The Structure of Mercury†

Nobuya IWAMOTO*, Takashi YAMANE and Satoshi MAEYAMA*****

Abstract

A x-ray diffractometer for the studies of liquid metals has been designed. Measurements up to 1500°C could be carried out, and scanning from 7° to 150° could be reached in this apparatus. The utility of this apparatus was demonstrated by obtaining the radial distribution function of mercury at room temperature and comparing with that reported by several workers. The nearest neighbour distance and first coordination number in present work are 3.07Å and 8.3 atoms (k_{max}= 12.0) respectively. They are in good agreements with those of previous works for mercury.

1. Introduction

Weld metals pass through the sudden transitions from melt to solidification in the course of a welding. Owing to the sudden transitions the quality changes of weld metals are unavoidable. For the improvement of the reliability of a weld zone, however, its quality changes must be controled. Therefore the physical researches of molten metals together with the physical studies of HAZ seem to be important.

The studies for structures and physical properties of liquid metals were undertaken in our laboratory. The x-ray diffraction method is one of the most important methods for the structural studies of liquids. The x-ray diffractometer for the studies of liquids has been constructed in our laboratory. The x-ray studies of mercury have been reported by many workers. Therefore a measurement of mercury was attempted in order to test the apparatus.

2. Apparatus

The x-ray diffractometer for the study of liquid structures requires the sample to be held in a stationary horizontal position. The diffractometer with a Bragg-Brentano focusing system has been designed, for satisfying the requirement. The x-ray source and detector in this diffractometer rotate about the sample in a vertical plane at equal speeds and in opposite directions as shown in **Fig. 1.** The maximum value of 2θ attainable is 150°.

A sample is held in a high temperature furnace chamber, composed of an enclosure and a sample stage. A vacuum of 10^{-5} mmHg can be obtained or gas can be passed through in this chamber. The

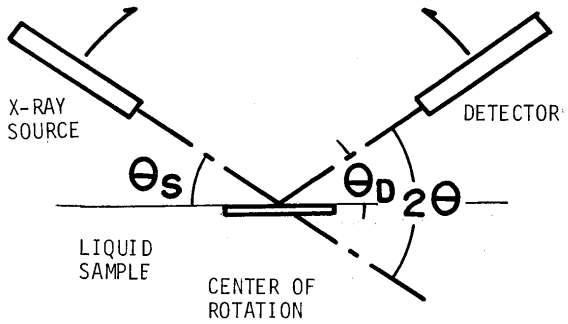

Fig. 1. Diffraction geometry.

x-ray beams entered and left the chamber through a beryllium window, 0.25 mm thick, 12 mm wide, curved to subtend an angle of 200° at the axis of a diffractometer.

The sample stage acts as a heater which heats the crucible directly by means of electric reistance. If molybudenum thin foil is used for a resistance element, a sample could be heated up to 1500°C.

The sample stage together with the crucible, could be adjusted optically from outside the chamber by elevation and azimuthal controls. The alignment was tested with the aid of silicon powder sample. Angular measurements were shown to be accurate to within 1/50° of arc over the whole angular range.

3. Experimental

Diffraction data were obtained with Mo-Kα radiation, using a curved graphite monochromator in the diffracted beam. The x-ray optics is illustrated in **Fig. 2.** The post-sample monocromator removed the fluoresent radiation from the sample. A scintillation counter with pulse-height analyzer was used as the detector.

† Received on Aug. 6, 1973
* Professor
** Research Associate
*** Graduate Student

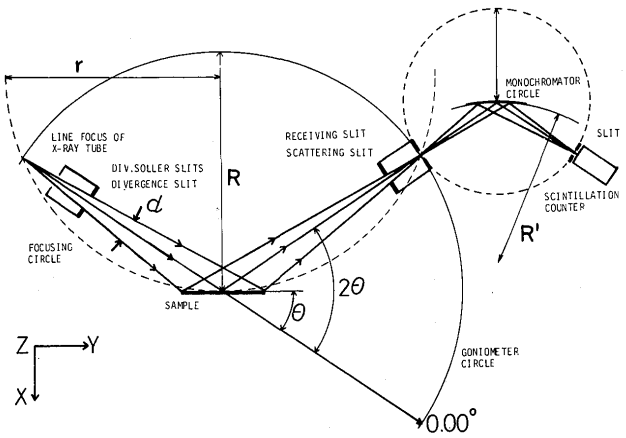

Fig. 2. Focusing conditions.

Mercury of 99.9% purity was distilled under reduced pressure. The sample is contained in an iron crucible of 25mm×25mm, which provided a sufficiently frat surface area, about 20mm×20mm. The crucible was seemed not to be amalgated during the course of a measurement at room temperature (about 23°C). The pressure in the chamber was reduced to 10^{-2}mmHg. Then hydrogen gas was flowed inside the chamber to prevent oxidation of the sample surface.

