Structures of Liquid Mercury and Dilute Liquid Mercury Alloys *

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The structures of liquid Hg and the dilute liquid Hg alloys with 0.5 and 2 atomic percent Cd, and 0.5 and 1 atomic percent Pb have been studied by x-ray diffraction using a theta-theta diffractometer with monochromator in the diffracted beam. The addition of 0.5 or 2 atomic percent Cd into Hg did not produce any detectable change in the interference function $I(K)$, where $K=4\pi(\sin\Theta)/\lambda$, whereas small additions of Pb seem to reduce the asymmetry of the first peak of $I(K)$ which is observed in pure Hg. Small additions of Pb also cause a slight shift of the second peak of $I(K)$ to smaller K-values. The present results have been used to offer a possible interpretation of the structure of Hg as observed in the liquid state.

Both theoretically and experimentally Hg occupies a unique place among other group II B metals. The Fermi energy of Hg is relatively high which prevents it from crystallizing in the regular hcp sequence similar to that of Zn and Cd. The solid Hg has two stable phases [1]. The α phase is rhombohedral ($a=2.993$ Å and $\beta=70°\,45'$) and stable to absolute zero under normal pressure. A phase transition from the α-phase to the β-phase which is a body centered tetragonal ($a=3.995$ Å and $c=2.825$ Å) takes place at higher pressures. Once it is formed, β-Hg is more stable than α-Hg below 70 °K at atmospheric pressure.

RIVLIN et al. [3] have recently studied liquid Hg and concluded that two correlation distances 3.07 Å and 2.85 Å exist in the liquid. They correlated these distances to the closest approach of the atoms in the two solid allotropes α- and β-Hg. RICHTER and BREITLING [3] deduced two distances of 3.04 Å and 2.86 Å from the analysis of the radial distribution function. This result, however, has not been reported previously [4–8]. MOTT [9] suggested that the intensity pattern of liquid Hg, which shows a subsidiary maximum or shoulder on the high angle side of the main peak, should change upon alloying to a structure similar to that of simple liquid metals. If this effect were found to be true, it should indicate that the liquid state of Hg was not as simple as it had been already thought in the past. ABOWITZ and GORDON [10] measured the sonic velocity, mass density and thermal expansion coefficient in a number of dilute liquid alloys of Hg and suggested that the structure of liquid Hg breaks down when presence of the solute atoms does not favor the covalent bonding in Hg any longer.

We therefore decided to study the effect on the structure of liquid Hg of adding a few solute atoms. The x-ray scattered intensities from dilute alloys of Hg – Cd and Hg – Pb were recorded. The results are discussed below.

1. Record of the Intensity Patterns

The experimental method of measurements of the scattered intensity was similar to that described previously [11], i. e., theta-theta diffractometer with statio-

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nary, horizontal sample and quartz crystal monochromator in the diffracted beam. The alloy samples were prepared using 99.999% pure Cd and Pb with 99.99% pure Hg at room temperature. The method of preparation has been described earlier [8, 12].

The scattered intensities from these liquids were recorded between $K = 4\pi(\sin\Theta)/\lambda = 1.5$ to 15.7 Å^{-1} and all corrections arising from diffraction geometry and sample positioning were applied. Then the intensity patterns were used to calculate the interference function $I(K)$:

$$I(K) = 1 + \int_0^\infty 4\pi r^2[\varrho(r) - \varrho_0]\frac{\sin K r}{K r}\,dr$$

where $\varrho(r)$ and ϱ_0 are respectively the weighted radial density and average density of the alloy which have been defined before (HALDER et al. [8]). In Fig. 1 are shown the plots of $I(K)$ for liquid Hg

