

## Structural Studies of Expanded Fluid Metals Using Synchrotron Radiation

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X-ray diffraction measurements for fluid mercury and rubidium in the wide density range up to the supercritical region have been carried out using synchrotron radiation at SPring-8. We obtained the structure factor  $S(Q)$  and the pair distribution function  $g(r)$  for expanded fluid Hg from liquid to the dense vapor. Based on these data, we discuss the structural changes in the local atomic arrangements with decreasing density in connection with the metal-nonmetal transition. Since fluid Rb is highly corrosive at high temperature we developed a special cell made of molybdenum which enabled us to perform x-ray diffraction measurements. The results suggest the possibility that dimers of Rb start to appear in the metallic liquid.

Key words: Fluid metals, Metal-nonmetal transition, Synchrotron radiation, Static and dynamic structure

### 1. INTRODUCTION

How are atoms condensed to a metal? In other words, what happens when a metal substantially expands? These questions are fundamental and important in materials science.

Metals change into insulators when they expand. A simple band model predicts that divalent metals such as mercury (Hg) are transformed to an insulating state with volume expansion by forming an energy gap between s and p bands. Monovalent metals such as alkali metals, on the other hand, are considered to transform to an insulating state in a different way. Conduction electrons in monovalent metals at normal condition behave as nearly free electrons which screen the positive charge of ions and occupy the half of the conduction band. When the density of electrons is sufficiently reduced the screening becomes weak and conduction electrons are not free any more. In such situation, the picture of one-electron band becomes incorrect and the correlation between electrons is considered to play a key role to force expanded monovalent metals to an insulating state.

pressure surrounding the liquid vapor critical point, without crossing the saturated vapor pressure curve as shown in Fig.1. In the expansion process the mean interatomic distance increases up to ten times larger than that at normal condition and the electronic properties change dramatically.

The evidence of the M-I transition with volume expansion has been obtained by the measurements of direct-current conductivity for fluid Hg [1] and fluid rubidium (Rb) [2] and cesium (Cs) [3]. These fluid metals have been extensively investigated so far because the critical temperatures and pressures are relatively low so that the physical properties can be investigated in the laboratory. It is widely known that the M-I transition in fluid Hg starts to occur when the density decreases down to  $9 \text{ g cm}^{-3}$  larger than the critical density of  $5.8 \text{ g cm}^{-3}$ . In fluid Rb and Cs the M-I transition occurs around the critical density.

It is interesting to study how atomic arrangements change in these fluids with expansion. The volume expansion of fluids is essentially caused by the thermal one, in which pressure is applied to suppress the boiling. The thermal expansion in fluids might be different from that of crystals. In crystals the thermal expansion is originated from the anharmonic nature of the vibration of constituent atoms and the crystal symmetry does not change during the thermal expansion, that is, the coordination number remains unchanged while the interatomic distance increases. The same type of expansion possibly occurs in fluids, in which atoms are randomly distributed, keeping the coordination number constant and increasing the interatomic distance as shown in Fig.2 (a). In contrast to this type of expansion, another one may be possible in fluids, in which the coordination number decreases and the interatomic distance remains constant as shown in Fig.2 (b). Which structural change occurs in the expansion process? Recent structural investigations revealed that the latter type of expansion occurs in fluid Hg [4], Rb [5] and Cs [6]. These fluid metals expand inhomogeneously as if

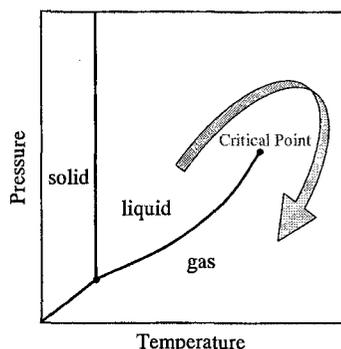
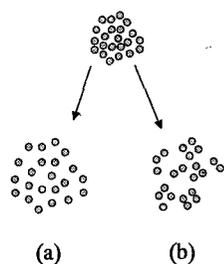


Fig.1 P-T diagram.