The divergence of the radiation in the surface plane in Fig. 2 was limited by the divergence slit. As the divergence length of Y direction was settled within 10mm, the following slit system was selected;

$\frac{1}{6}°$ for $7°<2\theta<30°$, $\frac{1}{2}°$ for $30°<2\theta<60°$, and $1°$ for $60°<2\theta<100°$.

Fixed count method was used. Counts were recorded at $\frac{1}{2}°$ intervals (2θ) between 7° and 100°.

4. Analysis and results

The observed intensities $I^{obs}(k)$ in arbitrary units were corrected for background and for polarization of the beam by both the sample and the monochromator. The corrected intensities $I^{cor}(k)$ were normalized to a scale of electron units per atom by the expression

$$I_{eu}^{cor}(k)=K\cdot I^{cor}(k) \tag{1}$$

where $k=4\pi\sin\theta/\lambda$, and K is a normalization constant.

The normalization constant was calculated from the High-Angle region method[1] and the Krogh-Moe-Norman method[2,3]. The corrected intensity can be related to the coherently scattering intensity in electron units I_{eu}^{coh}, and the Compton modified scattering intensity I_{eu}^{inc} by the following equation

$$I_{eu}^{cor}=I_{eu}^{coh}+I_{eu}^{inc} \tag{2}$$

The High-Angle region method is based on the assumption that the coherent intensity converges the squre of the dispersion corrected atomic scattering factor f^2 at the high values of k. Therefore the following equation is obtained

$$K\cdot I^{cor}=f^2+I_{eu}^{inc} \tag{3}$$

K can be actually determined as the mean of several values for different k. The High-Angle constant K_{HA} is given by

$$K_{HA}=\int_{k_{min}}^{k_{max}}(f^2+I_{eu}^{inc})\,dk/\int_{k_{min}}^{k_{max}}I^{cor}\,dk \tag{4}$$

where k_{min} is the minimum value of k beyond which I^{cor} shows only small oscillations, and k_{max} is the muximum k value of the observed data.

The normalization constant K_{KMN} obtained by using the Krogh-Moe-Norman method can be drived by

$$K_{KMN}=\frac{\int_0^{k_{max}}k^2\left(1+\frac{I_{eu}^{inc}}{f^2}\right)\cdot\exp(-\gamma k^2)\,dk-2\pi^2\rho_0}{\int_0^{k_{max}}k^2\cdot\frac{I^{cor}}{f^2}\cdot\exp(-\gamma k^2)\,dk} \tag{5}$$

where $\exp(-\gamma k^2)$ is a weighting factor proposed by Wagner, Ocken & Joshi[4].

For a liquid with one kind of atom, the radial distribution function (RDF) $4\pi r^2\rho(r)$ is given by[5]

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+\frac{2r}{\pi}\int_0^{k_{max}}k[I(k)-1]\times\exp(-\alpha^2k^2)\cdot\sin(kr)\cdot dk \tag{6}$$

where ρ_0 is the mean atomic density, $\exp(-\alpha^2k^2)$ is a convergence factor and I(k) is the interference function given by

$$I(k)=I_{eu}^{coh}(k)/f^2(k) \tag{7}$$

The normalization constants were calculated using the following value; $k_{min}=8.0$, $K_{max}=12.0$, $\gamma=0.008$, atomic scattering factors given by Cromer & Waber[6]. Anomalous dispersion corrections were refered to the values given by Cromer[7], and the Compton scattering factors calculated by Cromer & Mann[8]. The average of the two normalization constants were used. The absolute intensities $I_{eu}^{coh}(k)$ together with the interference functions I(k) are shown in **Fig. 3.** The radial distribution functions at $\alpha=0$ are shown in **Fig. 4.**

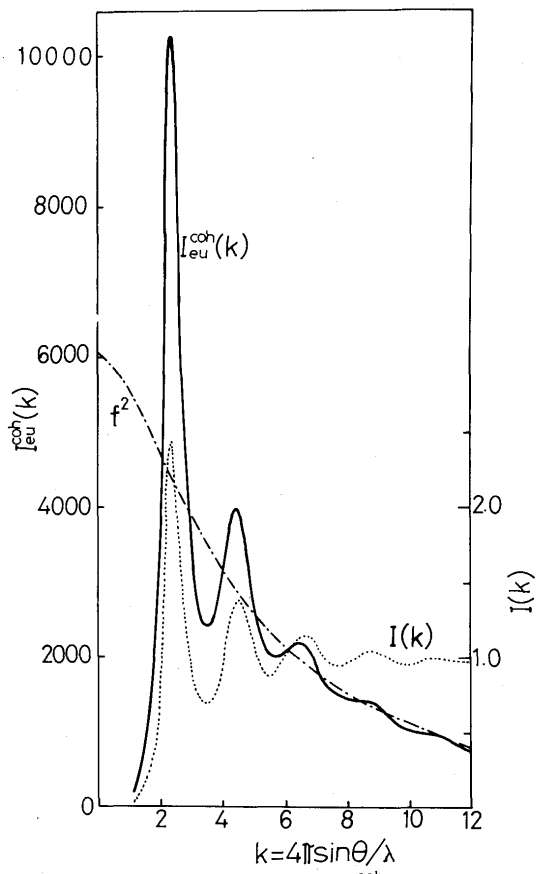

Fig. 3. The absolute intensity function $I^{coh}_{eu}(k)$ and interference function I(k).

