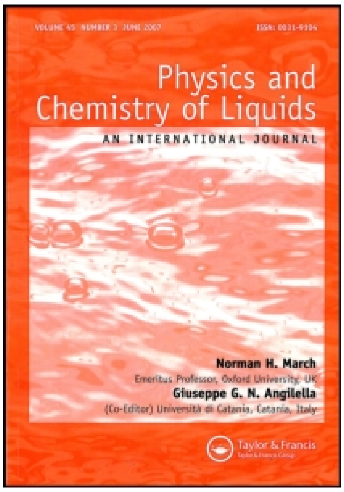

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Structural Properties of Liquid Ag-In System

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STRUCTURAL PROPERTIES OF LIQUID Ag-In SYSTEM

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The total structure factors, $S(q)$, of liquid Ag-In alloys have been derived by X-ray diffraction measurements. The concentration dependence of the first peak position is divided into three groups; on going from Ag to 70 at% Ag, the peak position decreases linearly and it goes to decrease with a more rapid proportion for the concentration range from 70 to 40 at% Ag, and furthermore it becomes nearly constant for the remained concentration range.

In order to know the information of a local configuration for this system, the partial structure factors are derived from the obtained total structure factors by assuming that they are independent for a concentration range. And they agree with the results obtained by the reverse Monte Carlo simulation method. From these partial structural information, we propose that the partial structure factors in Ag rich side are different from those in In rich side.

Keywords: Liquid Ag-In alloy; partial structure factor; $S_{CC}(q)$; Reverse Monte Carlo

1. INTRODUCTION

Structural measurements of liquid metals and alloys have been carried out by X-ray and neutron diffraction techniques by a number of workers [1].

Structure factors of the so-called simple liquid metals, such as Na, K and Al, agree with those calculated by the hard sphere approximation, quantitatively [1]. The structure factors of these simple liquid metals are also interpreted in terms of their effective ion–ion interactions [2, 3]. On the other hand, the structure factors of in liquid Bi, Sn and Zn are not represented by such a simple feature based on the hard-sphere approximation. $S(q)$'s of liquid Bi and Sn have a shoulder beyond their first peaks, and that of liquid Zn has an asymmetry around the first peak. These may be caused by an anisotropy in their atomic configurations [1] which may be ascribed to the anisotropy of the effective ion–ion interactions.

The structural properties of liquid alloys are more complicated because they are yielded by a complex combination of the three kinds of effective ion–ion interactions. However, from a point of view in the structural data [1], most of structure factors in liquid binary alloys are classified into three groups. The first group is that the structure factors of alloys are described by the hard sphere approximation as mentioned above and have neither subpeak nor asymmetry around the first peak. One of typical alloys belonging to this group is liquid Na-K system in which the structure factor is expressed in terms of the random mixtures of the two hard spheres. The total structure factors of the second group alloys, for example, Sn-Mg, Al-Au [1], display a pre-peak below the first peak. These pre-peaks may correspond to a compound-forming within a short range region. The third group alloys show an intermediate structural feature between the first and second ones. In a number of noble and polyvalent metal alloys belong to this group, there forms a characteristic structure at a concentration obeying the Hume-Rothery rule in the solid state.

Sometime ago, the partial structure factors of liquid Cu_6Sn_5 were determined by using the isotope-enrich method of neutron diffraction measurements [4]. The striking feature in the partial structures of liquid Cu_6Sn_5 is that the copper-tin correlation shows a long-range concentration fluctuations. Halder *et al.* [5] have estimated the three partial structure factors by averaging over the wide range of liquid Ag-Sn alloys. In these alloys, the unlike pair correlation is similar to the silver–silver one.

A knowledge on the partial structure factors allows us to evaluate the electrical resistivity and thermoelectric power of the liquid alloys

[6, 7]. The resistivities calculated by using the Faber-Ziman theory and the obtained partial structure factors agreed with experimental results [8].

Magnetic susceptibilities of some liquid alloys [9] belonging to the third group show a deviation from the linear change for the concentration which is called as the Wiedemann rule [10]. Recently magnetic susceptibilities, χ, of liquid Ag-In were measured by the present authors with emphasis on temperature dependence [11]. The $d\chi/dT$ and the density of states at the Fermi level was discussed in their report.

We have measured the X-ray diffraction for liquid Ag-In alloys and have obtained their total structure factors, from which the three kinds of partial structure factors were separated, assuming that they are independent for a concentration range.

