Instructions for use

Liquid structure of Rb-Hg alloys studied by neutron diffraction

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Abstract

The structures of liquid Hg-Rb alloys were studied as a function of composition with neutron diffraction. In the intermediate Rb concentration range, the obtained structure factors show a small prepeak, which may be evidence of the formation of Hg polyanion units in liquids. The reverse Monte Carlo (RMC) analysis was applied to separate the total radial distribution function into corresponding partial radial distribution functions. Up to 10 at.% Rb, no obvious changes are found for the first peak position of the partial radial distribution functions of the Hg-Hg pair and that of the Hg-Rb pair. Above 20 at. % Rb, the increase of the first peak position between the Hg-Rb pairs appears. At 60 at. % Rb, the nearest neighbor distance between Hg and Hg shows the closest value in the concentration range studied. These results indicate that with the proceeding of charge transfer the solvation structure in the dilute Rb concentration range changes into the structure containing the polyanion formation, composed of Hg species.

1. Introduction

Liquid alkali metal-mercury binary alloys show peculiar behavior in various physicochemical properties. Typical examples are shown on the concentration dependence curve of the thermoelectric power [1-3], the electrical resistivity [4,5], the magnetic susceptibility [6], the molar volume and the thermal expansion coefficient [4,7]. Among these the most curious phenomenon is the existence of a deep minimum in the concentration dependence curve of the thermoelectric power, which can be observed at a few (~5) at. % of the alkali metal such as Li, Na, K, Rb and Cs [1,2]. As for the electrical resistivity, it increases drastically with the addition of alkali metal to mercury and shows a small hump around 5 at. % alkali in the concentration dependence curve. On the more addition of alkali metals, it increases gradually and shows a maximum at 60 at. % alkali commonly to the liquid alkali-Hg binary systems [4,5]. Therefore, between 5 and 60 at. % alkali, a variation of the curvature can be observed around 20 at. % alkali in the concentration dependence curve of the electrical resistivity.

With respect to these curious phenomena, it has been pointed out that the crossover of the structures between the alkali-rich range and the Hg-rich range appears at about 20 at. % alkali in the isotherm curve of the electrical resistivity for liquid alkali-Hg alloys [4]. In the dilute alkali concentration range the solvation structure was speculated by taking into account the partial charge transfer from the alkali atom to Hg atoms, which was caused by the large difference in the electronegativity (for the present system, Pauling's value is 0.82 for Rb and is 2.0 for Hg [8]). In the intermediate alkali concentration range, the formation of a polyanion, such as Hg_4^{6-} found in the solid Na-Hg alloy [9], was speculated.

Recently, the XAS (x-ray absorption spectroscopy) study for liquid Rb-Hg alloys has been performed and indicated the formation of polyanionic units of Hg in the concentration range over 37 at.% Rb [10]. Below 37 at. % Rb, however, the data were not obtained because of the

experimental limitation of the transmission measurement for the high x-ray absorption of Hg atoms. In addition, a detailed analysis on the structure of liquid alkali-Hg alloys has not yet been performed, especially in the dilute alkali concentration range.

In order to obtain a better understanding of the structure and the properties of liquid alkali-Hg alloys, a neutron diffraction experiment has been carried out for liquid Rb-Hg alloys as a function of composition near the melting temperature. In this study, the structure analysis was mainly focused on the concentration range from dilute concentration region to the intermediate Rb concentration one.

2. Experimental

Alloy samples were made by mixing pure constituent elements (Rb 99.9 %, Hg 99.99 %) in an Ar gas filled glove box to prevent the contamination such as oxidation. Different compositions (x=5, 10, 20, 30, 40, 60 for Rb_xHg_{100-x}) of alloys were prepared by weighing the required quantities of each element. These samples were sealed under vacuum in a cylindrical quartz glass cell made for the present diffraction experiment.

The neutron diffraction experiments were performed with the use of the D4c diffractometer [11] at the Institut Laue-Langevin, Grenoble, France. The incident wavelength of the neutrons was 0.7021 Å and the scattered neutrons were counted by using the nine microstrip detectors, which are placed in a fan-shaped array from the sample position. The covered range of wave number, q, which is related to the momentum transfer, was from 0.3 to 16.6 $Å^{-1}$. The neutron diffraction measurements were carried out at 20-40 K higher temperature than the respective melting temperature of the sample alloy. To obtain the concentration homogeneity in liquid samples for the measurements, alloy samples were kept for a few hours at 50-100 K higher temperatures than their respective melting temperatures [12]. Data acquisition was repeated for which the stability of scattered intensity was kept to be satisfactory by comparing the

spectrum of each run.