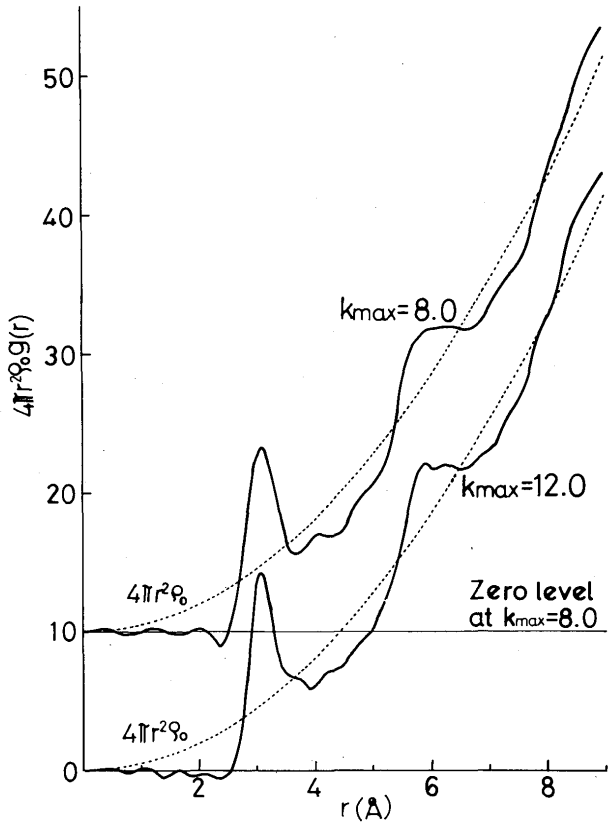

Fig. 4. The radial distribution function $4\pi r^2\rho(r)$.

Table 1. Summary of x-ray studies for mercury.

reference	Temp.	I (k)				RDF (Å)			coordination
		k_1	k_2	k_3	k_4	k_{max}	r_1	I (k_1)	number (atoms)
Wagner, Ock-n & Joshi[4]	28°C	2.27	(4.52)*	(6.76)*	(8.90)*	12.0	3.09	2.50	10.0
Black & Cundall[9]	room (about 20°C)	2.30	4.47	6.54	—	16.5	3.06	(2.06)*	7.4～8.0
Waseda & Suzuki[10]	15°C	2.32	4.55	—	—	12.0	3.07	(2.50)*	9.9～11.4
present work	room (about 23°C)	2.32	4.56	6.72	8.88	12.0	3.07	2.45	8.3

* These values in parentheses are evaluated by authors.

The nearest neighbour distance r_1 was obtained from the position of the first peak maximum of the RDF. The coordination number was obtained by integrating the first peak of the RDF. The results are summarized in **Table 1.**

5. Discussion

The interference function I(k) converges to the values slightly less than the unit at high values of k. Five peaks in the I(k) are found as shown in Fig. 3. The positions of the first and second peaks are in good agreements with those given by Waseda & Suzuki[10]. The positions of the third and fourth peaks are coincident with the results of Wagner, Ocken & Joshi[4], though the positions of the first and second speaks are significantly different from our results. The height of the first peak of the I(k), 2.45, is also in good agreement with other values. In the I(k), the subsidiary maximum on the high angle side of the first peak reported by Kruh, Clayton, Head & Sandalin[11] is not appeared.

In the radial distribution function RDF, the nearest neighbour distance $r_1=3.07$ Å is in good agreement with other results as summarized in Table 1. On the coordination number, our result at $k_{max}=12.0$ has a small value, as compared with those reported by many workers, but agrees with that given

by Black & Cundall[9]. The width of the first peak at $k_{max}=12.0$ is narrowly than that at $k_{max}=8.0$ as shown in Fig. 4. The coordination number at $k_{max}=8.0$ is 9.3.

As compared the RDF at $k_{max}=12.0$ with the RDF at $k_{max}=8.0$, the subsidiary maxima arising from the termination errorsare clearly found in the latter. They appear at

$$\Delta r=\pm 8\pi/(3k_{max}) \tag{8}$$

from the positions of the main peaks according to the analysis of Bragg & West[12]. The subsidiary maximum of the first peak on the high angle side at $k_{max}=8.0$ appears at r=4.10 Å, and Δr comes to 1.03 Å. This is coincident with the calculated value from eq. 8.

From these results, the apparatus described in this paper will be usefull for the structural studies of liquid metals.

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