Structural studies of expanded fluid rubidium up to the supercritical regions

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Abstract

X-ray diffraction measurements have been carried out for fluid rubidium up to enormous high temperatures and pressures beyond the liquid–vapor critical point ($T_c = 2017$ K, $P_c = 12.45$ MPa) using synchrotron radiation at SPring-8. We have developed a new sample cell made of molybdenum which is resistant to highly corrosive nature of hot alkali metals. Single crystalline molybdenum electrolytically thinned to 30 μm was used as X-ray windows of the cell. The crystal orientation of the disks was controlled to avoid the appearance of Bragg peaks from the cell in the diffraction spectra. All parts of the cell were assembled and brazed together using a high-temperature Ru–Mo alloy. The use of single crystal contributes to reduce the background noise from the cell and made it possible to achieve stable and precise measurements at the supercritical region of fluid rubidium.

Keywords: Fluid metal; Alkali metal; Rubidium; Supercritical fluid; X-ray diffraction; Structure; Metal–nonmetal transition

1. Introduction

A substantial and continuous volume expansion from liquid to vapor occurs by the change of the temperature and pressure surrounding the liquid–vapor critical point as shown in Fig. 1. In the expansion process, the mean interatomic distance increases up to 10 times larger than that at normal condition and the structural and electronic properties change dramatically.

Liquid alkali metals at the triple point are known to be a simple monatomic liquid consisting of neutral pseudo-atoms, i.e., well-screened ions by conduction electrons. Also the electronic properties show the nearly free-electron (NFE) character very similar to those of the crystalline state. On the other side, it is well known that alkali metal vapor is a typical insulator with the electrical conductivity less than $10^{-5}$ Ω$^{-1}$ cm$^{-1}$, the constituents of which are monomers and diatomic molecules in equilibrium [1]. These facts tell us that expanded alkali metals finally experience a metal–insulator (M–I) transition with volume expansion. The M–I transitions of fluid alkali metals occur around the critical density [2].

Experimentally accessible range of the critical constant of fluid alkali metals [2] (rubidium (Rb): $T_c = 2017$ K, $P_c = 12.45$ MPa, $\rho_c = 0.29$ g cm$^{-3}$, cesium (Cs): $T_c = 1924$ K, $P_c = 9.25$ MPa, $\rho_c = 0.38$ g cm$^{-3}$) allows a considerable amount of experimental work to investigate the physical properties of expanded fluid alkali metals, such as equation of state [3,4], electrical conductivity [5,6], magnetic susceptibility [7,8] and nuclear magnetic resonance (NMR) [9]. These measurements show that the physical properties of fluid alkali metals are strongly dependent on their thermodynamic state. The conductivity measurements have revealed that fluid alkali metals show a departure from the NFE character very early in metallic liquid range ($\sim 3\rho_c$). Also at the corresponding density regions, the magnetic susceptibility [8] showed a marked enhancement and the NMR data [9] strongly suggest the existence of antiferromagnetic spin fluctuations in the fluid. These experimental results indicate that the electrons in the fluid are in highly correlated state as the density of the fluid decreases.

It is of quite an interest to investigate how the effect of electron–electron correlations is coupled with the structural
properties. Several diffraction measurements have been carried out for expanded fluid alkali metals. Franz et al. [10] measured the neutron diffraction for fluid Rb up to the critical region. They reported that the local structure of expanded fluid Rb changes in the way that is similar to that of simple liquids; the coordination number decreases linearly while the nearest-neighbor distance is almost unchanged or slightly increased. Winter et al. [11] carried out neutron diffraction measurements for fluid Cs and reported the local structural variation essentially similar to that of fluid Rb.

Diffraction measurements using synchrotron radiation have been also carried out by Hosokawa et al. [12]. They performed X-ray diffraction experiments of Rb up to 1573 K using a sample cell made of sapphire. However, temperature range was limited to 1573 K due to highly reactive nature of hot alkali metal with sapphire.

Molybdenum (Mo) is a material resistant to chemical corrosion with alkali metals and widely regarded as a suitable material for those experiments at extremely high temperatures up to the critical temperature of fluid alkali metals such as the equation of state [3,4], electrical conductivity [5,6], and also the neutron diffraction [10,11].