To extract the structure factor, $S(q)$, standard procedures were applied for the measured intensity, including corrections for the self-absorption [13], the multiple scattering [14], the inelasticity [15] and the incoherent scattering [16]. The normalization was completed by using the data of a vanadium rod measured in the similar manner as the sample. For these corrections, the appropriate experimental density was used for the corresponding compositions of sample and temperatures [4]. The Fourier back transform was performed to reduce the normalization error and unphysical ripples in the radial distribution function (RDF), $g(r)$ [17].

In order to obtain the information of the partial radial distribution functions (or the partial structure factors), the obtained total structure factors were analyzed by means of the reverse Monte Carlo simulation (RMC) [18]. The particle number of 4000 was set in the cubic box, whose size was determined by the experimental density [4]. The cutoff distance was initially chosen to be 1 Å smaller than the distances of the first peak position of $g(r)$, which is obtained from the present experiment in pure liquid states of each constitute metal.

3. Results

The total structure factor, $S(q)$, of liquid Rb-Hg alloys is shown in Fig. 1 as a function of composition. Though some dispersion of the data is observed around 5, 7, 9,11, 13 and 15 Å because of a systematic error due to the overlap of the detectors with the different efficiency, the dispersion was reasonably reduced by Fourier back transform as can be seen in the figure. This indicates that important structure information of the alloys was not included in the present dispersed data. Accordingly, the reliable $S(q)$'s were obtained for liquid Rb-Hg alloys even in the rich concentration range of Hg, which is a highly neutron absorbing nucleus. As is shown in Fig. 1, the position of the first main peak and the second peak of $S(q)$ are shifted to

lower q values with the increase of Rb concentration. In addition, the width of the first main peak broadens and the oscillation is damped gradually on increasing the Rb content. From 30 to 60 at.% Rb, it should be noted that a small prepeak appears at lower q region (around 1 Å^{-1}) than that of the first main peak. It can be also observed that the prepeak is gradually pronounced with the increase of Rb concentration from 20 at. % Rb to 60 at.% Rb.

4. Discussion

The existence of the prepeak in $S(q)$ has been currently considered to be the evidence of the formation of polyanion, which is typically found for liquid K-Pb, Rb-Pb and Cs-Pb alloys at the equiatomic composition [19]. In the present case, even though the prepeak height of liquid Rb-Hg alloys is lower than that of these liquid alkali-lead alloys, the polyanion formation may occur and may be most probable at 60 at. % Rb, as also discussed later.

The total radial distribution function, $g(r)$, was obtained from the corrected $S(q)$ in terms of the Fourier transform, as shown in Fig. 2. The first peak of $g(r)$ around 3 Å corresponds to the Hg-Hg correlation and remains to be present even for lower Hg concentration of 60 at.% Rb. The peaks in the q range of 3.4-3.7 Å are observed from 30 at.% Rb to 60 at. %Rb and the peak height is pronounced gradually with the increase of Rb concentration. These peaks are situated between the first peaks in the constituent pure liquid states, 3.03 Å for Hg-Hg at 298 K (obtained from the present experiment) and 5.1 Å for Rb-Rb at 313 K [20]. These peaks are found to be related to the correlation of Hg-Hg pair, as discussed later.

The height of the second peak of $g(r)$ in liquid Hg in Fig. 2 decreases with the increase of Rb concentration over 20 at.%. In addition, with the increase of Rb content, the depth after the first main peak decreases and a width of the second peak broadens. This can be considered as the appearance of a correlation of the intermediate range order. Moreover, it is found that the

peak position of Hg-Hg correlation is slightly shifted to lower value of r with the increase of Rb content up to 60 at.% Rb.