2. EXPERIMENTAL RESULTS

The experimental arrangement and operating procedures for the X-ray intensity measurements on high-temperature melts were almost identical to those described in the previous work [15]. All data were obtained with Mo radiations using the step scan mode of operation. After several corrections [12] the total structure factors were derived. They are shown in Figure 1. The experimental errors of the heights of $S(q)$, most of which are caused by the normalization and also by statistical error of scattering intensity, have been estimated as ±1.5%, ±0.5% and ±2% around the small q region, the first peak and the second peak regions, respectively [15, 13, 14].

Figures 2 and 3 show the concentration dependencies of the peak positions and intensities of $S(q)$, respectively. As is seen in Figure 2, a distinct change occurs at about 60 at% Ag on going from Ag to In. However, the heights of first peaks show hardly such a tendency.

The total distribution functions $g(r)$'s obtained by performing the Fourier transformations of $S(q)$ are shown in Figure 4. This transformation is written as follows,

$$g(r) = 1 + \frac{1}{2\pi^2 r\rho_0}\int_0^\infty \{S(q) - 1\} q \sin(qr) dq \tag{1}$$

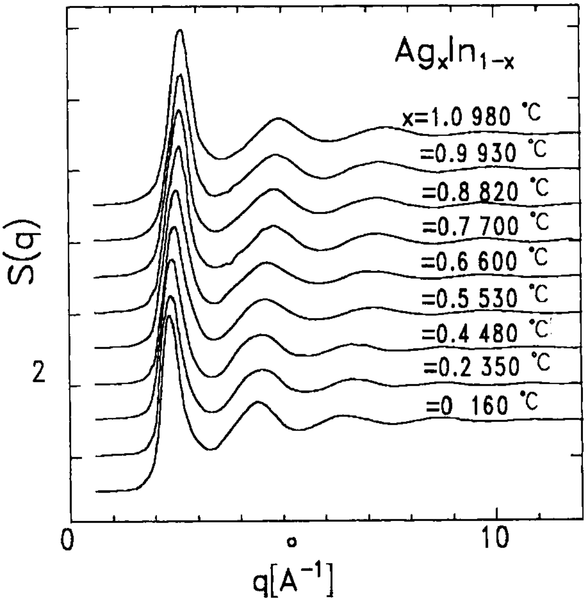

FIGURE 1 Structure factors of liquid Ag_xIn_{1-x} alloys.

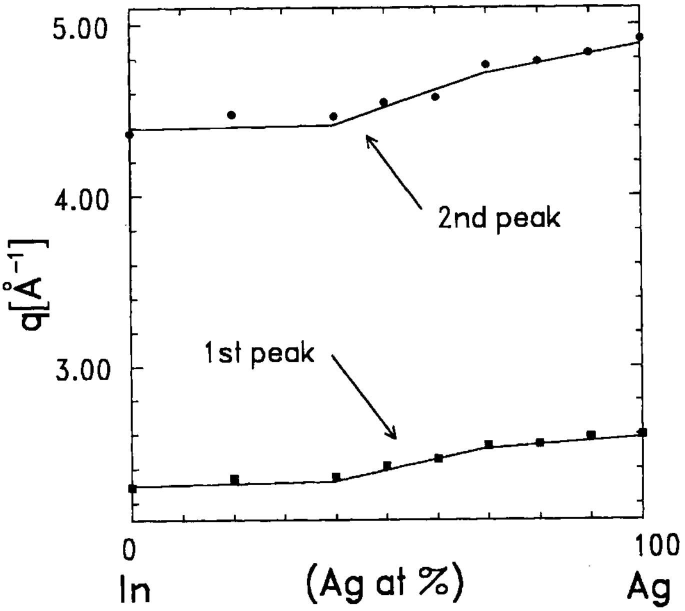

FIGURE 2 Concentration dependence of the peak positions of $S(q)$'s.

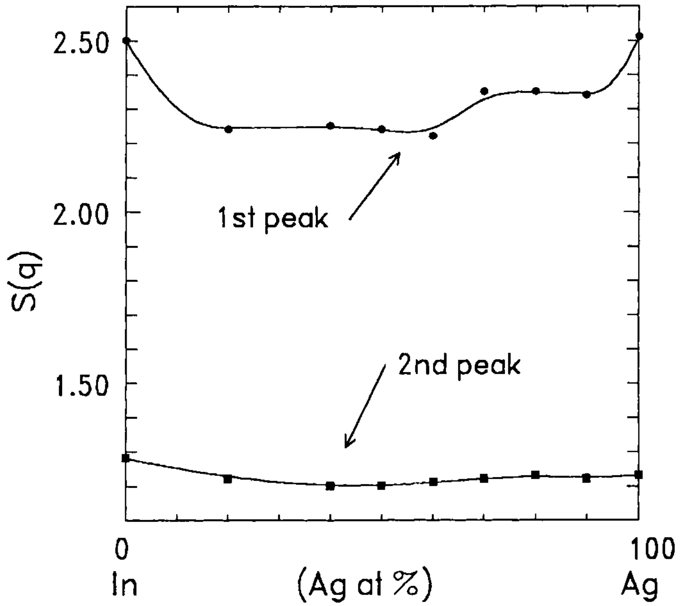

FIGURE 3 Concentration dependence of the intensities of $S(q)$ at the peak position.