While the advent of the third generation synchrotron radiation facilities provide great opportunities to perform precise structural experiments, the absence of sample container for fluid alkali metals have been hindering X-ray diffraction measurements up to the supercritical region. The use of a Mo cell for X-ray diffraction measurements of fluid alkali metals is quite attractive because it enables us to investigate the structural changes with volume expansion up to the supercritical region. In addition, combined with a synchrotron radiation as an X-ray source, more precise data on the structural changes might be obtained.

In the present paper, we report the design and the fabrication of a new sample cell made of Mo. We also report the results of X-ray diffraction measurements for fluid Rb over a wide range of temperatures and pressures using synchrotron radiation at SPring-8 in Japan, which have been achieved for the first time using the sample cell specially developed for this study.

2. Experimental

X-ray diffraction measurements for fluid Rb were carried out in the energy dispersive mode using synchrotron radiation on the beamline BL28B2 at SPring-8. White X-rays irradiated from a bending magnet and collimated 0.2 x 0.2 mm² were used as an incident beam on the sample and scattered X-rays were detected with a pure Ge solid-state detector (SSD).

High-temperature and high-pressure experiments were performed using an internally heated high-pressure vessel made of super-high-tension steel. Fig. 2(a) shows a side view of the high-pressure vessel for X-ray diffraction measurements. The vessel permits high-temperature and high-pressure experimental conditions up to 2123 K and 200 MPa beyond the supercritical condition of fluid Rb. The vessel consists of a main cylinder (50 mm in inner diameter, 105 mm in outer diameter, and 140 mm in length) and two flanges with thickness of 43 and 49 mm. The fluid Rb contained in the sample cell is located at the central axis of the vessel and the sample cell is held by alumina disks that are not described in the figure. The vessel is pressurized by He gas of high-purity grade (99.9999%), which has a low absorption factor in the energy range of the experiment carried out. Fig. 2(b) shows a top view of the high-pressure vessel. The vessel has pressure-sealed beryllium (Be) windows located at different angles of 20° (4°, 7°, 11.5°, 15°, 20°, 25°, 33°) through which scattered X-rays go out and are detected by a pure Ge SSD.

In order to achieve high temperature and high pressure experiments of fluid alkali metals, the fluid sample must be contained in a cell made of a special material resistant to high reactivity of hot alkali metals. We have devised a sample container made of Mo, which is resistant to highly corrosive nature of alkali fluids. The design of the cell which was fabricated is shown in Fig. 3(a). The cell mainly consists of three components, an outer pipe which is indicated by (1) in the figure, an inner pipe (2) and a reservoir (3). All parts of which were made of Mo. These three components were made of polycrystalline Mo and were all fabricated with conventional machining techniques. They were screwed with each other and then sealed with high temperature Ru–Mo brazing alloy. Fig. 3(b) shows an enlargement of the area enclosed with the circle in Fig. 3(a). A sample spacer with thickness of 0.4 mm (4) was located between two thinned disks made of single crystalline Mo (5), (6). The thickness of the disk was 30 μm. The disks were fabricated from a bulk single crystalline Mo by cutting and electrolytically polishing.

Liquid sample contained in the reservoir is introduced into the sample space through the hole with 0.5 mm in diameter (as shown in Fig. 3(a)) and the narrow path between two pipes. Incident X-rays come from the right-hand side as indicated by the arrow in Fig. 3(b). Scattered
X-rays go out to the direction of the left-hand side. The left end was tapered for allowing the scattered X-rays with large scattering angles to pass.

The most important point in the cell construction is the use of single crystalline Mo as a material for the X-ray windows of the cell indicated by (5) and (6) in Fig. 3(b). As has been described, the diffraction from the sample is measured by the energy-dispersive mode using white X-rays as an incident beam. Therefore, the use of polycrystal disturbs the signals from the fluid sample with a huge background including Debye–Scherrer pattern. The use of single crystal is crucial importance in terms of obtaining diffraction spectra with high signal-to-background ratio. However, even if single crystal is used the diffraction spectra might contain the Bragg peaks from the cell. We avoided the appearance of the Bragg peaks from the cell in the diffraction spectra by controlling the crystal orientation of the Mo disks as described below.