Figure 3 shows the partial radial distribution functions, $g_{\alpha\beta}(r)$'s, for liquid Hg alloy containing 5 at. % Rb obtained by the RMC simulation. The first neighbor distance of Rb-Hg pairs is close to that of Hg-Hg pairs. On the other hand, the reliability of the $g_{RbRb}(r)$ is rather insufficient due to small numbers of Rb atoms in the alloy and the smaller neutron scattering cross section of Rb nuclei than that of Hg nuclei. The Hg-Rb-Hg bond angle distribution within 4.5 Å (corresponds to the first minimum of the $g_{RbHg}(r)$) obtained from the corresponding atomic configuration is shown as an inset in Fig.3. It can be seen that a peak is pronounced around 55 deg., which is slightly shifted to lower angle from 60 deg. to be estimated from the normal closest packed distribution of same size atoms. In addition, the average coordination number of Hg atoms around Rb atom within 4.5 Å was obtained as 14.4. These results indicate that Hg atoms distributed closely around a Rb atom. This may be derived from the charge transfer from Rb atoms to Hg ones [4].

Figure 4 shows partial structure factors, $S_{\alpha\beta}(q)$'s obtained for liquid $Rb_{40}Hg_{60}$ alloy by the RMC simulation. The small prepeak in the total $S(q)$ was well reproduced by the RMC fitting as can be seen in the inset. From the partial structure factors, it turns out that the prepeak is derived from the $S_{HgHg}(q)$ and the $S_{HgRb}(q)$. Figure 5 shows partial radial distribution functions corresponding to the partial structure factors in Fig.4. In Fig.5, the Hg-Hg-Hg bond angle distribution within 4.0 Å is also demonstrated as an inset. It can be seen that an additional sub-peak of the $g_{HgHg}(r)$ pair appears around 3.7 Å. Hereafter, the first peak of Hg-Hg pair is called as Hg-Hg peak (1) and the sub-peak of Hg-Hg is called as Hg-Hg peak (2). The Hg-Hg peak (2) in the $g_{HgHg}(r)$ was observed above 30 at. % Rb concentration. In Fig. 2 the peaks in the distance of 3.4-3.7 Å are found to appear from 30 to 60 at. % Rb. These peaks correspond to Hg-Hg peak (2). The first peak of the $g_{HgHg}(r)$ moves inwardly and that

of the $g_{HgRb}(r)$ moves outwardly. On the other hand, the average coordination number of Hg atoms around a Hg atom was obtained as 3.9, which is lower than the average coordination number 7.2 estimated from a simple substitutional model assumption without taking into account the difference of the size of atoms. These results indicate that the further charge transfer from Rb atoms to Hg atoms induces the Hg polyanion formation. That is, compared with the case of 5 at.% Rb liquids, the closer distance between Hg atoms may appear in polyanion units, whereas the coordination number is decreased. Rb atoms may be more distant each other because of the existence of polyanion units among them.

Figure 6 shows the concentration dependence of the peak position of $g_{\alpha\beta}(r)$ obtained for liquid Rb-Hg alloys by the RMC simulation. It can be seen that the first peak positions of the $g_{HgHg}(r)$ and that of the $g_{HgRb}(r)$ are nearly constant in the dilute Rb concentration range up to 10 at.% Rb. In this concentration range, since the atomic volume increases with the addition of Rb [4], the average distances of each pair should be increased if we adopt the uniform dilatation assumption of volume. Therefore, the present result indicates that liquid Hg containing dilute Rb may have a structure in which the Rb atom is surrounded compactly by the Hg atoms, such as the solvation structure. Such a view was observed in a snapshot of the atomic configuration in the RMC analysis.

As can be seen in Fig. 6, with the increase of Rb concentration, the Hg-Hg nearest neighbor distance (Hg-Hg peak (1)) decreases and the Hg-Rb nearest neighbor distance increases abruptly around 20 at.% Rb, and then these changes continues gradually up to 60 at.% Rb. In addition, a sub-peak of Hg-Hg pair appears over 30 at. % Rb. The Hg-Rb and Hg-Hg (1) distances at $Hg_{40}Rb_{60}$ in Fig. 6 are consistent with the mean atomic distance of Hg-Rb (3.60 Å) and of Hg-Hg (2.95 Å) obtained by the XAS study [10], which also supported the existence of polyanions composed of Hg atoms. At present the distance of Hg-Hg peak (2) is not clear. At 60 at. % Rb, the ratio of the distance of peak (2) to that of peak (1) can be

estimated to be 1.40, which is very close to $\sqrt{2}$. This implies that the square structure for polyanions of Hg atoms is formed, which contributes to the broadening of the bond angle distribution. Nothing to say, more detailed consideration should be performed for the meaning of Hg-Hg peak (2).