To see the metal-insulator (M-I) transition in actual materials, it can be used that a substantial and continuous volume expansion from the liquid to the rarefied vapor occurs by a change of the temperature and



**Fig.2** Schematic drawings of how the structural change of fluid metals occurs in the microscopic sense with volume expansion (see text).

atoms in the random array are taken away one by one and favor the increase of configurational entropy. This is the gross feature of structural changes in the expansion process from liquid to vapor.

It seems that such an inhomogeneous expansion stimulates the formation of clusters or molecules in sufficiently expanded fluids. Especially when the electronic states dramatically change accompanying the M-I transition, electrons may assist the formation of clusters. Recent investigation on expanded fluid Rb [7], for instance, suggests that dimers are already formed in the metallic region far from the critical point. It has been pointed out [8] that the existence of dimers in the metallic region of fluid Rb is helpful to understand the structural changes in the metallization process of compressed fluid hydrogen (H); quite recently metallic fluid H have been obtained at high temperature and high pressure by a shock compression [9], the metallization takes place at much lower pressure than that predicted by the static compression at room temperature and probably occurs without complete dissociation of H<sub>2</sub>. Since it is impossible, at present, to perform the experimental studies on the structural changes from insulating fluid H<sub>2</sub> to metallic fluid H, the structural studies of fluid alkali metals are quite helpful.

Thus, it is important to obtain precise and detailed information on the structural changes of expanded fluid metals. In the present paper we report advanced results of x-ray diffraction measurements for fluid Hg and Rb using synchrotron radiation at SPring-8. Changes of the local structure of fluid Hg accompanying the M-I transition are discussed in details. For fluid Rb our attention is focused on the possibility of the presence of Rb dimers in the metallic liquid.

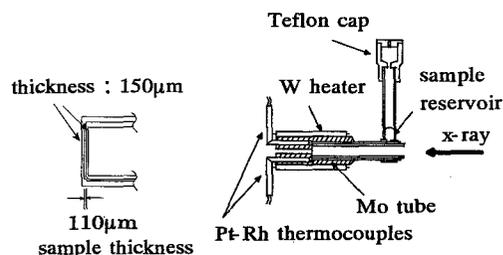
## 2. EXPERIMENTAL

We have performed energy-dispersive x-ray diffraction measurements for expanded fluid Hg and Rb using synchrotron radiation on the beam line BL04B1 and BL28B2 at SPring-8. The storage ring at SPring-8 was operated at 8 GeV with 100 mA during the experiments. White x-rays irradiated from a bending magnet and collimated to 0.2x0.2 mm<sup>2</sup> using slit at upper stream were incident on the sample and scattered x-rays were detected with a pure Ge solid-state detector. The details of the experimental setup are described elsewhere [10,11].

The experiments at high temperature and high pressure were performed using an internally heated high-pressure vessel made of super-high-tension steel. The apparatus permits measurements to be made up to

2000 K and 200 MPa. The high-pressure vessel for x-ray diffraction measurements has seven Be windows for the scattered x-ray beams, which are located at the scattering angles of 2θ of 4, 7, 11.5, 15, 20, 25 and 33 degrees, to cover a sufficiently wide range of scattering wave number  $Q$  ( $Q=4\pi E \sin\theta/hc$ , where  $h$  is Planck's constant,  $c$  is the velocity of light and  $E$  is the energy of the x-ray). The construction of the high-pressure vessel is shown elsewhere [11]. The vessel is pressurized by He gas of high-purity grade (99.9999%).

Supercritical fluid Hg must be contained in a cell made of a special material being transparent to x-rays and resistant to chemical corrosion by hot fluid Hg. A single-crystalline sapphire cell was developed for this purpose. Since white x-rays were used for the measurements of energy-dispersive diffraction, the polycrystalline sapphire could not be used because the x-ray scatterings from the poly-crystal produce a huge background disturbing the signals from Hg. Figure 3