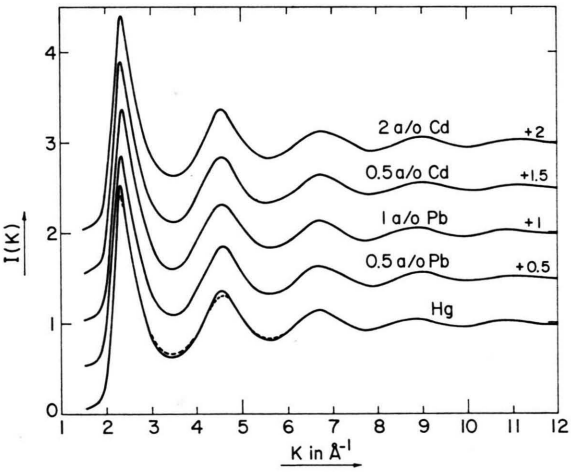

Fig. 1. Interference function $I(K)$ of liquid Hg, Hg—0.5 a/o Pb, Hg—1.0 a/o Pb, Hg—0.5 a/o Cd and Hg—2.0 a/o Cd.

and its alloys. The Fourier transform of $I(K)$ yielded the reduced distribution function $G(r)$:

$$G(r) = 4\pi r[\varrho(r) - \varrho_0] = \frac{2}{\pi}\int_0^\infty K[I(K) - 1]\sin(K r)\,dK .$$

These are indistinguishable from those of Hg which have been published previously [8, 12].

2. Effect of Alloying on the Interference Functions

The interference function reflects the arrangement of the atoms in the liquid and is a measure of the constructive interference of the neighboring atoms within a certain distance r from an arbitrary reference atom. It is related to the Fourier transform of the atomic distribution $\varrho(r)$ which is affected by changing the size and number of atoms within the first coordination shell. If there is any change in the structure of a metal or alloy in the liquid state, we should be able to see it on the interference function plots provided the change is large enough to be distinguishable from the spurious fluctuations resulting from the experimental and computational errors.

The $I(K)$ patterns of most liquid metals, at a glance, look similar. For liquid metals which exhibit close packed structure and might be called "normal" liquids such as Ag, Tl, Pb and In, the first peak of $I(K)$ is quite symmetrical and the ratio K_2/K_1 (see Table 1) of the positions of the first peak maximum K_1 (calculated from the apex position of the para-

Alloys	Atomic Percent	K_1 Å^{-1}	$K_2' = K_2/K_1$
Hg–Cd alloys	0.5	2,32 ± 0.02	1.96 ± 0.02
	2.0	2.32	1.94
Hg–Pb alloys	0.5	2.35	1.95
	1.0	2.34	1.93
Hg–Tl alloys	5	2.31	1.97
	16	2.30	1.97
	28.6	2.30	1.92
	40	2.28	1.90
Hg–In alloys	5	2.34	1.95
	12	2.34	1.94
	25	2.33	1.94
	35	2.30	1.94
	42	2.31	1.94
	50	2.32	1.93
	62	2.30	1.93
Pure metals	Hard sphere (0.35 packing) density)	—	1.96
	Hg (25 °C)	2.32	1.97
	Sn (335)	2.27	1.90
	Tl (350)	2.26	1.87
	In (170)	2.30	1.87
	Pb (340)	2.20	1.87
	Ag (1050)	2.62	1.86
	Hard sphere (0.45 packing density)	—	1.86

Table 1. The positions of the first and second maxima of the interference function curves. The values K_1 and K_2 have been obtained from the position of the apex of the parabola calculated with three points near the peak maximum. The atomic percentages of the solute atoms Cd, Pb, Tl and In are only given.

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bola obtained with 3 points near the peak maximum) to the second peak maximum K_2 is a constant ($\cong 1.86$). This value agrees with that obtained from the theoretical interference function using the Percus-Yevick equation with packing density $\eta = 0.45$ [13].

The evidence from x-ray and neutron diffraction is that $I(K)$ for liquid Hg is significantly different from what it is for the "normal" liquids. Thus, most workers agree that the first peak is asymmetric and the value $K_2/K_1 \cong 1.97$ is abnormally high, which can be obtained with the hard sphere model of packing density 0.34. However, the absolute positions K_1 and K_2 of the hard sphere $I(K)$ do not agree with the experimental curve as shown in Fig. 2.