The interatomic distance between Hg and Rb (3.6~3.7 Å) in Fig. 5 is less than 4.0 Å which is the average atomic distance between Hg-Hg and Rb-Rb. This also implies the strong charge transfer and the polyanion formation in intermediate Rb concentration range. In the concentration range studied here, at 60 at. % Rb, the distance of Hg-Hg peak (1) shows a minimum value and that of Hg-Rb peak shows a maximum value. The polyanion formation may accomplish at 60 at. % Rb at which the very small value is found for the distance of Hg-Hg peak (1). The accomplishment of the polyanion formation may be responsible to the maximum of the electrical resistivity at this concentration for all alkali-mercury alloys.

5. Conclusions

The structure factors of liquid Rb-Hg alloys were obtained as a function of composition with the neutron diffraction. In terms of the concentration dependence of the pair distribution function, it is revealed that the structural change may be occurred drastically from the dilute Rb concentration to the intermediate Rb concentration range. In this study, the partial pair distribution functions for each constituent are extracted with the use of the RMC method. The concentration dependence of the peak distance of the partial radial distribution functions suggest that the crossover of the structures exists around 20 at. % Rb. In addition, the existence of polyanionic units of Hg, which was indicated by the prepeak of the structure factor, was suggested also from the peak positions in the partial pair distribution function.

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Figures captions

Fig.1 Concentration dependence of the static structure factor $S(q)$ obtained for liquid Rb-Hg alloys above the melting temperature. Dots represent the measured data and lines indicate the corrected data by the Fourier back transform. The deviations between them are within 0.5 % for pure Hg and within 1 % for $Rb_{60}Hg_{40}$.

Fig.2 The radial distribution function, g(r), of liquid Rb-Hg alloys plotted as a function of composition.

Fig.3 Partial radial distribution functions, $g_{\alpha\beta}(r)$'s, obtained from the RMC simulation for liquid Rb_5Hg_{95} alloy. The Hg-Rb-Hg bond angle distribution within 4.5 Å obtained from the corresponding atomic configuration is shown as an inset.

Fig.4 Partial structure factors, $S_{\alpha\beta}(q)$'s, obtained from the RMC simulation for liquid $Rb_{40}Hg_{60}$ alloy. Comparison between the experimental total structure factor (circles) and the fitting result (solid line) is shown as an inset.

Fig.5 Partial radial distribution functions, $g_{\alpha\beta}(r)$'s, obtained from the RMC simulation for liquid $Rb_{40}Hg_{60}$ alloy. The Hg-Hg-Hg bond angle distribution within 4.0 Å obtained from the corresponding atomic configuration is shown as an inset.

Fig.6 Evolution of the peak position of the partial radial distribution functions, $g_{\alpha\beta}(r)$'s, obtained for liquid Rb-Hg alloys as a function of composition.

Structure factor, $S(Q)$ plotted against $Q/$ Å^{-1}

Rb$_{60}$Hg$_{40}$ at 453 K

Rb$_{40}$Hg$_{60}$ at 533 K

Rb$_{30}$Hg$_{70}$ at 543 K

Rb$_{20}$Hg$_{80}$ at 483 K

Rb$_{10}$Hg$_{90}$ at 408 K

Rb$_5$Hg$_{95}$ at 373 K

Hg at 293 K

Rb$_{60}$Hg$_{40}$

Rb$_{40}$Hg$_{60}$

Rb$_{30}$Hg$_{70}$

Rb$_{20}$Hg$_{80}$

Rb$_{10}$Hg$_{90}$

Rb$_5$Hg$_{95}$

Hg

Radial distribution function, $g(r)$

$r/$ Å

Partial RDF $g_{\alpha,\beta}(r)$ vs Distance r / Å^{-1}

Inset: $P(\theta)$ vs θ(deg.)

Legend: Rb-Rb, Rb-Hg, Hg-Hg