The Structure of Liquid Hg-Na and Hg-K Alloys

The Structure of Liquid Hg–Na and Hg–K Alloys*

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Synopsis

The X-ray scattering intensity of liquid Hg-Na and Hg-K alloys have been measured along their liquidus temperatures. The change in the total structure factors by alloying is small up to 70 at.% of alkali metals in both systems, although the category of compound forming has been frequently discussed in these liquid alloys. The partial structure factors of these alloys were also obtained assuming that each partial structure is independent of concentration at their liqudius temperatures. The partial structure factor of mercury atom pairs in both alloy systems showed the deviation from that of pure liquid mercury, i.e., the profile of the partial structure factor was more like that of the hard sphere fluids.

I. Introduction

The electron transport properties of liquid Hg-Na and Hg-K alloys have shown anomalous behaviour (Faber[1]). The knowledge of the structure factors of these alloys have long been required in concerning the above facts. The neutron diffraction for the mercury alloys is incapable because of large absorption for neutrons by mercury atoms and therefore the measurements of X-ray scattering intensity are most convenient way to obtain the structure factors of the mercury alloys.

Schuhmann[2] has reported X-ray diffraction study of liquid NaHg at 225°C, $NaHg_5$, KHg_5 and KHg at 200°C, and KHg_2 at 300°C. They are of considerable interest, but the accuracy of his results is still limited to allow a reliable interpretation, because the peak profile of his intensity data shows too much deviation from those of various liquid metal alloys reported previously. As pointed out by Faber[1], it is more convenient to measure the X-ray scattering intensity along the liquidus temperature of these alloys, since the structure factor varies as a function of $(T\text{-}T_m)$, T_m being the liquidus temperature.

The main purpose of this work is to provide the structure factors of liquid Hg-Na and Hg-K alloys along the liquidus temperatures by means of the X-ray diffraction technique.

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(1) T.E. Faber, *An Introduction to the Theory of Liquid Metals*, London, Cambridge University Press (1972).

(2) H. Schuhmann, Z. anorg. allgem. Chem., **317** (1962), 204.

II. Experimental procedures

The experimental set-up, as well as the procedures for handling the X-ray scattering intensities, the correction of the observed intensity data, and its analysis, are essentially the same as the procedures employed in our previous works (Waseda and Tamaki[3,4]) and is therefore not duplicated here. The samples were melted in 18/8 stainless steel crucible with thin-walled window made of beryllium containing pyroritic graphite supports. The materials used had the following purities: Na and K (99.95%) and Hg (99.99%).

III. Results and discussion

The angular range measured corresponds to a range from $Q=0.5$ to $Q=15.0$ Å^{-1}, where $Q=4\pi \sin\theta/\lambda$. The uncertainty in the structure factor obtained in this work is as follows. According to the usual method for evaluating errors in normalization proposed by Rahman[5] and the detailed discussion for systematic errors in X-ray diffraction of liquid metals by Greenfield *et al.*,[6] the total error in the structure factor $S(Q)$ was estimated to be 2.3%. Thus the error bars in the

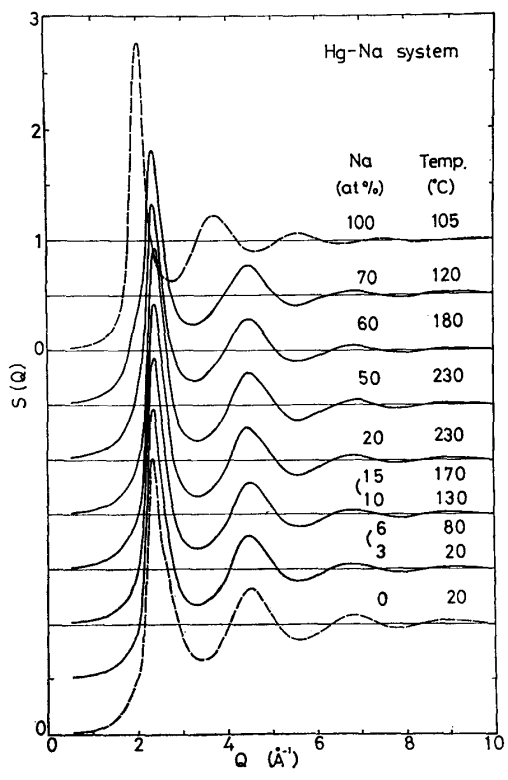

Fig. 1.