**Fig.3** The construction of the sapphire cell.

shows the construction of the sapphire cell. The details are described elsewhere [12]. The cell consists of a hot part and a sample reservoir kept around the melting temperature of the liquid sample. The liquid sample was introduced from the reservoir to the small gap between two closed-ends of sapphire cell at the hot part. The closed-ends through which x-rays pass were made as thin as possible and the thickness of them was 150 µm. Since the sapphire cell containing fluid Hg was put in the high-pressure vessel filled with compressed He gas, no strain was applied to the closed-ends of the cell. The hot part was heated by a tungsten (W) heater surrounding a molybdenum (Mo) tube of 6 mm in outer diameter and 4 mm in inner diameter to keep the temperature uniform. The sapphire cell of 4 mm in outer diameter was put into the Mo tube. The temperature of the sample was measured by two Pt-30%Rh-Pt-6%Rh thermocouples, which were inserted in the holes of the Mo tube and were in close contact with the wall of the sapphire cell. Cells with sample thickness of 110 and 260 µm were prepared and the Hg sample of high-purity grade (99.999%) was used for the present experiments.

The observed data were analyzed using the same procedure reported in the previous paper [13]. Several corrections described in the literature [4] were performed for each spectrum obtained at different angle settings. Then structure factors  $S(Q)$  obtained at different angles were overlapped and averaged in a suitable  $Q$  ranges.

To measure the energy dispersive x-ray diffraction for fluid Rb the same high-pressure vessel was used. Special care was taken to construct the cell because fluid Rb is

highly corrosive to sapphire at high temperatures. Fluid Rb must be contained in a cell made of a special material being transparent to x-rays and resistant to chemical corrosion by hot fluid Rb. A special cell made of Mo was developed for this purpose and the details are described elsewhere [13]. Figure 4 shows the construction of a Mo cell. The cell was designed for x-ray transmission geometry similar to the sapphire cell and mainly consists of three components, an outer cylinder, an inner cylinder and a reservoir. These three

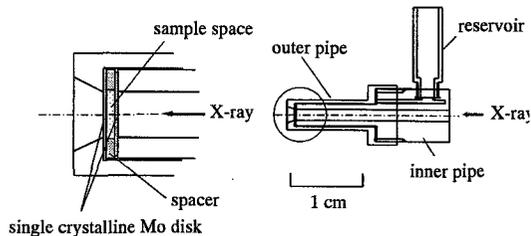


Fig. 4 The construction of the Mo cell.

parts were made of polycrystalline Mo and screwed with each other and sealed with high temperature brazing metal. In the figure an enlargement of the area enclosed with the circle is shown. A spacer of 0.4 mm in thickness made of polycrystalline Mo was located between two thinned disks made of single-crystalline Mo. Liquid sample contained in the reservoir is introduced into the space between disks through the narrow space of cylinders. The most important point in the cell construction is that a single crystal of Mo was used for the disk through which white x-rays pass. The reason for using the single crystal of Mo was the same as that for sapphire cell. The disk was mechanically polished down to 100  $\mu\text{m}$  and the central region through which x-rays pass was polished electrochemically down to 40  $\mu\text{m}$ . Single-crystalline disks were soldered to the ends of cylinders using high-temperature brazing metal.

### 3. RESULTS AND DISCUSSION

#### 3.1 Fluid Hg

Figure 5 shows the  $S(Q)$  for expanded fluid Hg in different temperatures and pressures from liquid to dense vapor through the M-I transition and the critical density regions. Dots denote the experimental data. Figure 6 shows the pair distribution function  $g(r)$  calculated from the Fourier transforms of  $S(Q)$ , of fluid Hg shown in Fig. 5. The data for  $g(r)$  at 298 K and 1.0 MPa have several features; the first peak has an asymmetric shape, the first minimum is invariant in the region from 0.4 to 0.5 nm, and the second peak is rather small. With increasing temperatures and pressures, with decreasing density, long-range oscillation of  $g(r)$  diminishes. The broadening of the first peak gradually occurs but no change of the peak position is observed and the asymmetry of the first peak remains at temperatures and pressures up to 1768 K and 194.0 MPa. While the first peak is observable even in the M-I transition region, the second peak around 0.6 nm is substantially damped. It should be noticed that the shape and the position of the first peak change when the density further decreases and the dense vapor region is approached.