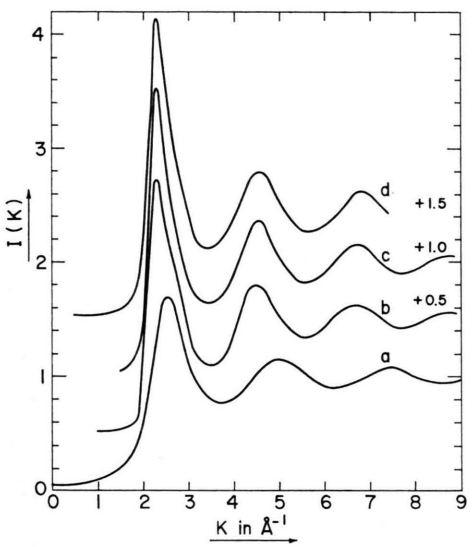

Fig. 2. Interference functions of liquid Hg. a) Hard sphere model with packing density $\eta = 0.35$ and atomic density $\varrho = 0.0407$. b) Model $I(K)$ based on distribution function of KAPLOW et al. [6]. c) $I(K)$ of present investigation. d) $I(K)$ calculated from $I_{eu}^{coh}(K)$ of RIVLIN et al. [2].

The interference functions $I(K)$ of the dilute Hg alloys plotted in Fig. 1, do not show any striking change with alloying. Nevertheless, the values K_2/K_1 given in Table 1 decrease from 1.97 for dilute Hg alloys to a value about 1.90 for Hg – 40 a/o Tl [8] and about 1.93 for Hg – 62 a/o In [12]. The shift of the second peak K_2 towards a smaller value is more rapid in Hg – Pb alloys than in Hg – Cd alloys because the size of Pb atoms (3.50 Å) is larger than that of the Cd atoms (2.97 Å). This effect can readily be noted when plotting $I(K)$ in reduced coordinates $K' = K/K_1$. Such figures show that the asymmetric nature of the first peak of Hg vanishes with the increasing solute concentration.

KAPLOW et al. [6] have calculated the atomic distribution function of liquid Hg with a model based on the structure of solid rhombohedral Hg and showed that their theoretical distribution function $G(r)$ was in agreement with the experimental curve. We have made the Fourier transform of their theoretical distribution function $rG(r)$ and obtained a model $I(K)$ function for Hg. This is also included in Fig. 2. From the published intensity pattern of RIVLIN et al. [2] for Hg we also computed the corresponding $I(K)$ function shown in Fig. 2. Only a small difference in the peak height between the model interference function and those measured experimentally is observed, otherwise all the features of the curves agree very well including the positions of the two maxima. The little quantitative disagreement can perhaps be accounted for by the normalization procedures which are employed to scale the measured intensity into electron units. The model $I(K)$ of KAPLOW et al. [6] is based on the damped and broadened structure of rhombohedral solid Hg with particle size of 40 Å. As can be seen from Fig. 2, it also predicts the asymmetric nature of the first peak. The small hump which RIVLIN et al. [2] called shoulder is the consequence of the distorted rhombohedral structure and can be described by the model which does not require a presupposition of the presence of body centered tetragonal structure of Hg. RICHTER and BREITLING [3] deduced a double structure in liquid Hg from the $G(r)$ function which showed modulation in the shape of the third and fourth maxima. Such modulation is a consequence of minute errors in the interference function $I(K)$. The dotted curve for liquid Hg in Fig. 1 represents an interference function which had been measured on the same theta-theta diffractometer as the one represented by the solid curve. The dotted $I(K)$, however, yields $G(r)$ of similar shape as that shown in Fig. 1 c of the paper by RICHTER and BREITLING [3]. Application of the refinement procedure as proposed by KAPLOW et all. [6] will yield an $I(K)$ eventually indistinguishable from that represented by the solid curve for Hg in Fig. 1.