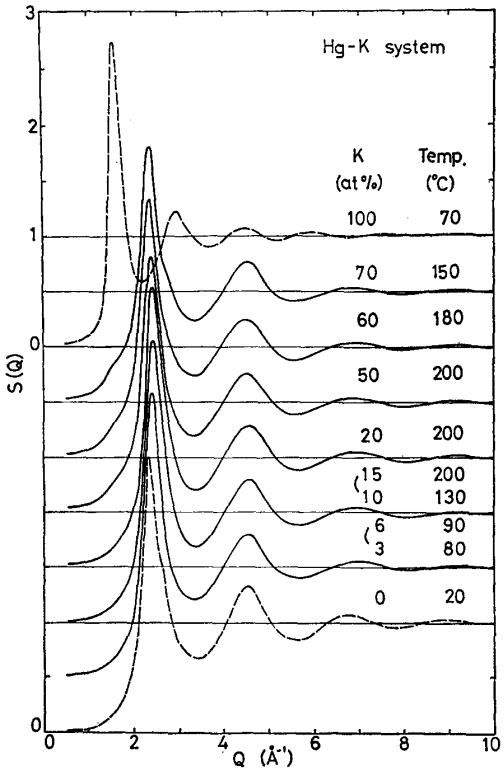

Fig. 2.

Fig. 1. Total structure factors of liquid Hg-Na alloys.
Fig. 2. Total structure factors of liquid Hg-K alloys.

(3) Y. Waseda and S. Tamaki, Philos. Mag., **32** (1975), 273.
(4) Y. Waseda and S. Tamaki, Z. Naturforsch., **30a** (1975), 1655.
(5) A. Rahman, J. Chem. Phys., **42** (1965), 3540.

value of $S(Q)$ are of order of ± 0.7 over the first peak, ± 0.03 near the value of $Q=4.0$ Å^{-1} and ± 0.02 beyond $Q=6.0$ Å^{-1}.

The measurements of the Hg-Na and Hg-K systems were carried out over the composition with 3, 6, 10, 15, 20, 50, 60, 70 and 100 at. % of Na and K at temperatures about 30°C above their liquidus. The obtained total structure factors of these liquid alloys are shown in Figs. 1 and 2. The basic profile of the total structure factors for alloys up to 70 at. % of alkali metal are rather similar to that of pure liquid mercury. This implies that the alloying would be attained by the substitutional configuration rather than the interstitial one, in both liquid Hg-Na and Hg-K alloys. However, the value of the total structure factor for liquid alloys beyond the alkali metal concentration of 50/50 toward the alkali metal rich side is asymmetric, in which the low Q region of the first peak is less steep than the high Q region. This behaviour was also confirmed by the measurements with Cu ratiation. In this analysis, the separation of the scattered intensity from the primary beam in the low angle region ($Q \leq 1.5$Å^{-1}), the correction for air scattering and absorption and the elimination of the Laue monotonic scattering term to evaluate the total structure factor were carefully taken account of. The asymmetric first peak observed may be related to the contribution of alkali metal atoms. The difference of the structure factor between 3 and 6 at. % Na and K and that between 10 and 15 at. % Na and K were not quantitatively observed because of lying within the experimental error. It is noted, however, that the characteristic structure of pure liquid mercury, so-called shoulder at about $Q=2.6$ Å^{-1} disappears with the addition of a small amount of alkali metals (3 and 6 at. % Na and K).

