X-RAY DIFFRACTION MEASUREMENTS FOR EXPANDED LIQUID MERCURY AROUND THE METAL-NONMETAL TRANSITION REGION

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Abstract-The energy-dispersive X-ray diffraction measurements for expanded liquid Hg have been carried out for the first time in the density region from 13.55 to 8.78 g/cm³ including the metal-nonmetal transition region. It was found that the volume expansion of liquid Hg in the metallic region, namely down to the reduced density of about 10 g/cm³, is not accompanied by a uniform increase of interatomic distance, r_1 , but mainly caused by a decrease of coordination number, N_1 . When the transition region is approached the decrease of N_1 becomes rather small and r_1 starts to elongate.

1. Introduction

A great deal of efforts have been devoted to the study on the electronic and thermodynamic properties of fluid Hg over the range of temperature and pressure sufficiently wide to include the liquid-gas critical point (critical data of Hg /1/: $T_c=1478^\circ\text{C}$, $p_c=1673$ bar, $d_c= 5.8$ g/cm³). Much of the efforts have been concerned with the metal-nonmetal (M-NM) transition which occurs in the liquid when it is expanded beyond the critical point. A number of measurements of physical properties such as electrical conductivity /2-5/, thermopower /3,6-8/, Hall coefficient /9/, optical reflectivity /10,11/, NMR /12/, sound velocity /13/ and equation of state /1,2,4,5/ show that, as the density is reduced, the M-NM transition starts to occur at the density of about 9 g/cm³.

It is obvious that the structural data around the transition region are quite important to the understandings of the M-NM transition. However, information on the structure of expanded liquid Hg has been quite limited mainly because there have been several technical problems accompanied by such an extreme experimental condition. Recently we have reported for the first time the structural data of expanded liquid Hg in the temperature and pressure range up to 1200°C and 830 bar, in the density range between 13.55 and 10.26 g/cm³ /14/, by the energy-dispersive X-ray diffraction method using new type of high pressure vessel and sample cell developed in our laboratory /14,15/. We have obtained the result that the nearest neighbour distance, r_1 , remains almost constant in the measured density range and the coordination number, N_1 , decreases substantially and almost linearly with decreasing density /14/. It is interesting to study how liquid Hg is expanded with further decrease of density beyond the M-NM transition region.

In this paper we report the results of the X-ray diffraction measurements for expanded liquid Hg in the temperature and pressure range up to 1450°C and 1750 bar, in the density region

from 13.55 to 8.78 g/cm³ including the M-NM transition region.

2. Experimental

We have carried out X-ray diffraction measurements for expanded liquid Hg using the energy-dispersive method. This technique has already been employed in our structural studies of expanded liquid Se near the liquid-gas critical point /15/ and expanded liquid Hg in the metallic region /14/. For the measurements of expanded liquid Hg in the lower density region, we have constructed another new internally heated autoclave. Figure 1 shows the side view of the autoclave which was constructed of a main cylinder with an smaller inner-diameter of 58 mm than that of the previous one and two flanges. As seen in the figure, the sample was located at the center of the autoclave. The primary and scattered X-ray beams passed through Be windows with the thickness of 5 mm and diameter of 4 mm. The Be windows were supported by the flat area of a screws. Figure 2 shows the top view of the autoclave. As seen in the figure, there were eight windows, one of which was for the incident X-ray beam and the rest for the scattered ones. The windows for the scattered X-ray beams were located at the scattering angle, 2θ , of 5, 7.5, 11, 15, 20, 25 and 35°. He gas was used as pressurizing medium.

Expanded liquid Hg must be contained in a cell made of special material being transparent to X-ray and resistant to chemical corrosion by Hg at high temperature. A single-crystal sapphire cell was developed for the purpose, the construction of which is illustrated in figure 3(a). The details around the liquid sample is also shown in figure 3(b) on an enlarged scale. The cell construction is essentially the same as the previous ones /14,15/ but the size has become much smaller.

Figure 1.

Side view of the autoclave for X-ray diffraction studies.

