\rho_{ij}(r)$ means the number of j-type atoms per unit volume at a distance r from i-type atom. Then we also obtain the reduced partial distribution function $G_{ij}(r)$ from $S_{ij}(Q)$ by the following relation:

$$G_{ij}(r) = 4\pi r\left[\frac{\rho_{ij}(r)}{c_j} - \rho_o\right] = \frac{2}{\pi}\int_o^\infty Q\,[S(Q)-1]\sin(Qr)\,dQ. \quad (6)$$

In this work, the three partial structure factors were derived from the total structure factors experimentally obtained at several compositions by solving three set of simultaneous equation based on Eq.(4). The numerical calculation was performed on the NEAC-2200, Model-700, in Computer Center, Tohoku University.

4. RESULTS AND DISCUSSION

4.1 Atomic distribution in liquid Pb-Bi alloys

The total structure factors are shown in Figure 1. These were measured at temperatures about 50°C above the liquidus temperature. The positions of

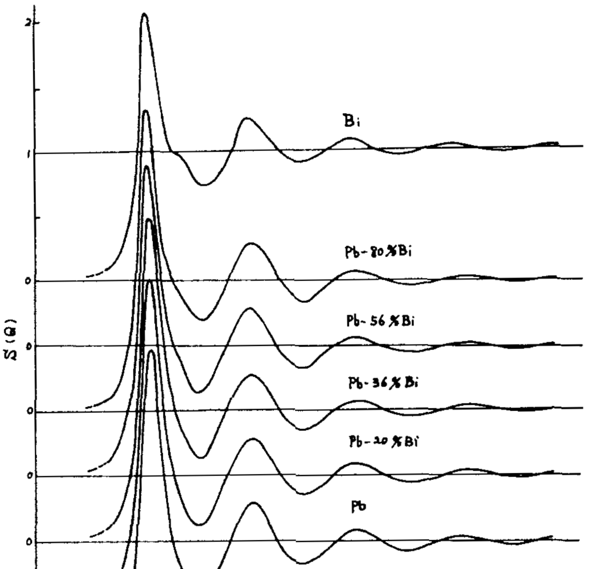

FIGURE 1 Total structure factors for liquid Pb-Bi alloys.

TABLE I

Summary of the information of total structure factors

Composition at % Bi	Measured temp. °C	ρ_0 atoms/Å^3	Q_1	Q_2	Q_3	r_1	n_1	n_a
0	340	0.0310	2.28	4.23	6.20	3.33	10.9	10.8
20	300	0.0304	2.20	4.21	6.19	3.34	10.1	9.9
36	250	0.0300	2.17	4.18	6.17	3.34	9.9	9.9
56	200	0.0294	2.15	4.16	6.15	3.36	9.5	9.5
80	270	0.0290	2.13	4.13	6.03	3.38	9.1	8.8
100	300	0.0289	2.11	4.12	6.00	3.38	8.8	9.0

ρ_0 is the average number density of atoms, Q_i is the position of the i-th peak in S(Q), r_1 and n_1 are the interatomic distance and coordination number of atoms derived from $4\pi r^2 \rho(r)$, and n_a is the value calculated by Eq. (8).

peak maximum of the total structure factors were determined from the position of apex of the parabola obtained with three points near the peak maximum and are given in Table I together with average density of atoms.[12] These positions decrease gradually from 2.28 Å^{-1} for pure Pb to 2.11 Å^{-1} for pure Bi for the first peak and from 4.23 Å^{-1} to 4.12 Å^{-1} for the second peak. The structure factor of liquid Bi shows the small hump on the high angle side of the first peak. The small hump of the structure factor was also found in the case of pure liquid Ga, Sn[13] and Bi.[14] In all the cases this small hump is not specified as the temperature rises, but the asymmetry of the first peak is observed. In addition, the electronic structure of these liquid metals is quite different from the value expected by the nearly free electron model.[15] For these reasons, it is deduced that the small hump of these liquid metals is connected with the anisotropy of their crystal structure. At present time, a definite answer on this problem is not available. In liquid Pb-Bi alloys this small hump becomes less evident with an increase in the Pb-concentration as shown in Figure 1.