Since the change of the total structure factors of these alloys is gradual, on going from pure mercury to alloys of 70 at. % Na and K, the concentration dependence of the partial structure factors seems to be small. Assuming each structure factor is almost independent of the relative abundance of the constituent elements in these alloys in a certain composition range, say 3 (or 6), 10 (or 15) 20 at. % of alkali metals, then the partial structure factors are able to be estimated. However, the temperature dependence of the structure factor of liquid metals is fairly remarkable and it might be doubtful to use the isothermal data for evaluating the partial structure factors, if the liquidus temperature is drastically changed by alloying. In the Hg-Na system, the liquidus temperature of 10 at. % Na alloy is nearly equal to 100°C and thus its structure factor is considered to be blurred with increase of temperature up to 360°C which is close to the melting point (350°C) for $NaHg_2$. A similar situation is maintained in the Hg-K system, some of physical quantities relating to the structure factors of liquid metals are experimentally reduced to unified values at their melting points. For example, the packing density of various liquid metals near the melting point is around 0.45 if the first peak of the structure factor is fitted to the hard sphere model. In this sense, it is reasonably accepted the assumption of the concentration independence for the partial structure factors along the liquidus temperatures.

Based on this idea, the partial structure factors $S_{ij}(Q)$ in liquid Hg-Na and Hg-K alloys were estimated from the data for 3 (or 6), 10 (or 15) and 20 at. % of Na and K. The results are given in Figs. 3 and 4. It has been confirmed that these partial structure factors also reproduce the total structure factors of the alloys in

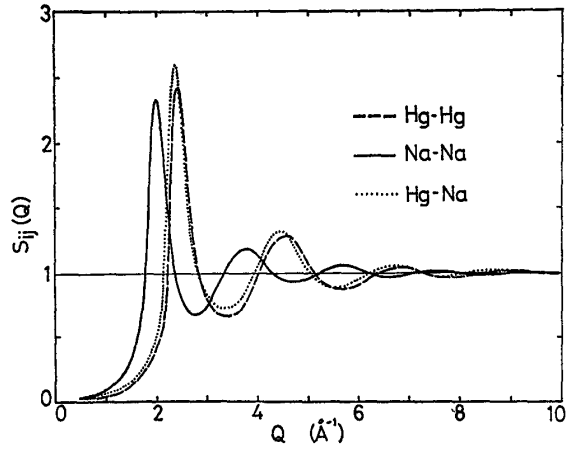

Fig. 3. Partial structure factors of liquid Hg-Na alloys.

the composition range from 50 to 70 at. % of Na and K, within the error of the present measurements. This fact strongly supports that our method for the derivation of the partial structure factors is reasonably accepted.

The profile of the partial structure factors of like atom pairs of alkali metals, $S_{Na-Na}(Q)$ and $S_{K-K}(Q)$ is close to those of pure sodium and potassium (Greenfield *et al.*[6]), although the decrease in the peak height is observed. On the other hand,

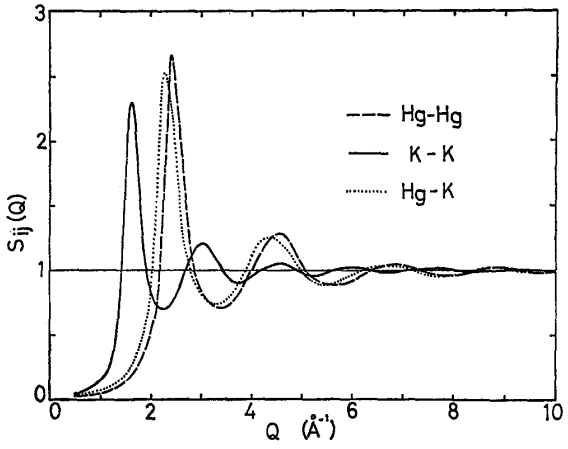

Fig. 4. Partial structure factors of liquid Hg-K alloys.

the partial structure factors of unlike atom pairs, $S_{Hg-Na}(Q)$ and $S_{Hg-K}(Q)$ are no closer to the average values between those of two like atom pairs than are the partial structure factor of mercury atom pairs, $S_{Hg-Hg}(Q)$. Such behaviour which

(6) A.J. Greenfield, J. Wellendorf and N. Wiser, Phys. Rev. A, **4** (1971), 1607.

corresponds to the deviation from the distribution of random mixture, has been observed in some liquid alloys (Waseda[7]). One of the most striking results in the present work is the fact that the partial structure factor of mercury atom pairs $S_{Hg-Hg}(Q)$ in liquid Hg-Na and Hg-K alloys differs from that of pure liquid mercury as shown in Fig. 5. Namely the partial structure factor of mercury atom pairs shows the following characteristic features; the first peak shifts toward the high Q direction and thus the profile of the first peak becomes more like to that of the hard sphere model (Aschroft and Lekner[8]). This contrasts with the structure factor of pure liquid mercury.

