On the Structure of Liquid and Solid Mercury studied with Cathode Ray Diffraction
(Temperature-Effect, Part III)[1]

By

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Abstrac

Diffraction patterns of Debye-Scherrer rings were taken by the method of cathode ray reflection on the surface of liquid and solid mercury. The author observed that both patterns belonged equally to the face centric rhombohedral unit of the crystalline system, and that the diameters of the rings of solid mercury were larger than those of liquid mercury by 10%. It is therefore concluded that liquid and solid mercury have the same structures but the intermolecular distance of solid state is contracted compared with liquid state by this percentage.

Introduction

On the structure of liquid only a little is known compared with the structures of gas or solid. The molecules in gaseous state are considered to be isolated from each other and those of solid state are situated at almost definite places, but the aggregate state of the molecules of liquid are very, complicated, as liquid crystals, etc. Some liquids show diffraction patterns, but the patterns are mainly due to the atoms arranged regularily in the complex molecules such as cyclic compounds, and they are not necessarily due to the arrangement of molecules in liquid itself. Then in order to exclude such innermolecular diffraction patterns which are meaningless for the study of structure of liquid, it is desirable to adopt the liquids of monoatomic molecules, if possible. Mercury is very suitable for this purpose. In addition to this, low vapour tension of mercury makes it adaptable to

1. Part I, II, These Memoirs **17**, 35, 1934.

be introduced into high vacuum of the chamber of the cathode ray apparatus.

The author has carried out an investigation on liquid mercury by the method of reflection of cathode rays. The cathode rays which struck the meniscus head of mercury gave diffraction patterns on the photographic plate behind it, similar experiment was already reported by R. Wierl[1] but his result was somewhat different from the present author's. He determined the structure of liquid mercury to be face centric cubic but the present author found it to be face centric rhombohedral.

Next the author carried out the same experiment with liquid upon solid mercury. The solid mercury was obtained in the cathode ray camera by freezing the mercury by liquid air. The theory of melting i. e. the intermolecular relations between liquid and solid states were almost unknown, so it should be studied at first how the structure of liquid differs from the solid in the same substance. For this purpose the present experiment was attempted. To give it greater weight, more trials should be made.

Regarding the problem of the scattering of electrons by mercury several interesting investigations have been done. The electrons which took part in this problem, however, were exclusively slow electrons of some hundred volts. The scattering of such slow electrons by mercury vapour was studied by F. L. Arnot[2], first and by others. The scattering of slow electrons by liquid mercury was investigated by R. Brode and E. Jordan[3].

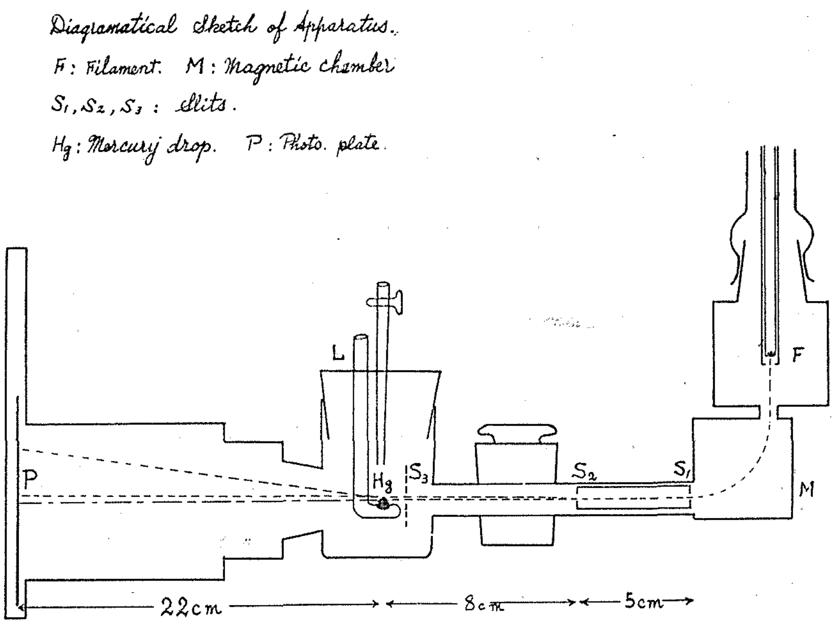
Experiment

The apparatus is shown in Figure 1. F is a filament where the electrons are produced. The electrons which have been accelerated by fifty or sixty kilovolts are deflected in a circular path by a magnetic field M, and select suitable monochromatic cathode rays by slits S_1 and S_2. The slits S_1 and S_2 have holes of diameters 0.3mm. The rays passing through the slits, strike the mercury Hg, and go on to the photographic plate P. The slit denoted as S_3 which had always been used for experiments of solid crystal[4] to obtain sharp patterns,