The total reduced distribution function G(r) and the pair probability function $W(r) = \rho(r)/\rho_0$ are shown in Figures 2 and 3. All the curves of G(r) oscillate about zero. Asymmetry of the first peak is found for all alloys. The first peak of pure Pb is sharp unlike those of pure Bi and alloys which are comparatively broad. This slight asymmetry of the first peak is also found in W(r). These curves do not indicate any fine structures, for example, the double headed peak in the Au-Sn system.[16] Therefore, one can not expect drastic changes of the structure in liquid Pb-Bi alloys.

The interatomic distances r_1 were obtained from the curves of $4\pi r^2(r)$. The area under each first peak of $4\pi r^2\rho(r)$ was used to estimate the coordination number of nearest neighbour atoms n_1. As we have no unique method of evaluating the coordination number of atoms[17], only a value obtained by Eq.(7) is given in Table I and Figure 4 together with the interatomic distances.

$$n_1 = \int_{r_0}^{r_2} 4\pi r^2 \rho(r)\, dr, \tag{7}$$

where r_0 is the edge of the left-hand side of the first peak and r_2 corresponds to the first minimum on the right-hand side of the first peak in $4\pi r^2\rho(r)$ curves. This method is considered mathematically the best one though the validity of this method is unfortunately doubtful when ripples appear due to the errors.[18] We see from Figure 4 that the interatomic distance r_1 increases linearly with concentration. The dotted line in this figure joining the two

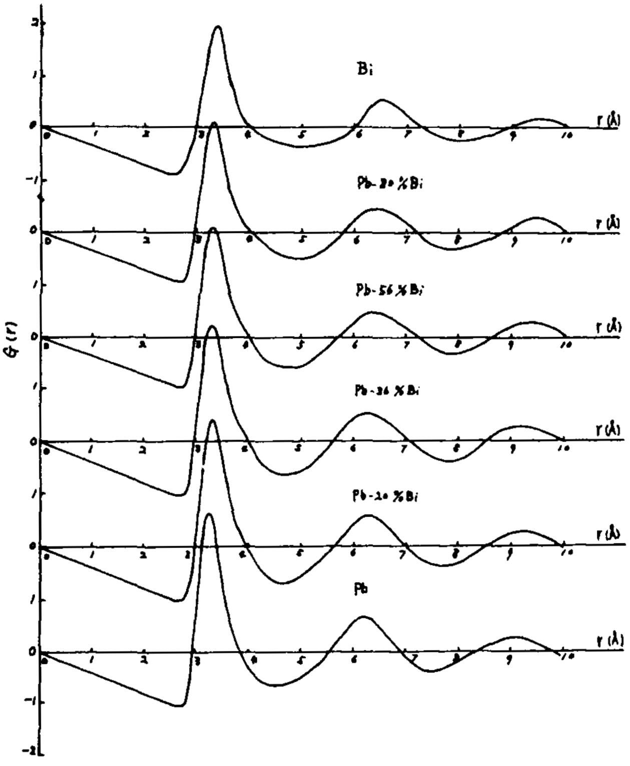

FIGURE 2 Total reduced distribution functions for liquid Pb-Bi alloys.