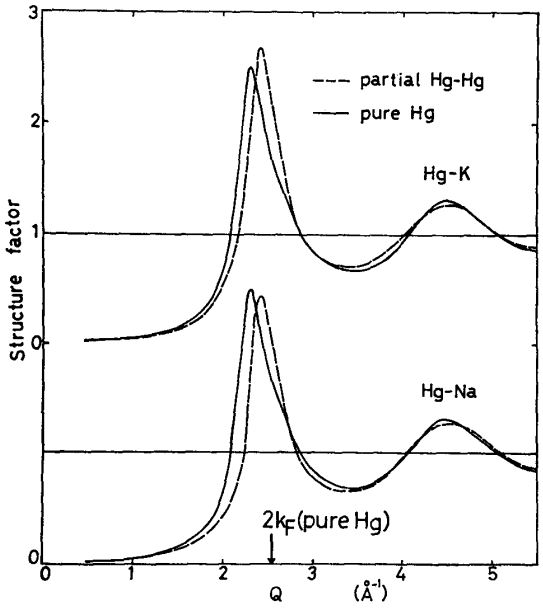

Fig. 5. Comparison of the partial structure factor of mercury atom pairs in liquid Hg-Na and Hg-K with the structure factor of pure liquid mercury.

The electron transport properties of liquid Hg-Na and Hg-K alloys show somewhat complicated features; the electrical resistivity isotherm for these alloys has a maximum at a small amount of alkali concentrations around 6 at. % and it decreases down until the composition of $NaHg_2$ or KHg_2. In the concentration range from MHg_2 to M, M being alkali metals, the curve of resistivity isotherm shows ordinal parabora (Müller[9]). The thermoelectric power isotherm of liquid Hg-K alloys gives a similar behaviour (Fielder[10], Itami and Shimoji[11]). Regarding these behaviour in the electron transport properties, liquid Hg-Na and Hg-K alloys are classified into the category of compound-forming alloys from the thermodynami-

(7) Y. Waseda, Proc. 3rd Inter. Conf. on Liquid Metals, Bristol, The Inst. Phys. Conf. Ser., No. 30 (1977), 230.
(8) N.W. Ashcroft and J. Lekner, Phys. Rev., **145** (1966), 83.
(9) P. Müller, Metallurgie, **7** (1910), 730.
(10) M.L. Fielder, Adv. Phys., **16** (1967), 681.
(11) T. Itami and M. Shimoji, Philos. Mag., **28** (1973), 85.

cal point of view (Hultgren *et al.*[12]). In concerning with the above facts, the following qualitative comments could be derived from the structural information obtained in this work within the framework of the Ziman nearly free electron theory.

The increase of the resistivity isotherm by the addition of a small amount of alkali metals into liquid mercury may be related to the shift of the first peak in the partial structure factor of mercury atom pairs (see Fig. 5), i.e., the position of the first peak approaches to the value of $2k_F$ (k_F: Fermi wave vector) by alloying so as to yield a large contribution to the resistivity increment. As mentioned previously, the present structural data suggest that the alloying in both systems seem to be substitutional type, thus the category of the compound-forming at $NaHg_2$ or KHg_2 is rather likely to be an idea of ordered structure. In addition, these liquid alloys have no correlation of pseudogap (Mott[13]) in the electronic structure, because the numbers of their valence electrons are lying between one and two. Therefore, it is well accepted that there is no extraordinary resistivity increase in these alloys, which is consistent with the experimental facts. A more detailed discussion with respect to the relationship between structure and electron transport properties will be given in elsewhere.

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(12) R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser and K.K. Kelly, *Selected Values of the Thermodynamic Properties of Binary Alloys*, Ohio, American Soc. for Metals (1973).

(13) N.F. Mott, Philos. Mag., **13** (1966), 989.