1. H. Mark und R. Wierl. „Die exp. und theor. Grundl. d. Electronenbeugung," p. 68, 1932.
2. F. L. Arnot, Proc. Roy. Soc. London, A **130**, 655, 1931, A **140**, 334, 1933.
3. R. Brode and E. Jordan, Phy. Rev. **44**, 872, 1933.
4. H. Kakesita, These Memoirs **17**, 35, 1934.

was removed in the present experiment, so that the beams of cathode rays were somewhat divergent. As a consequence, the image of the specimen on the photographic plate became about twice as large as the original size.

Fig. 1



L in the figure was a glass tubes of *L*-letter-type, on whose lower end the specimen was put, and in the experiment of low temperatures liquid air was poured into this tube.

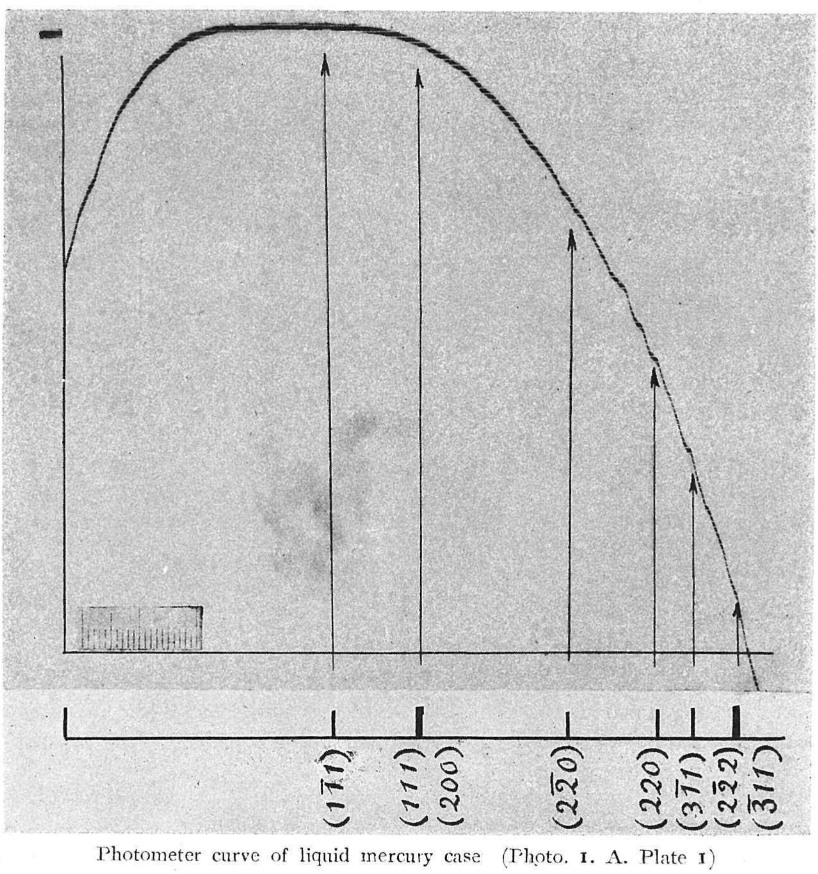
The purity and clearness of the mercury are essential to this experiment, because the penetrating power of cathode rays is very weak while foreign substances float and cover the surface of mercury. Then the mercury was showered down in the 10% nitric acid again and again and distilled under reduced pressure just before the experiments. A drop of mercury of 1 gram weight was taken from this purified mercury and put on the *L*-glass tube in the crystal chamber. Of course the vessels which were used had been carefully cleaned.

The drop of mercury thus introduced in the apparatus formed a spheroid on the glass tube. As the cathode rays which struck the mercury were diverging conical beams, ignoring the diffracted part, the direct spot marked on the photographic plate became a new moon form (Photo. 2, a, b) and the inner arc of this new moon was obviously the shadow of the meniscus head of mercury.

The photographing of solid mercury was quite analogous to the above, as shown in Photo. 2, b. As the freezing temperature of mercury is −39°C and the temperature of liquid air is about −180°C, so the solidification would be ensured even with the bombardment of cathode rays. The inner arcs of the direct spots, which are the shadows of the mercury, are as a matter of course smooth in the case of liquid (Photo. 2. a.), whereas they are zigzag in the case of the frozen solid (Photo. 2. b).