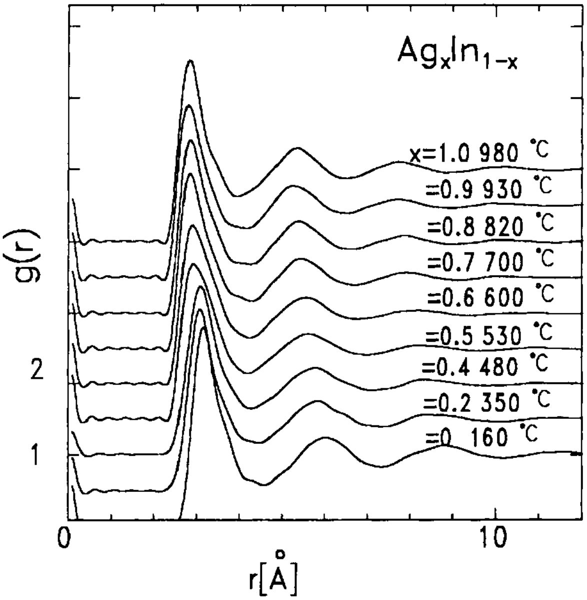

FIGURE 4 Total pair distribution functions of liquid Ag_xIn_{1-x} alloys.

where ρ_0 is the averaged number density of atoms in the sample. The concentration dependences of the peak positions and intensities of $g(r)$ are shown in Figures 5 and 6, respectively. As seen in Figures 2, 5 and 6, profiles of $g(r)$ and $S(q)$ are classified into three types, in regard to the peak positions and heights. The total structure factors of pure silver and of the alloys up to 30 at % In are assigned to one group. Alloys of In rich region more than 60 at % In are allotted to another group. The structure factors of remained alloy compositions are a mixed state of the former two cases.

3. DISCUSSION

The results of magnetic susceptibility and $S_{cc}(0)$ [11, 16] indicate that the electronic and structural properties in Ag-rich side are different from those of In-rich side. Hence the derivation of partial structure

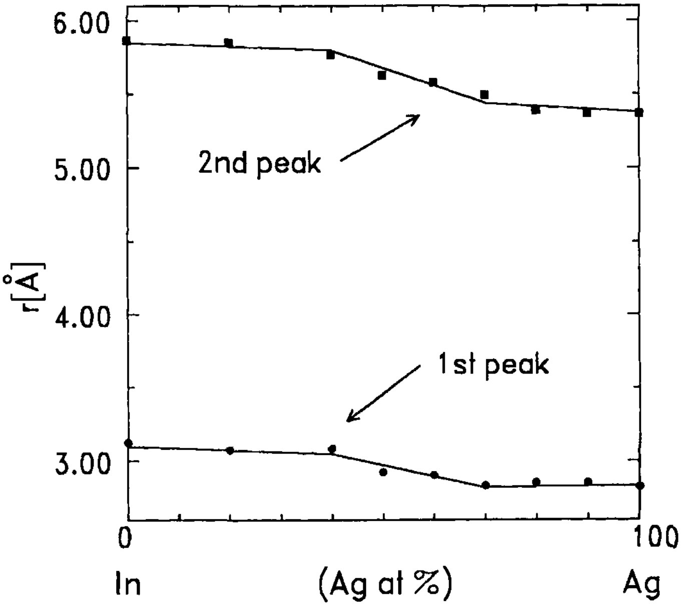

FIGURE 5 Concentration dependence of the peak positions of $g(r)$'s.