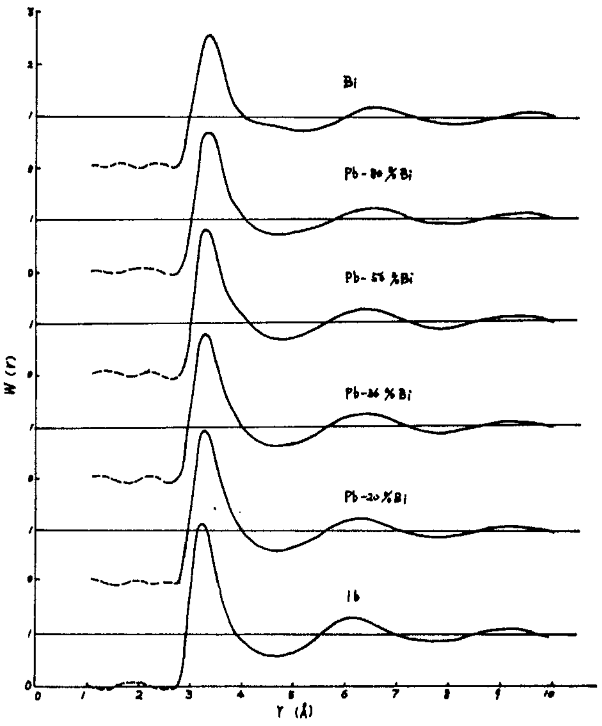

FIGURE 3 Pair probability functions for liquid Pb-Bi alloys.

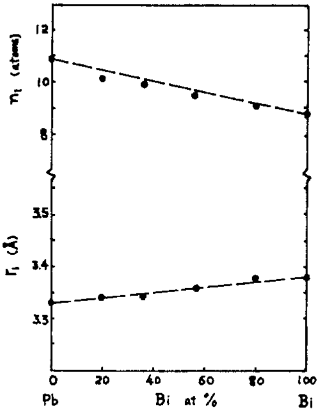

FIGURE 4 Plots of interatomic distance r_1 and coordination number n_1 against concentration for liquid Pb-Bi alloys.

points corresponding to r_1 for pure Pb and Bi (3.33 Å and 3.38 Å respectively), indicates a linear relationship of Vegard's law in the solid solution.[19] The variation of the coordination number n_1 with concentration is similar to that of the interatomic distance. From these results, the contribution of the difference of crystal structures to the atomic arrangement for liquid Pb-Bi alloys is found to be insignificant. It is easy to see that this agrees with the conclusion from a quasi-face centered cubic lattice model by Furukawa[20] and supports that there is no preferential grouping or molecular arrangement in liquid Pb-Bi alloys.

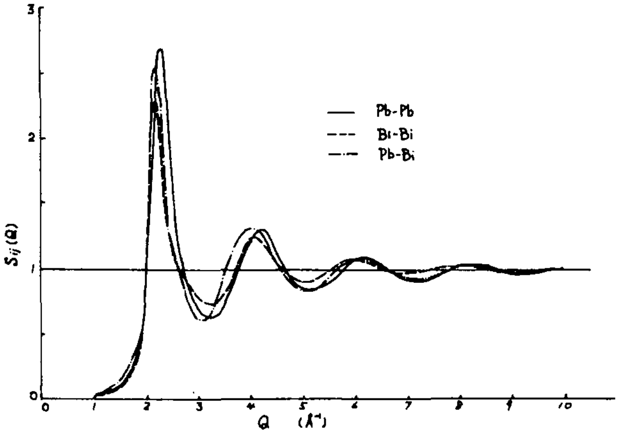

FIGURE 5 Partial structure factors for liquid Pb-Bi- alloys.

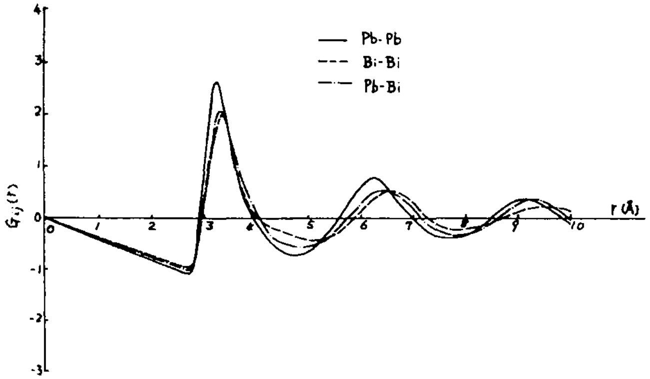

FIGURE 6 Partial reduced distribution functions for liquid Pb-Bi alloys.