After the photograph of liquid mercury had been taken, the same mercury was frozen at that place by pouring liquid air in the *L*-glass tube, and after a few minutes the photograph of the solid was taken.

Fig. 2. Curve A.



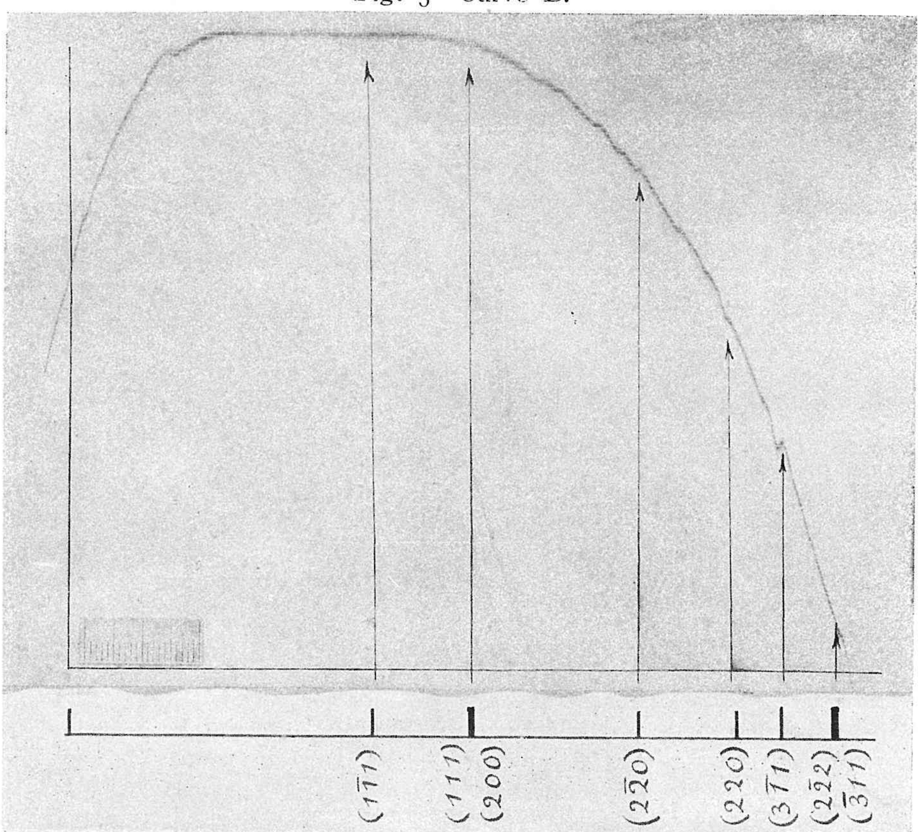
Photometer curve of liquid mercury case (Photo. 1. A. Plate 1)

The diffraction of cathode rays by liquid mercury is seen in Photo. I. A; and that by solid mercury in Photo. I. B. By carefull examinations it was found that the Debye-Scherrer rings of solid mercury were larger in diameters and sharper than those of liquid. The details of these photographs were examined by taking their photometer curves.

Results

Several photographs of liquid as well as solid mercury were taken. Photo. 2 shows the inner parts of patterns of Photo. I by strongly printing from the same negative plates. The patterns of these photographs are very diffusive partly because of the present method of photographing. The photographs of solid crystals taken in the same condition as the case of mercury were also diffused, as is shown in Photo. 3, which is a photograph of a rectangular block of brass.

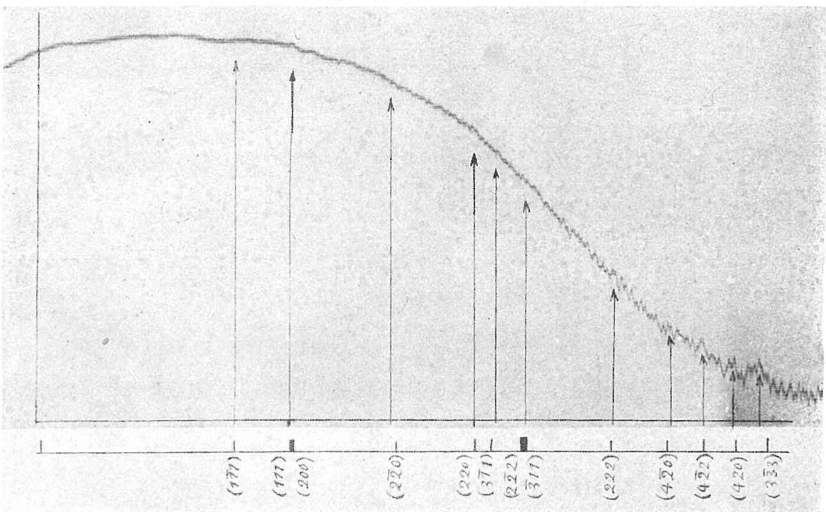
Fig. 3 Curve B.