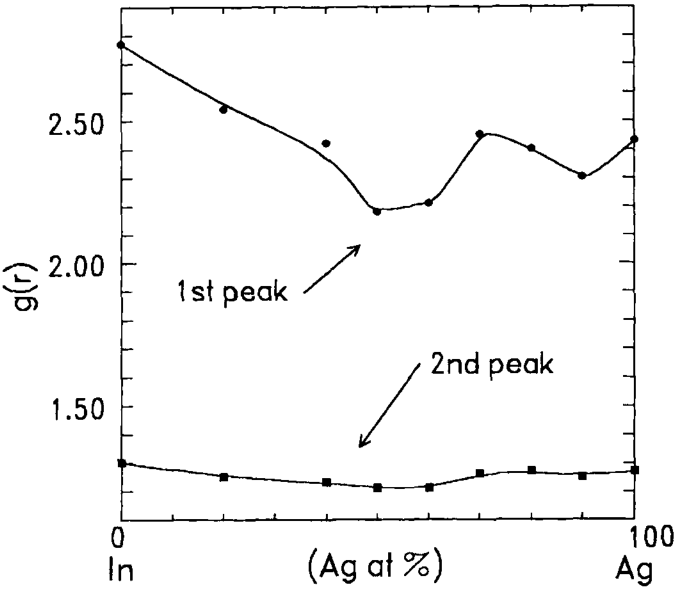

FIGURE 6 Concentration dependence of the intensities of $g(r)$ at the peak positions.

factors seems to be a good clue to interpret the properties at the concentration range.

The previous works on the partial structure factors for some of liquid binary system [1, 5] show that the concentration-independent partial structure factors could reproduce the observed total structure factors in a given concentration range if the peak positions of $S(q)$ changed linearly with concentration. And as shown in Figure 2. The above condition is satisfied for the two regions. Then, three partial structure factors are derived to discuss the local structure of liquid Ag-In system.

The three partial structure factors $S_{\mathrm{AgIn}}(q)$, $S_{\mathrm{AgAg}}(q)$ and $S_{\mathrm{InIn}}(q)$ are obtained for the concentration of *Ag*- and In-rich regions by solving the three simultaneous equations involving the observed total structure factors such as

$$S_{k_{\mathrm{total}}}(q) = w_{k_i}^2 S_{ii}(q) + w_{k_j}^2 S_{jj}(q) + 2w_{k_i} w_{k_j} S_{ij}(q) \qquad (2)$$

Three total structure factors for three different concentrations, for example, $S_{\mathrm{Ag}0.7\mathrm{In}0.3}(q)$, $S_{\mathrm{Ag}0.8\mathrm{In}0.2}(q)$ and $S_{\mathrm{Ag}0.9\mathrm{In}0.1}(q)$ are used to solve the equations, $w_{k_i} = c_{k_i} f_i / \langle f \rangle$ and $\langle f \rangle = \sum_i c_{k_i} f_i$, c_{k_i} being the atomic concentration of k alloys, f_i the form factor of the constituent i. And the w_{k_i} changes gradually the concentration. Therefore, under the assumption that the partial structures are the same, the total structure factors should be gradually changed for a concentration range and their peak positions and heights are also smoothly changed as appeared in the case of liquid Na-K system.

In Ag-rich side, the three partial structure factors are derived from three obtained total structure factors. The profile of $S_{\mathrm{AgAg}}(q)$ seems to be plausible because its profile is similar to that of pure liquid silver. However, the profiles of the $S_{\mathrm{AgIn}}(q)$ and the $S_{\mathrm{InIn}}(q)$ are slightly affected by the experimental error due to a lower amount of In. Hence the smoothing of the curves of the $S_{\mathrm{InIn}}(q)$ and the $S_{\mathrm{AgIn}}(q)$ has been carried out by using the modification-function [17] and the reversal Fourier methods [18]. The smoothing for $S_{\mathrm{InIn}}(q)$, $S_{\mathrm{AgAg}}(q)$ and the observed total structure factor $S_{\mathrm{Ag}0.7\mathrm{In}0.3}(q)$ bring out the $S_{\mathrm{AgIn}}(q)$ using equation (2) and this obtained $S_{\mathrm{AgIn}}(q)$ compares with initially estimated $S_{\mathrm{AgIn}}(q)$. Furthermore the smoothing for $S_{\mathrm{AgIn}}(q)$, $S_{\mathrm{AgAg}}(q)$ and $S_{\mathrm{Ag}0.7\mathrm{In}0.3}(q)$ bring out the $S_{\mathrm{InIn}}(q)$ using equation (2) and this obtained $S_{\mathrm{InIn}}(q)$ compares with the initially estimated $S_{\mathrm{InIn}}(q)$. These differences between the initial $S_{ij}(q)$ and the smoothed$S_{ij}(q)$ are regarded as errors of this method. The estimated $S_{ij}(q)$'s for the liquid $S_{\mathrm{Ag}0.7\mathrm{In}0.3}(q)$ alloy are shown in Figure 7. As is shown in Figure 7, the correlation of Ag-In is similar to that of In–In. The peak position of Ag–Ag correlation is located at a higher q than those of the other two correlations. In a similar way, the $S_{ij}(q)$'s for the liquid $\mathrm{Ag}_{0.2}\mathrm{In}_{0.8}$ alloy are also estimated and are shown in Figure 8. The peak position of $S_{\mathrm{AgAg}}(q)$ is located at a higher q than those of In–In and slightly lower than those of Ag-In.