4.2 Partial structures in liquid Pb-Bi alloys

The calculation was performed to derive the partial structure factors on three sets of data (pb-20, 36, 56 at % Bi; Pb-36, 56, 80 at % Bi; Pb-20, 56,80 at % Bi) and then the best fit values of $S_{Pb\text{-}Pb}(Q)$, $S_{Bi\text{-}Bi}(Q)$ and $S_{Pb\text{-}Bi}(Q)$ were determined by the least square analysis of four S(Q) with different Bi concentrations. Figures 5 and 6 show the partial structure factors $S_{ij}(Q)$ and the reduced partial distribution functions $G_{ij}(r)$ respectively. The peak positions of $S_{ij}(Q)$ and $G_{ij}(r)$ are summarized in Table II.

As shown in Figure 5, $S_{Pb\text{-}Pb}(Q)$ and $S_{Bi\text{-}Bi}(Q)$ closely resemble the structure factors of pure liquid metals reported by our group.[13] This seems to indicate that the partial structure factors are independent of the composition of alloys. $S_{Pb\text{-}Bi}(Q)$ and $G_{Pb\text{-}Bi}(r)$ have the peak maxima at the positions between those of pure elements. Such a behaviour is predicted from the random mixing model of hard spheres. The value of the partial quantities of unlike atom pair (Pb-Bi), for example the position of peak maxima, interatomic distance and so on, is in moderately good agreement with the mean value between those of like atom pairs (Pb-Pb and Bi-Bi). On the other hand, the total structure factors and their Fourier transforms have no anomalies at any particular compositions, as shown in Figures 1 and 2. These results

TABLE II

Summary of the information of partial structure factors and partial distribution functions

Position of i-th peak	$S_{Pb\text{-}Pb}(Q)$	$S_{Bi\text{-}Bi}(Q)$	$S_{Pb\text{-}Bi}(Q)$	mean value
1st peak	2.28	2.12	2.18	2.20
2nd peak	4.23	4.09	4.05	4.16
3rd peak	6.17	5.96	6.16	6.07
	$G_{Pb\text{-}Pb}(r)$	$G_{Bi\text{-}Bi}(r)$	$G_{Pb\text{-}Bi}(r)$	mean value
1st peak	3.28	3.36	3.33	3.32
2nd peak	6.24	6.59	6.35	6.42
3rd peak	9.13	9.47	9.31	9.30
Interatomic distance r_{ij}	3.30	3.38	3.36	3.34
Coordination number n_{ij}	10.8	9.0	9.3	9.9

Peak positions of $S_{ij}(Q)$ are represented in A^{-1} and those of $G_{ij}(r)$ and interatomic distance are in A, mean value denotes average value between those of pure elements.

suggest that the structure of the crystalline compound, for example the ϵ-phase (Pb_3Bi), never influences the liquid structure of alloys.

According to the method of Halder and Wagner[2], the coordination number for an alloy n_a can be written in terms of the partial coordination numbers n_{ij} in the following form;

$$n_a = \frac{c_1^2 f_1^2}{\langle f \rangle^2} n_{11} + \frac{c_2^2 f_2^2}{\langle f \rangle^2} n_{22} + \frac{2 c_1 c_2 f_1 f_2}{\langle f \rangle^2} n_{12} \tag{8}$$

The calculated coordination number for an alloy n_a is listed in Table I. It is interesting to note that agreement is shown between the calculated and observed values. This result at least confirms that the structure of liquid Pb-Bi alloys is represented by the combination of the three partial distribution of atom pairs (Pb-Pb, Bi-Bi and Pb-Bi) within the framework of the assumption that the partial distribution of atom pairs is independent of composition.

Here, we have employed one simple approach, the hard sphere mixture model to calculate the partial structure factors in a liquid binary alloy. The model structure factors which are calculated from the concentration, hard sphere diameter and total packing fraction are frequently used[21] in the case of quantitative analysis of electron-transport properties in liquid binary alloys because the partial structure factors of any binary systems do not obtained experimentally. In this section, a comparison is made between the partial and total structure factors obtained in this work and those calculated from the hard sphere mixture model.