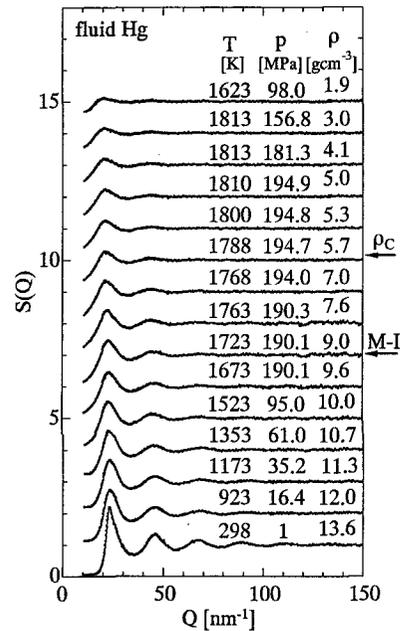


Fig. 5 Structure factor  $S(Q)$  for expanded fluid Hg.

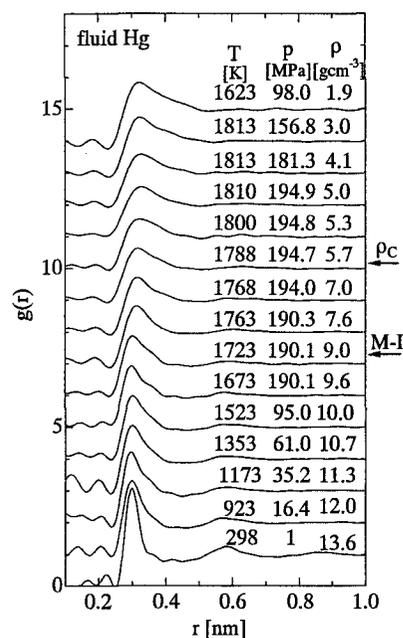
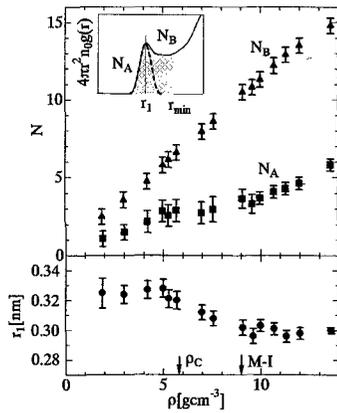


Fig. 6 Pair-distribution function  $g(r)$  for expanded fluid Hg.

Figure 7 shows the density variation of the coordination number  $N$  and the maximum position of  $g(r)$ ,  $r_1$ , which gives the nearest-neighbor distance. To obtain the definite  $N$  from the broad  $g(r)$  pattern of the liquid we employed two different methods to define and to integrate the first neighbor peak as shown the inset of Fig. 7. The first one (method A) is the method of integrating  $4\pi r^2 n_0 g(r)$  up to  $r_1$ , and taking twice the integral, where  $n_0$  denotes the average number density of fluid Hg. The second one (method B) is the method of integrating  $4\pi r^2 n_0 g(r)$  up to the first minimum position of  $g(r)$ ,  $r_{\min}$ . We fixed  $r_{\min}$  as 0.45 nm in the whole density range because  $r_{\min}$  does not change so much except in the dense vapor region.

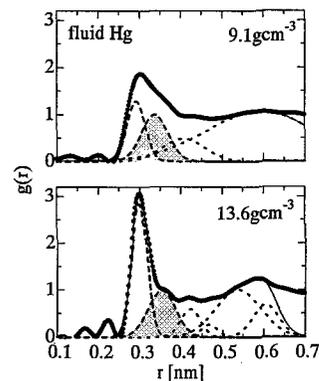


**Fig.7** The density variation of the coordination number  $N_A$ ,  $N_B$  and the nearest neighbor distance  $r_1$  (see text).