From this discussion we might suggest that the conclusion that the two allotropes of Hg exist in the liquid is ambiguous.

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3. Evaluation of Electron Transport Properties

An evaluation was made of the electrical resistivity and thermoelectric power of the dilute alloys with the substitutional model of FABER and ZIMAN [14]. In calculating the electrical resistivity ϱ_R and thermoelectric power Q we used the matrix elements of the pseudopotential computed by ANIMALU and HEINE [15] for Hg, Pb and Cd. Recently ASHCROFT and LANGRETH [16] have used a pseudopotential for Hg which deviates markedly from that of ANIMALU and HEINE [15]

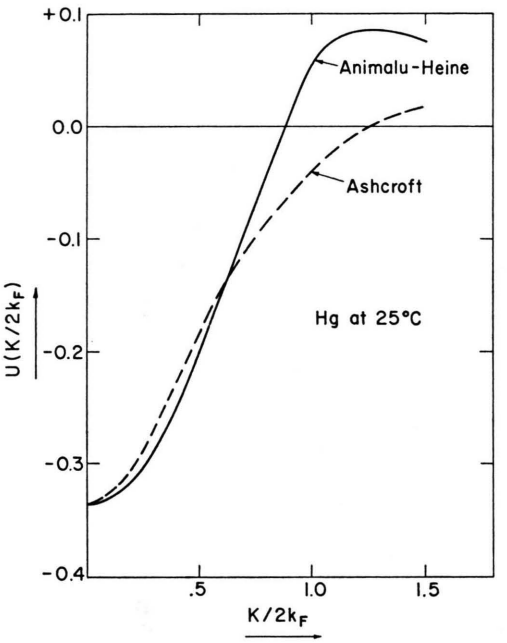

Fig. 3. Pseudopotential elements of Hg. Animalu-Heine [15], Ashcroft (see Ashcroft-Langreth [16]).

Alloys	$2k_F$	ϱ_R	Ashcroft		Animalu	
			ϱ_R	Q	ϱ_R	Q
Hg (pure)	2.68	96	101.9	− 2.26	29.3	1.23
Hg–0.5Cd	2.68	94	104.6	− 2.29	31.2	1.07
Hg–2.0Cd	2.68	92	105.0	− 2.25	32.5	1.20
Hg–0.5Pb	2.68	93	109.4	− 2.26	32.7	0.98
Hg–1.0Pb	2.68	90	103.1	− 2.26	30.6	1.13

Table 2. Resistivity ϱ_R and thermoelectric power Q for dilute alloys of Hg calculated using the measured $I(K)$ and pseudopotential elements of Ashcroft, and Animalu and Heine for Hg, and Animalu and Heine for Pb and Cd. $2k_F$ is in $Å^{-1}$, ϱ_R is in $\mu\Omega$ cm and Q in $\mu V/°K$.

as shown in Fig. 3, but explains some results on Hg, which could not be done with the ANIMALU-HEINE pseudopotential [15]. For this reason we also used here ASHCROFT-LANGRETH pseudopotential elements [16] for Hg. Table 2 shows all these results.

Qualitatively, the asymmetry of the first peak in $I(K)$ seems likely to increase the value of the resistivity predicted by ZIMAN's theory [17] and the measured resistivity for Hg is indeed rather high. This raises the possibility that the well-known fall in resistivity which occurs when small amounts of impurity are added to Hg may be due to the disappearance of the asymmetry [9]. The additions of up to 1 atomic percent of Pb and 2 atomic percent of Cd are sufficient to lower the resistivity by 6 percent and 4 percent, respectively, but small enough to keep the Fermi diameter $2k_F$ fixed. The measured interference function $I(K)$ (Fig. 1) is a weighted mean of three partial interference functions [12]. For small concentrations of these solute atoms the alloy was assumed to be substitutional [12, 14] and hence all partial $I(K)$ were approximately equal to the mean $I(K)$. The changes induced in $I(K)$ by small amounts of Cd and Pb, are very slight, but if K_2/K_1 is used as an index of the shape of the $I(K)$ curve there is some indication that this ratio is reduced, especially by Pb, and that Pb does something to reduce the asymmetry in the first peak.