A closed-end sapphire tube with inner diameter 2.5 mm, outer diameter 3.5 mm was put into another closed-end tube with the inner diameter 3.5 mm, outer diameter 4.5 mm. The sample reservoir was connected to the outsides of the tubes. The sapphire components were cemented with a high-temperature glaze providing a uniform gap between the closed ends of the tubes as shown in figure 3(b). The thickness of the closed ends was 150 μ m and that of the gap was 15 μ m. In measuring X-ray diffraction from liquid sample contained in the sapphire cell, the problem is that the strong Bragg diffraction from the sapphire cell may disturb the obtained X-ray spectrum. This was overcome by employing the suitable procedure on the cell construction /14,15/.

The cell was heated by a heating element made of W wire with diameter

0.4 mm. The temperature of the sample was measured by two Pt-30%Rh:Pt-6%Rh thermocouples which were located in the holes of Mo tube and were close contact with the wall of the closed end of the outer sapphire tube. It is noticed that a slit was made on the left hand side of the Mo tube so diffracted X-rays were able to go out through it. The cell and the heater were held by alumina disks as seen in figure 1. The space between the alumina disks and the inner wall of the autoclave was filled with alumina powder to obtain good thermal insulation and to prevent convection of the compressed He gas. As seen in figure 3(a) liquid Hg in the sample space was connected with that in the sample reservoir through a small path. The balance between the compressed liquid Hg pressure and He pressure on the outside was achieved by making a small hole in the upper part of the Teflon cap.

Figure 2.
Top view of the autoclave for X-ray diffraction studies

White X-ray was generated by operating a commercial W tube at 50 kV and 25 mA. The diffracted X-ray photons from expanded liquid Hg were detected by a pure-Ge solid-state-detector (SSD) located at 2θ of 5, 7.5, 11, 15, 20, 25 and 35° . Since the spectrum in the energy region 16-42 keV was used for the data analysis, the magnitude of scattering vector, k , $k = (4\pi \sin\theta / hc)E$, E : photon energy, h : Planck constant, c : velocity of light, ranged from 0.7 to $13 \text{ \AA}^{-1}$. A photon accumulating time at scattering angles of 5, 7.5, 11, 15 and 20° was one hour and that at 25 and 35° was two hours.

In order to obtain the structure factor, $S(k)$, of expanded liquid Hg from the experimental scattering intensity, several data corrections had to be made such as taking account of the escape-effect of the Ge SSD, the energy spectrum of the primary X-ray beam, the energy dependence of the polarization of the primary beam, the absorption by the sapphire cell, compressed He gas, Be windows and liquid Hg itself, and finally Compton scattering from liquid Hg and the sapphire

Figure 3.
(a) The construction of the sapphire cell used for X-ray diffraction studies of expanded liquid Hg.
(b) Details of the sample space. See text for further details.

cell /14,16/. The first and second corrections are rather unique for the energy-dispersive X-ray diffraction. Detailed descriptions about the procedure of the data analysis are given in the literature /15/.

Figure 4 shows $S(k)$ of liquid Hg at 20°C and 5 bar obtained for the different angle settings. Circles show the $S(k)$ data obtained for angle settings of $2\theta=5$ and 20° , triangles for $2\theta=7.5$ and 25° , squares for $2\theta=11$ and 35° and reversed-triangles for $2\theta=15^\circ$. As seen in the figure, the consistency of the data in the same k -region is quite good.

3. Results and discussion

Figure 5 shows $S(k)$ of expanded liquid Hg in the temperature and pressure ranges up to 1450°C and 1750 bar along the saturated vapour-pressure curve and with densities ranging from 13.55 to 8.78 g/cm³. Note that these results include the data in the M-NM transition region. Dots represent the experimental data and the full curves show the Fourier transforms of the corresponding pair dis-

Figure 4.
The structure factor, $S(k)$, of liquid Hg at 20°C and 5 bar obtained for different angle settings.

Figure 5.
The structure factor, $S(k)$, of expanded liquid Hg.