Ashcroft Langreth[5] and Enderby-North[6] have independently suggested to apply the Fourier transforms of the hard sphere solutions of the Percus-Yevick equation for binary mixtures presented by Lebowitz.[7] The detailed formulas are given in their original works.[5-7] Hence only the method for selection of the parameters, namely the hard sphere diameter and total packing fraction, is given below. Waseda and Suzuki[22] showed that the hard sphere diameter (σ) for one component liquid metals is close to the distance (r_0) of the first node in the effective interionic potential. Using the assumption $\sigma = r_0$ and the density of liquid Pb-Bi alloys observed experimentally[12], the total packing fraction is 0.43 ± 0.02. This is good agreement with the value (0.45) used by Ashcroft and Langreth.[5] From these results, the model partial structure factors for Pb-56 at % Bi alloy are calculated with r_0 (Å) = 2.97 and 3.04 for Pb and Bi respectively[22] instead of σ and the total packing fraction 0.43.

Figure 7-(A) shows the partial structure factors of the unlike atom pair

(Pb-Bi) obtained in this work and calculated from the hard sphere mixture model. Adequate agreement is readily observed for the first peak maximum, but the disagreement between curves is evident with respect to the damping behaviour and the phase. We may suggest that this is because the repulsive core in the effective interionic potential for liquid metals is softer than that of the liquids of rare-gas elements.[22] Therefore the hard sphere model which neglects the softness of the repulsive core in the pair potential does not explain properly the quantitative aspects of the structure factor for liquid metals though it seem to be fairly good as a first approximation.

Figure 7-(B) shows the total structure factor of liquid Pb-56 at % Bi alloy according to the hard sphere mixture model together with the curve

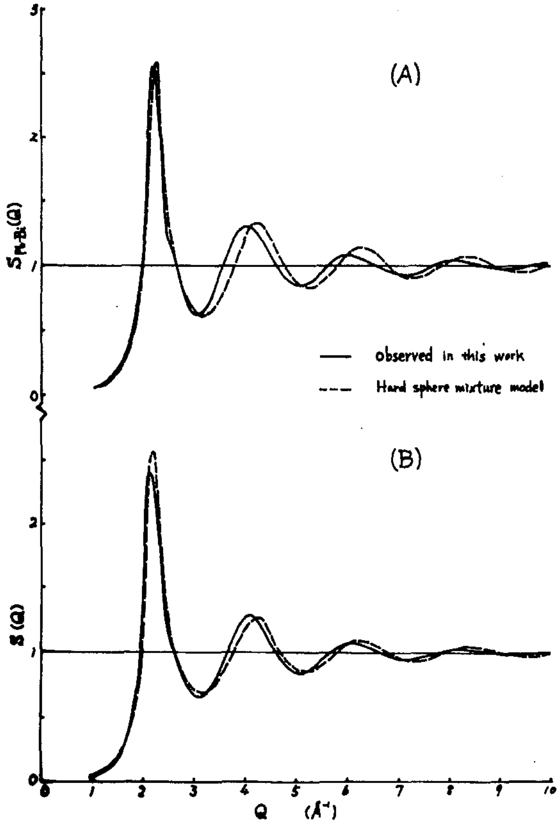

FIGURE 7 A comparison between partial and total structure factors of liquid Pb- 56 at % Bi alloy observed in this work and those calculated by the hard sphere mixture model.

measured in this work. Although there are differences in detail good agreement is found with respect to the position and the height of the first peak. For this calculation, we may suggest that the hard sphere mixture model seems to be fairly good as a first approximation at least for liquid Pb-Bi alloys though the detailed information evidently differs from the results observed experimentally. In addition, a new approach for liquid metals to give the best fit to the observed structure factor should include the characteristic of the softness of the repulsive core in pair potential. But this problem is to be discussed in a later work after performing some further diffraction experiments and consideration.

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