The large quantitative disagreement (one is about three times the other) between the two sets of ϱ_R obtained with two different pseudopotential elements deserves some discussions. ϱ_R for Hg obtained with the ASHCROFT-LANGRETH pseudopotential elements [16] is in good agreement with the experimental value 96 $\mu\Omega$cm. In previous publications [8, 12] we reported that the ANIMALU-HEINE pseudopotential elements [15] yielded ϱ_R which was about one third the experimental value and suggested that the effect of low density of states for Hg at the Fermi level should be considered. In this context we referred to the hyothesis which has been put forward by MOTT [18] and later supported by BRADLEY [19] and BUSCH and GÜNTHERODT [20] from experimental observations on liquid Hg alloys. Making use of MOTT's idea we were able to explain the low value of ϱ_R for Hg. It

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is now apparent that if ϱ_R were calculated with the ASHCROFT-LANGRETH pseudopotential elements and our measured $I(K)$, the results will be in accordance with those obtained for the other liquid metals.

It must be re-emphasized that the pseudopotentials which are available from the theoretical calculations do not give us any guarantee that they represent uniquely the electron-ion interaction in the liquid metals. A calculation on pseudopotentials can yield the right value of ϱ_R for a liquid metal but may fail to satisfy its many other electronic properties. This is the subject of criticism in a number of publications [21–24]. The most critical region of the pseudopotential elements is the point K_0 where the first node of the pseudopotential elements occurs (Fig. 3). A little adjustment of the position K_0 can bring about a remarkable agreement between the predicted and measured values of ϱ_R. It must be clearly stated that the value of $K_0 = 3.40$ Å^{-1} obtained by ASHCROFT and LANGRETH [16] is much larger than the value of $K_0 = 2.38$ Å^{-1} obtained by ANIMALU and HEINE [15] besides some obvious differences in the sign and magnitudes of the potential elements at $K = 2\,k_F$.

ASHCROFT and LANGRETH [16] rely on a theoretical model for $I(K)$ (the Percus-Yevick equation) which contains as adjustable parameters the effective hard-sphere radii for the ions concerned. In order to secure any sort of agreement for amalgams they are compelled to choose a radius for Hg which corresponds to $\eta = 0.346$ in pure Hg at 20 °C, whereas $\eta = 0.45$ for most liquid metals. Although this value η does reproduce the anomalously high value observed for K_2/K_1 in Hg, it does not accurately reproduce the position and shape of the first peak which is most important. We, therefore, rely on the direct experimental determination of $I(K)$ rather than on the Percus-Yevick hard-sphere model.

The ANIMALU-HEINE pseudopotential [15] for Hg gives quite the wrong answer for pure Hg and for this metal it may be preferable to choose the ASHCROFT-LANGRETH pseudopotential [16], which is deliberately adjusted to give the right answer. But whichever is used, calculations suggest that ϱ_R should be decreased by adding Pb or Cd rather than the reverse.

4. Conclusion

X-Ray scattering from liquid metals which possess a close packed structure in the solid state yields interference functions $I(K)$ which agree well with that of the hard sphere liquid of packing density 0.45, when plotted in reduced coordinates. The asymmetric nature of the first peak of $I(K)$ and a slight shift of the position of the second peak towards a higher value, place Hg outside the general description of most liquid metals. The peak asymmetry and the peak shift of the first and second peak, respectively, disappear very slowly when Hg is alloyed with Cd, Pb, Tl, and In. The interference functions of the dilute alloys are strongly influenced by the Hg structure and fail to indicate distinguishable change in the electrical resistivity and thermoelectric power when a calculation is made with the substitutional model proposed by FABER and ZIMAN [14].

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