Figure 6.
The pair distribution function, $g(r)$, of expanded liquid Hg.

tribution functions, $g(r)$, which are shown in figure 6. The $S(k)$ at 20°C and 5 bar is in good agreement with previous data obtained by the usual angle-dispersive method /17/. The characteristic feature of the temperature and pressure variations of $S(k)$ is that the oscillation damps and the peak width becomes broad with increasing temperature and pressure. This tendency is noticed in the first peak, whereas the second peak seems to damp rather slowly. As clearly seen in the figure, the values of $S(k)$ at low k region, say at $0.7 \text{ \AA}^{-1}$, gradually increase with increasing temperature and pressure. Further, there appears the minimum of $S(k)$ in the low k region below $1 \text{ \AA}^{-1}$ for the data at 1450°C and 1750 bar.

Figure 6 shows $g(r)$ deduced from the Fourier transformation of $S(k)$. In the Fourier transformation, the values of $S(k)$ in the small k region between 0 and $0.7 \text{ \AA}^{-1}$ were estimated by interpolating the values of $S(0)$ and $S(k)$ above $0.7 \text{ \AA}^{-1}$, where $S(0)$ were calculated using the experimentally obtained isothermal compressibility of expanded liquid Hg /1/. With increasing temperature and pressure, the long-range oscillation of $g(r)$ diminishes. The broadening of the first peak gradually occurs but no remarkable change of the peak position is observed. The small peaks of $g(r)$ in the region $r < 2.5 \text{ \AA}$ may be due to termination effects on the Fourier transformation.

Figure 7 shows the coordination number, N_1 , together with the nearest-neighbour distance, r_1 , as a function of density. As is well known, it is not easy to obtain the definite value of N_1 from the diffuse $g(r)$ pattern of liquid. Because there is overlap between the first- and second-neighbour peak, N_1 depends quite sensitively on the method employed to define and integrate the first-neighbour peak. However, variations of N_1 as a function of temperature, pressure or density can be determined with more reliability as long as a consistent definition of N_1 is used. We employed three different methods as shown at the upper of the figure. The first, (a), is the method integrating the radial distribution function, $4\pi r^2 \rho_0 g(r)$, up to the maximum position, r_{max} , and taking twice the integral, where ρ_0 denotes the average number density of Hg. The second, (b), is the method integrating $4\pi r^2 \rho_0 g(r)$ up to the maximum position of $g(r)$, r_1 , and taking twice the integral. The third, (c), is a special method taking account the asymmetry of the first-neighbour peak. We regard the triangle area below the tangent line as that due to the penetration of the second-neighbours.

As is clearly seen in figure 7, N_1 decreases substantially and almost linearly with decreasing density in the metallic region, that is, down to about 10 g/cm^3 , whatever method might be employed. On the contrary, r_1 remains constant. This is consistent with our previous results /14/.

Figure 7.

Coordination number, N_1 , and first-neighbour distance, r_1 , of expanded liquid Hg as a function of density. See text for further details.

When the M-NM transition is approached, however, the deviation from the linear plots of N_1 becomes evident and r_1 starts to elongate. From these findings we can speculate how the structural change of liquid Hg occurs in the microscopic sense with volume expansion. As schematically illustrated in figure 8, the atomic arrangement indicated by (a) represents a uniform expansion in which r_1 increases and N_1 remains unchanged. On the contrary, (b) shows an inhomogeneous expansion in which r_1 remains constant and N_1 decreases. The volume expansion of liquid Hg in the metallic region occurs in such a way as shown in (b). This is the same as that observed in liquid alkali metals [18,19]. However, it is changed to the way as shown in (a) when the M-NM transition region is approached. It is interesting to note that the M-NM transition seems to take place when N_1 decreases to a minimum value and r_1 may be forced to elongate.

Figure 8.
Schematic drawings of two ways how the structural change of liquid Hg occurs in the microscopic sense with volume expansion. See text for further details.

The X-ray diffraction measurements extending to the lower density region, especially under the supercritical condition, are now in progress.

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