Photometer curve of solid mercury case. (Photo. I. B)

Curve A and Curve B of Figures 2 and 3 are the intensity distribution curves of Photo. I, A and Photo, I, B respectively. These curves were taken with a microphotometer, newly manufactured in the Institute of Physical and Chemical Research, Tokyo, from the original plates of Photo. I, A, B, by crossing radially from centers to the outer rings. The curve of Figure 4 is that taken from another plate tracing up to higher orders of index, which were missed in the curves A and B.

Fig. 4 Curve C.



Photometer curve of another plate, showing the higher order of index.

As the original plate was very black at the central parts, the contrast of the intensities in the photometry curves at those parts were not distinct even of the direct spots. But the small kicks observed in the curves well accord with the values of X-rays investigations[1]. By assuming the rhombohedral unit of hexagonal system of crystalline form and using formula

$$d_{hkl} = \frac{a_0\sqrt{1+2\cos^3\alpha-3\cos^2\alpha}}{\sqrt{(h^2+k^2+l^2)\sin^2\alpha+2(hk+hl+kl)(\cos^2\alpha-\cos\alpha)}}$$

or

$$\frac{1}{d_{hkl}} = \frac{1}{a_0}\sqrt{(h^2+k^2+l^2)-2\cos\alpha(hk+hl+kl)}$$

the following numerical table was obtained where the value 98° 14′ was adopted for the axial angle α. The scales A, B and C attached to the curves of figures were made from the table:

[1] M. Wolf, *Zeitschrift f. Physik*, **53**, 72, 1929.

Table

index	$(h^2+k^2+l^2)$ $+2\cos\iota(hk+hl+kl)$	$\sqrt{\text{sum}}=a_0/d_{khl}$	d_{hkl}/a_0	d (Å)
$(1\bar{1}1)$	2.72	1.62	0.622	2.72
(111)	3.84	1.96	0.512	2.24
(200)	4.00	2.00	0.500	2.20
$(2\bar{2}0)$	6.88	2.62	0.382	1.72
(220)	9.12	3.03	0.330	1.48
$(3\bar{1}1)$	9.72	3.14	0.328	1.47
$(2\bar{2}2)$	10.88	3.30	0.303	1.36
$(\bar{3}11)$	11.28	3.35	0.298	1.34
(311)	12.96	3.60	0.278	1.20
(222)	15.36	3.92	0.256	1.15
$(4\bar{2}0)(\bar{4}20)$	17.74	4.22	0.237	1.07
$(\bar{4}22)$	20.64	4.55	0.220	0.99
(420)	22.24	4.71	0.212	0.95
$(3\bar{3}3)$	24.48	4.95	0.202	0.92

The agreement of the calculated scales and the observed curves which is clearly seen in the figures 2,3 and 4, shows that liquid and solid mercury have the same structures : both are face centric rhombohedral forms. The face centric is seen in the above table.

It is evident that the scale B is larger than the scale A, as if the scale B were enlarged as a whole by 10%. The difference in the size of rings is seen in the original Photographs, i. e. Photo. I, A and Photo. I, B, but it is more remarkable in these photometer curves. It has been verified here that this enlargement is neither due to the change of wave length during photographing nor to accidents during photometring. The constancy of the wave length has been ensured by the magnetic field even with the change of voltage supplied to the cathode. In order to find the correspondence between two photometry curves the author marked light marks on the curves during photometring at the time when the centre of rings, direct spot and intensive rings came to be illuminated, and the corresponding lines had been roughly found before the exact analysis of index was done.

The enlargement of diameters of the rings of diffraction patterns means the contraction of lattice distance, if the wave length is unchanged. Therefore it can be concluded that the intermolecular distances of solid mercury are contracted by 10% over those of liquid mercury, and their lattice constants are calculated as 4.5 Å and 4.95 Å respectively.