To confirm the above analysis of the present structural data, we perform the Reverse Monte Carlo (RMC) simulation for those. RMC has been developed by McGreevy *et al.* [19]. It is based on the standard Monte Carlo simulation method with Markov chain sampling without any effective pair potentials. The densities of each alloy are taken from experimental values [20] and the number of total particles is 864. The results of RMC simulation and the experimentally derived $g_{ij}(r)$

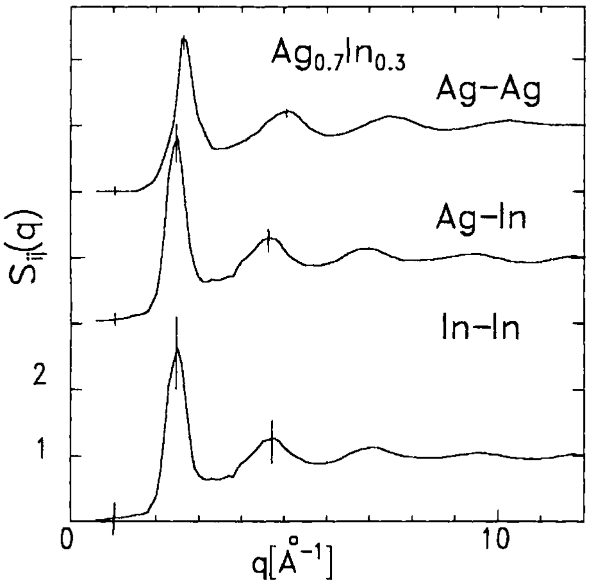

FIGURE 7 Partial structure factors of liquid $Ag_{0.7}In_{0.3}$.

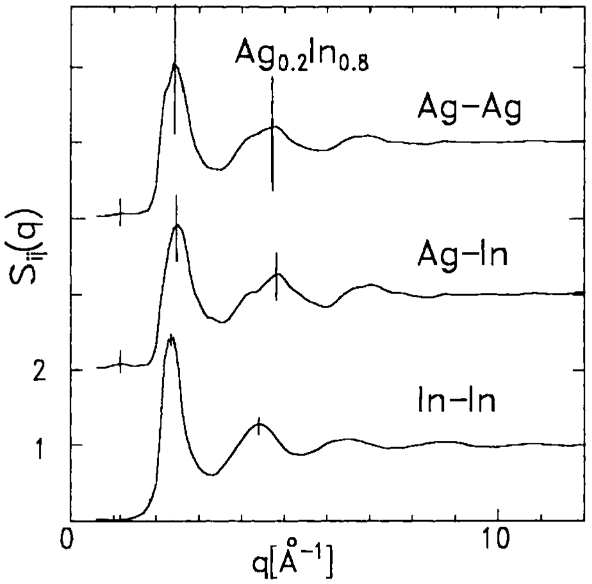

FIGURE 8 Partial structure factors of liquid $Ag_{0.2}In_{0.8}$.

performing for Fourier transform from $S_{ij}(q)$ assuming the concentration independence for $S_{ij}(q)$ are shown in Figures 9 and 10. $g_{ij}(r)$'s derived by these two different methods agree, qualitatively and semiquantitatively with each other.

We have also derived the partial structure factors of Bhatia-Thornton type, $S_{NN}(q)$,$S_{NC}(q)$ and $S_{CC}(q)$ as shown in Figures 11,12 and 13 by using the three partial structure factors $S_{ij}(q)$ and the following expression [1],

$$\begin{aligned} S_{NN}(q) &= c_1^2 S_{11}(q) + c_2^2 S_{22}(q) + 2c_1c_2S_{12}(q) \\ S_{CC}(q) &= c_1c_2[1 + c_1c_2\{S_{11}(q) + S_{22}(q) - 2S_{22}(q)\}] \\ S_{NC}(q) &= c_1c_2c_1[c_1\{S_{11}(q) - S_{12}(q)\} - c_2\{S_{22}(q) - S_{12}(q)\}] \end{aligned} \tag{3}$$

The shapes of concentration–concentration fluctuations $S_{CC}(q)$'s in both terminal sides are quite different to each other. In the In-rich, side $S_{CC}(q)$ has a distinct peak at about 2Å^{-1}. And the whole shapes of