The coordination numbers  $N_A$  and  $N_B$  obtained by the methods A and B, respectively, are plotted in Fig. 7. It should be noted that  $N_A$  gives the coordination number in the nearest region of the first neighbor, and  $N_B$  is that when the region of the first neighbor is taken as widely as possible. As seen in the figure,  $N_B$  decreases substantially and linearly with decreasing density in the wide region from liquid to dense vapor. On the other hand,  $N_A$  also decreases almost linearly with decreasing density in the metallic region but when the M-I transition region is approached, around  $9\text{--}10 \text{ gcm}^{-3}$ , the deviation from the linear dependence comes out. It should be noted that the density around which the deviation starts to occur coincides with the region where the M-I transition starts to occur. On the contrary, no anomalous behavior is observed in that of  $N_B$  around this density region. In the region near the critical density, variation of  $N_A$  changes again. As seen in the figure,  $r_1$  in the metallic region remains almost unchanged with decreasing density but when the M-I transition region is approached,  $r_1$  starts to slightly increase. Such a behavior coincides with the deviation from linear dependence of  $N_A$ . In the region near the critical density,  $r_1$  becomes about  $0.33 \text{ nm}$ . The value of  $r_1$  seems close to the interatomic distance of Hg dimers in the rarefied vapor [14]. From these results we can conclude that the density decrease of fluid Hg is essentially caused by the reduction of the coordination number through the whole density region as seen in the behavior of  $N_B$ . The volume expansion of liquid Hg in the metallic region is not a uniform expansion with a fixed coordination number, but is caused by a decrease of coordination number with a fixed nearest neighbor distance.

To see the volume dependence of the local structure in liquid Hg more clearly, we tried to reproduce  $4\pi r^2 n_0 g(r)$  of fluid Hg from the liquid to the M-I transition region using a summation of Gaussian peaks. Since the x-ray diffraction measurements for liquid Hg by Kaplow et al. [15], the local structure of liquid Hg has been pointed out to be similar to that of crystalline  $\alpha$ -Hg with rhombohedral form. The crystal has an atomic configuration of distorted structure, where six neighboring atoms are hexagonally arranged at  $0.35 \text{ nm}$  around a central atom and other six atoms are located in upper and lower planes three by three. As shown in Fig. 8 the asymmetrical first peak of  $g(r)$  for liquid Hg at

$13.6 \text{ gcm}^{-3}$  is well reproduced using two Gaussian peaks, whose positions are  $0.30$  and  $0.36 \text{ nm}$ , respectively. Their coordination numbers are  $6$  and  $5$ , respectively. These results appear to be consistent with those reported by Kaplow et al. [15] and may suggest that the local structure of a liquid near the melting point is related that of the crystal below the melting point. With decreasing density, the height of the first peak in  $g(r)$  decreases. Figure 8 also shows the Gaussian fittings for  $g(r)$  at  $9.1 \text{ gcm}^{-3}$ . The positions of two peaks are not changed but the number of atoms coordinated at  $0.30 \text{ nm}$  substantially decreases while the decrease of the number at  $0.36 \text{ nm}$  is smaller. These results may suggest that the first stage of volume expansion, Hg atoms are not randomly taken away one by one from the atomic position but especially from closer neighbors. This result suggests that the decrease of atoms coordinated at  $0.30 \text{ nm}$  is closely related to the M-I transition in fluid Hg.



**Fig.8** Pair-distribution function  $g(r)$  reproduced using four Gaussian peaks (see text).

Reverse Monte Carlo modeling technique to the x-ray diffraction data of expanded fluid Hg using in-house x-ray source [4] were applied by Nield and Verronen [16] and Arai and McGreevy [17]. Their analysis pointed out that the variation of the near neighbors at shorter and longer distance in the first coordination shell is important to understand the nature of the M-I transition. The suggestion by these studies is consistent with the results of the Gaussian fitting.

To understand the nature of the M-I transition in connection with the structural changes of fluid Hg, several band structure calculations were carried out for the hypothetical forms of crystalline Hg. One of the approaches whose principle was consistent with the present experimental results was that of Mattheis and Warren [18]. They assumed that the nearest-neighbor distance was constant, so the density variation in expanded fluid Hg was due entirely to the changes in the coordination number for crystalline Hg with fcc, bcc, sc and diamond structures. They found that the trend of the density dependence of the theoretically calculated density of states is in good agreement with that of the Knight shift in the density range down to about  $9.5 \text{ gcm}^{-3}$ . However, it was found to be necessary to increase the lattice constant by  $1\%$  to fully open a band gap.