This percentage of the enlargement is too large compared with the ordinary rate of expansion of solid crystalline lattice. According to the theory of melting, the amplitudes of lattice vibrations grow up by the anharmonic vibrations due to heat motions until at last the molecules of lattice points strike against neighbouring ones and free themselves from the binding of crystallization. In such a circumstance extraordinary expansion of lattice distances might be possible. But this is not a satisfactory explanation. The density of liquid mercury at ordinary temperature is 13.59 and that of solid mercury, according to recent observation[1], is 14.47 at the temperature of $-191^{\circ}C$, so the rate of contraction of mercury is 6.5% in density.

In conclusion, the author wishes to express his hearty thanks to Professor M. Ishino for suggesting this problem and for valuable advice.

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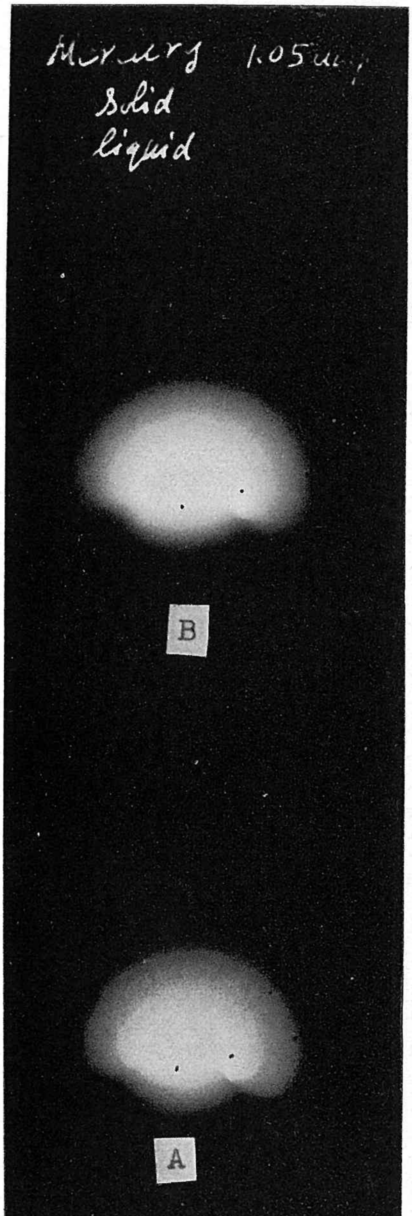
1. E. Grüneisen und O. Sckell, *Ann. d. Physik*, **19**, 389, 1934.

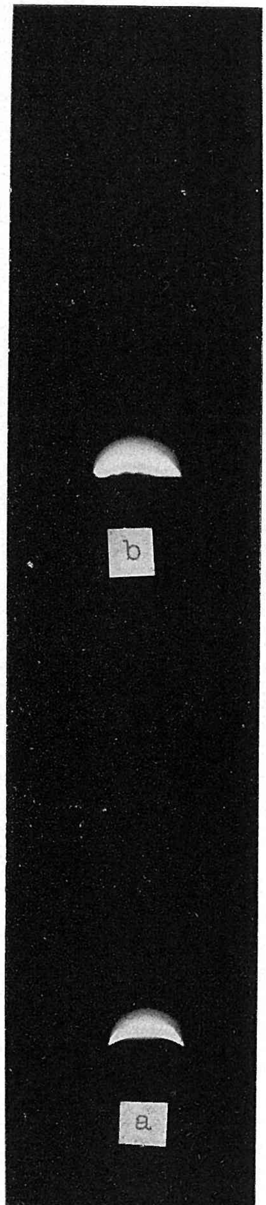
Plate I

Photo. 1.



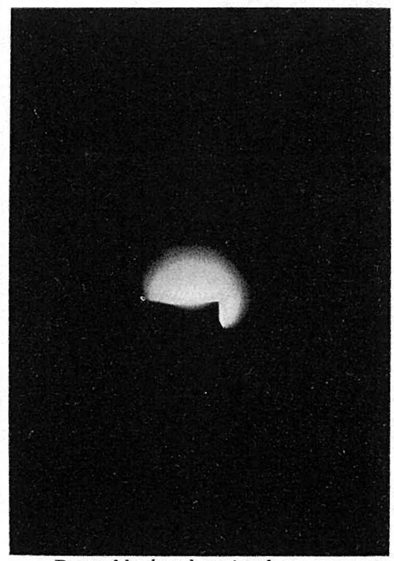
Reflection by solid and liquid Mercury

Photo. 2.



Central parts of patterns of Photo. 1

Photo. 3.



Brass block taken in the same condition as Photo. 1. $\lambda=0.0565$Å (45 K. V.)