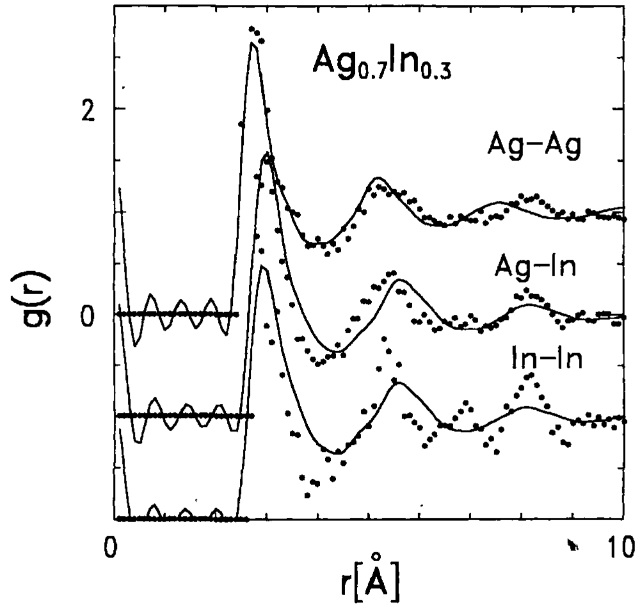

FIGURE 9 Partial pair distribution function of $g_{ij}(r)$'s of liquid $Ag_{0.7}In_{0.3}$. Solid line:- estimated by concentration independence, dotted line: • derived by RMC simulation.

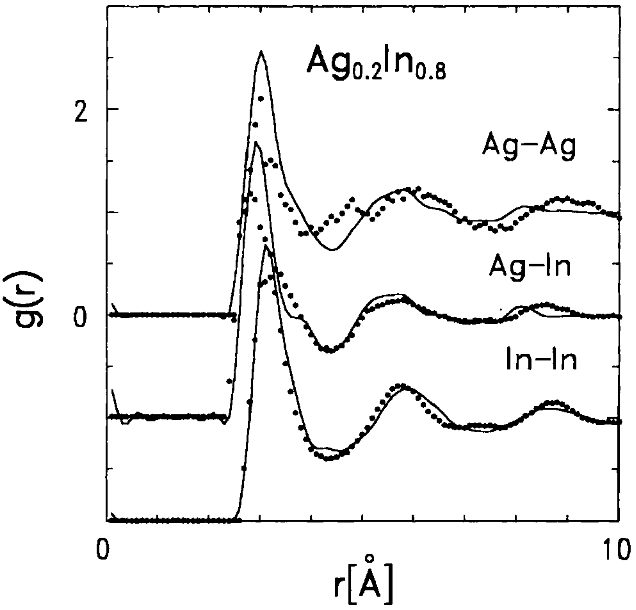

FIGURE 10 Partial pair distribution function of $g_{ij}(r)$'s of liquid $Ag_{0.2}In_{0.8}$. Solid line:-estimated by concentration independence, dotted line: • derived by RMC simulation.

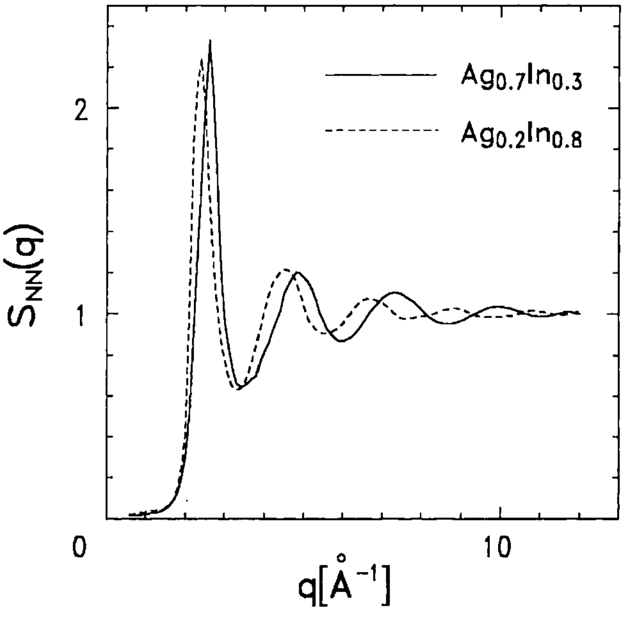

FIGURE 11 $S_{NN}(q)$ curves of liquid $Ag_{0.7}In_{0.3}$ and $Ag_{0.2}In_{0.8}$.