By taking fluctuations in the local coordination number into account, Franz [19] showed that a band gap opens at the correct density of  $9 \text{ gcm}^{-3}$ . The model was based on the assumption that average coordination

number decreases linearly with decreasing density but that actual local coordination numbers would be randomly distributed over a range allowed physically. Franz postulated that the local gap at the atom with coordination number smaller than 4 play a role as if a vacancy in hopping of conduction electrons and that a real gap appears when such vacancies against the transport propagate throughout the liquid.

Recently we have measured small angle x-ray scatterings of fluid Hg at SPring-8 and found that there exists a weak scattering in the M-I transition region, in addition to the critical scattering. The correlation length,  $\xi$ , of the density fluctuation related to the M-I transition, obtained by a curve-fit analysis using Ornstein-Zernike formula is about 1 nm. Also the amplitude of density fluctuation,  $S(0)$ , was found to be quite small compared with that of liquid-vapor critical scattering. Such a weak density fluctuation may be correlated with that of local coordination number suggested by Franz [19].

### 3.2 Fluid Rb

We have succeeded to measure x-ray diffraction for fluid Rb using Mo cell in the wide density region up to the critical point and for the dense vapor.

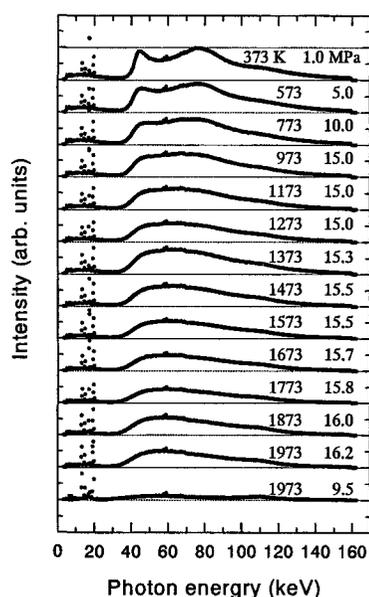


Fig.9 The diffraction intensity vs. photon energy for fluid Rb.

Figure 9 shows raw spectra of energy-dispersive x-ray diffraction obtained at scattering angle  $2\theta$  of 4 degree. The sample thickness was 2 mm. The spectrum at 373 K and 0.1 MPa has three maxima located around 42, 80 and 115 keV corresponding to the first, second and third maxima in  $S(Q)$  of liquid Rb. With increasing temperature and pressure the oscillation damps. It is noted that any diffractions from the single-crystalline Mo disk of the cell do not appear in the spectra. By analyzing these data we can get  $S(Q)$  and  $g(r)$  the details of which are to be described elsewhere. In the present report we summarize the main results obtained.

The first result is that the coordination number, estimated by using the method A in the section 2, decreases almost linearly with decreasing density down to the critical density. The results are consistent with

those of previous results by Franz et al. [5] and by Hosokawa et al. [20]. The second one, the most important, is that the nearest-neighbor distance,  $r_1$ , decreases with decreasing density;  $r_1$  decreases slightly or remains almost constant from 1.5 to about 1.0  $\text{gcm}^{-3}$  and then decreases with further decrease of density. The result is in contrast to those by Franz et al. [5] and by Hosokawa et al. [20] which show that  $r_1$  increases with decreasing density.

Recently *ab initio* molecular-dynamics simulation of expanded liquid Rb has been made by Shimojo et al [21]. They studied the temperature dependence of the structural and electronic properties. The simulations were carried out at 350 K, near the triple point, and at 1400 K. The pair distribution functions at both temperatures are in agreement with our results, in which  $r_1$  decreases with decreasing density. They also calculated the electron density distribution. The snapshots of contour plots of the electron density at 350 K and 1400 K show that the electron distribution spreads over all space except in the neighborhood of atomic positions at 350 K, while at 1400 K the distribution tends to localize and the electronic charge piles up in the areas where the ions come together. The results may suggest the formation of Rb dimers. Since liquid Rb near the melting point has loosely packed structure and the coordination number substantially decreases with decreasing density, it is not so unreasonable to consider that Rb dimers tend to form more easily. However, it does not immediately mean that there appear the same neutral dimers as those existing in the rarefied vapor. The dimers appearing in the liquid state may co-exist with conduction electrons screening the dimers and must be unstable. It is noticed that the temperature of 1400 K is located in the liquid and metallic region far from the critical point.