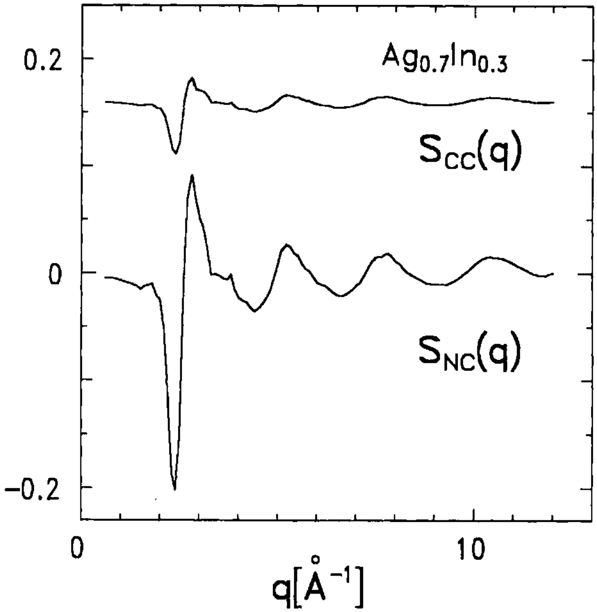

FIGURE 12 $S_{NC}(q)$ and $S_{CC}(q)$ curves of liquid $Ag_{0.7}In_{0.3}$.

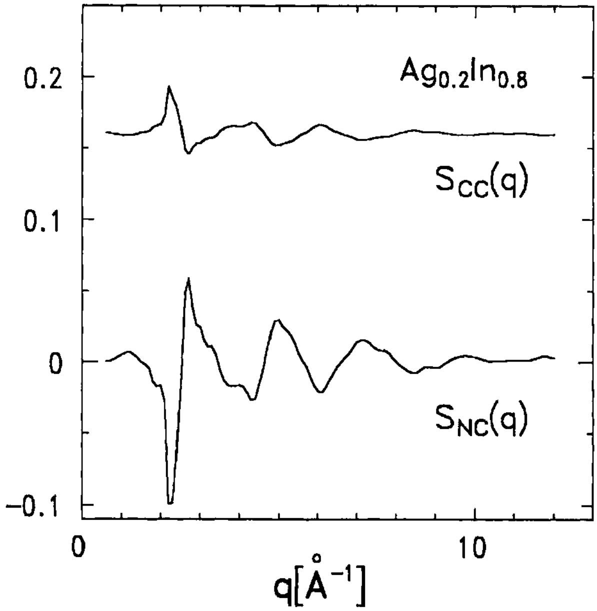

FIGURE 13 $S_{NC}(q)$ and $S_{CC}(q)$ curves of liquid $Ag_{0.2}In_{0.8}$.

$S_{CC}(q)$ in In-rich side is similar to that calculated by using the hard sphere Percus-Yevick model with $\sigma_1/\sigma_2=0.7$ [21], as shown in Figure 14, where σ_i is the hard sphere diameter of the element i.

The ratio of the hard sphere diameters of pure liquid Ag and In is nearly equal to 0.9 which can be deduced by assuming that the packing fractions of both metals are nearly equal to 0.45. The discrepancy between these ratios in the In-rich region may be ascribed to the change of the hard sphere size of constituents by alloying. This is an evidence that the partial structure factors of some compound forming liquid alloys, in which the electronegativities of the constituents are different to some extent, are represented by the hard sphere model.

On the other hand, $S_{CC}(q)$ of the present system in Ag-rich side has a large dip at about 2Å^{-1} and oscillates with an opposite phase against that in In-rich one. Such an oscillation seems to infer, not the mixture of hard sphere, but the existence of a kind of short-range order in the liquid alloys of Ag-rich region. Actually, the magnetic susceptibility and thermodynamic analysis of Ag-rich side in this system indicate the

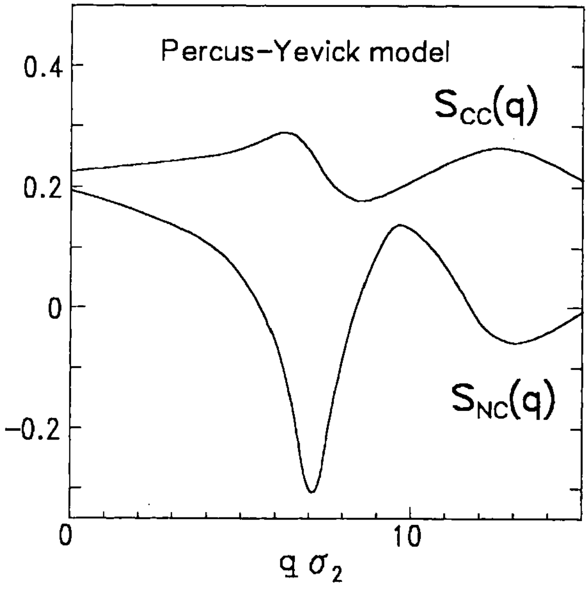

FIGURE 14 S_{NC} and S_{CC} curves derived from the hard sphere Percus-Yevic model calculations [21] with $c_1=0.6$ and $\sigma_1/\sigma_2=0.7$.