The evidence suggesting that Rb dimers exist in the liquid region was obtained by the measurements of the dynamic structure factor  $S(Q, \omega)$  by means of the inelastic neutron scattering technique [7]. The measured  $S(Q, \omega)$  for expanded liquid Rb show [7] that collective excitations are observed over a very wide temperature range up to 1673 K. Their results also show that liquid Rb up to this temperature is basically monatomic and the screened forces control the liquid dynamics. However, when the temperature is further increased the evidence of *intra*-molecular vibrations appears. The temperature is 1873 K and the density is 0.61  $\text{gcm}^{-3}$ . In the current-current correlation function three peaks can be identified as resulting from excitations at 3.2, 6.4 and 9.6 meV. This feature was assigned to the excitation of local harmonic oscillations in the environment of their neighboring atoms in the liquid.

Thus, the investigations of static and dynamic structures together with *ab initio* molecular-dynamics simulation strongly support that there exist 'dimers' in liquid Rb in the metallic state far from the critical point. When liquid Rb expands the seeds of dimers start to appear much earlier than the M-I transition takes place; the dimerization does not coincide with the M-I transition. From the view point of the condensation process, in other words, when neutral dimers in vapor are condensed to liquid, the dissociation of dimers are not completed being accompanied by the insulator-metal

(I-M) transition near the critical point. The I-M transition occurs much earlier than the complete dissociation of dimers. The complete dissociation occurs in the liquid side.

As pointed out by Hensel [8], this view mentioned above is quite helpful to understand the process of the metallization in fluid hydrogen. Metallic hydrogen was made for the first time in the fluid state by Weir et al [9] by using a shock compression technique. They found that the conductivity increases with increasing pressures and temperatures, and at pressures of 93 to 120 GPa liquid H is in a semiconducting state, but at a pressure of 140 GPa the conductivity becomes more than 1000  $\text{ohm}^{-1}\text{cm}^{-1}$  and liquid H becomes metallic [9]. The metallization takes place at much lower pressure than that predicted by the static compression at room temperature for solid H. The density variation of conductivity of fluid H was found to be quite similar to those of fluid Rb and Cs, which has been pointed out for the first time by Hensel and Edwards [22]. The similarity of the behavior of fluid H to fluid alkali metals tells us that liquid H consisting of dimers may be transformed to metallic state before and without complete dissociation of  $\text{H}_2$  and the I-M transition may be induced by the band overlap of the bonding and anti-bonding bands of compressed hydrogen molecules. The fact that the metallization of fluid H starts to occur at lower pressure is quite important when it is connected with the planet Jupiter; fluid H in the core of the planet becomes metallic at the shallower location from the surface which is helpful to clarify the origin of the strong magnetic field of Jupiter [23].

Thus, the structural studies of fluid Rb is especially important when connected with the I-M transition in fluid H because it is impossible to perform detailed structural investigations on fluid H at present.

#### 4. Summary

X-ray diffraction measurements for fluid Hg and Rb in the wide density range from liquid to dense vapor using synchrotron radiation at SPring-8. For the present measurements of fluid Rb with highly corrosive nature, a special Mo cell with single crystalline disks was developed and successfully used.

It was confirmed that fluid Hg and Rb expand essentially accompanied by the reduction of the first coordination number, expanding inhomogeneously as if atoms in the random array are taken away one by one. This is the gross feature of structural changes in the expansion process from liquid to vapor. However, the detailed analysis reveals the following aspects of structural changes in the local atomic arrangements. In fluid Hg, the number of closer atoms in the first neighbor is selectively reduced and the reduction must be strongly related to the M-I transition. The changes of the local structure concerning the M-I transition is not simple. It is not easy to draw a concrete picture on the structural changes accompanying the M-I transition in the three dimensional space. In fluid Rb, it was found that  $r_1$  decreases in spite of the volume expansion. The fact suggests the possibility that Rb dimers appear in the liquid state. The importance of dimers was discussed in the connection with metallic fluid H.

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