existence of a kind of short-range order [11]. The Fourier transform of $S_{CC}(q)$ yields $\rho_{CC}(r)$ as in the following form,

$$\rho_{CC}(r) = \int q(S_{CC}(q) - c_1c_2)\sin(qr)dq/2\pi^2 rc_1c_2 \tag{4}$$

If unlike pairs prefer to coordinate at the nearest neighbour distance, the value of $\rho_{CC}(r)$ at its distance tends to be negative, and vice versa [22]. These are shown in Figure 15. $\rho_{CC}(r)$'s in Ag rich side imply that it prefers to occupy by like atoms in the first coordination shell, and therefore the first peak positions of $g_{\mathrm{AgAg}}(r)$ and $g_{\mathrm{InIn}}(r)$ are smaller than that of $g_{\mathrm{AgIn}}(r)$. In In rich side, on the other hand, unlike atoms tend to coordinate in their nearest neighbors, and so the first peak position of $g_{\mathrm{AgIn}}(r)$ is the smallest. These behaviors are consistent with the results of the pair distribution functions $g_{ij}(r)$ as shown in Figures 9 and 10, respectively.

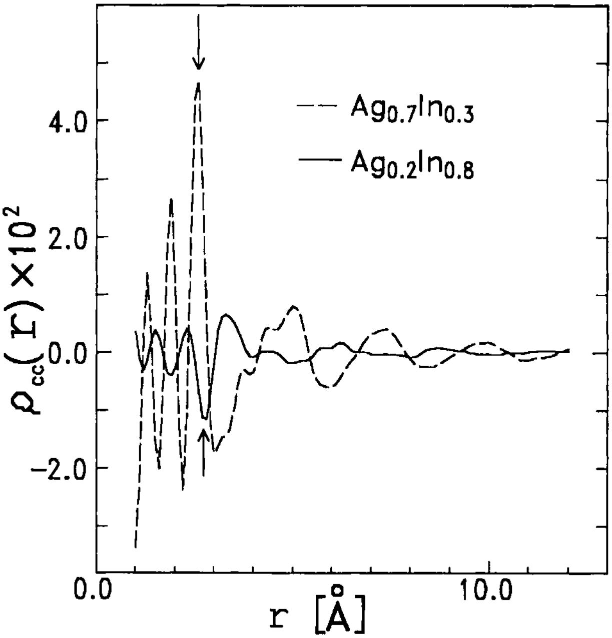

FIGURE 15 $\rho_{CC}(r)$ curves of liquid $Ag_{0.7}In_{0.3}$ and $Ag_{0.2}In_{0.8}$. Arrows indicate the nearest neighbor correlation.

4. CONCLUSION

The concentration dependences of $S(q)$ and $g(r)$ are divided into three groups in liquid Ag-In system. These results are consistent with those of the magnetic susceptibility and $S_{cc}(0)$. In taking account of these situations, we assume that the concentration-independence of the partial structure factors in the region satisfied the condition of linear change of peak position, and derive $S_{ij}(q)$, $g_{ij}(r)$ and $\rho_{cc}(r)$.

In the liquid Ag-In system of Ag-rich side, the $\rho_{cc}(r)$ curves show that Ag or In atoms prefer to coordinate by like atoms in the nearest neighbors. The position of the first peak of the pair distribution function $g_{ij}(r)$ indicates that the distance of Ag–Ag correlation is shorter than the others, and those of Ag-In and In–In correlations are almost the same. If the structure of this system is constructed by a random mixture, then the peak positions in the obtained partial structure factors are basically shifted in the order from In – In, In-Ag to Ag–Ag correlations. However the results do not show such an order.

While, the curve of $\rho_{CC}(r)$ for In-rich side gives a contrasting result to that of Ag-rich one, which shows that the nearest neighbors prefer to coordinate by the unlike atoms. From the first peak position of $g_{ij}(r)$, the distance of In–In is longer than the others, and those of Ag–Ag and Ag-In are almost the same. Above results of In-rich side seem to indicate that the structure is described in terms of the hard sphere mixture.

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