The main oscillations of the structure factor \( S(Q) \) of liquid Rb near the melting point appear at lower \( Q \) region than those of liquid Hg [13], it is important to choose the crystal axis of Mo which gives no Bragg peaks in the region of small angles of 4°, 7° and 11.5°. We carried out the simulation of the Bragg reflection peaks from Mo crystal when the incident X-rays are scattered from the window of the cell and examined which crystal orientations should be normal to the surface of the Mo disks. We found that the selection of the crystal axis with Miller index of \( \langle 123 \rangle \) is appropriate, which is located around the center of the standard stereo-triangle of a cubic crystal system and apart from \( \langle 100 \rangle, \langle 110 \rangle \) or \( \langle 111 \rangle \) axis. In the present experiments, we adopted the axis with \( \langle 123 \rangle \) index. The reason for selecting \( \langle 123 \rangle \) is to prevent the orientation such as \( \langle 100 \rangle, \langle 110 \rangle \) and \( \langle 111 \rangle \) from being close to the direction normal to the surface of X-ray windows of the cell. If such orientations with relatively lower Miller indexes are selected as the normal direction to the surface of Mo disks, the Bragg reflection condition tends to be satisfied within the energy range of the measurement at 20 angles of 4°, 7° and 11.5° unless these orientations align perfectly normal to the surface of X-ray windows (the orientations which satisfy the extinction rule are excluded from the beginning.). Therefore, in consideration of the experimental controllability of crystal orientation in this
work, we adopted the axis with $\langle 123 \rangle$ index avoiding the appearance of Bragg peaks from the cell in the diffraction spectrum. If the axis with $\langle 123 \rangle$ is selected, the energy which fulfills the Bragg reflection goes outside the energy range which is required for data analysis to deduce structure factor of Rb.

Also it is very important to reduce the thickness of windows to be transparent to X-rays. It is desirable to reduce the thickness of windows as thin as possible while keeping mechanical strength of the windows. In the present experiment, we have successfully fabricated the disk with thickness of 30 $\mu$m.

The process of single crystal Mo disks is as follows. Back scattering Laue method was employed for determining the crystal orientation of a bulk single crystal made by a technique of crystal growth in the solid state [14]. Single crystalline Mo disks with thickness of 250 $\mu$m were cut from the bulk single crystal by electro-discharge machining. Then the disks were mechanically polished down to 100 $\mu$m. To maintain mechanical rigidity of the disk only the central region through which X-rays pass was polished electrolytically down to 30 $\mu$m using methanol–$\text{H}_2\text{SO}_4$ (volume fraction 7:1) solution.

Assembling of the cell was carried out as follows. The fabrication process is shown in Fig. 4. Each component of the cell was assembled using a brazing technique using 43 wt% Ru–Mo alloy powder [15].

First, an inner pipe and a reservoir were screwed each other and the end of the hole with 0.5 mm in diameter was sealed with a small Mo pin as shown in the Fig. 4(a). Then 43 wt% Ru–Mo powder was filled into the connected area between these components (Fig. 4(b)). Furnace heating was carried out at 2000 °C for 5 min in the vacuum ($10^{-3}$ Pa) followed by the cooling process in the furnace. The rate of the temperature increase was 10 °C/min. In this process, the brazing metal melted and the components were connected. Second, a single crystalline disk and a spacer were inserted into the outer pipe and positioned at the end. Another single crystalline disk was set on the end of the inner pipe (Fig. 4(c)). The brazing metal was filled into the contact area of each component and the brazing at the same condition was performed (Fig. 4(d)). Finally, the two pipes were screwed each other and the brazing metal was filled into the connected area. The brazing was carried out again (Fig. 4(e), (f)). After each step of brazing process was finished, the seal around the connected area was checked with a helium (He) leak detector. In each step the same brazing process was repeated until no leakage is found.

Fig. 5 shows a photograph of a fabricated Mo cell in (a) and a cross-section of the left end of the cell in (b). It is understood from the figure that a sample space is created between two thinned Mo disks.

Before the structural measurements, Rb sample is introduced into a Mo cell in a glove box filled with highly purified He gas. The cell filled with Rb is put in a high-pressure vessel and the vessel is closed. The procedure of which is also carried out in the glove box. Then the high-pressure vessel was conveyed to the beam line at SPring-8. X-ray diffraction measurements were carried out over a wide range of temperatures and pressures from 373 K, 1.0 MPa up to
2123 K, 22.1 MPa, which corresponds from the triple point region up to the supercritical region. By combining the Mo cell with high-pressure and high-temperature apparatus, we have succeeded to perform X-ray diffraction measurements from the triple point up to the supercritical regions using synchrotron radiation at SPring-8 in Japan.

Fig. 6 shows the phase diagram of Rb in which open circles indicate the temperatures and pressures where the diffraction experiments were carried out.

3. Results and discussion

Fig. 7 shows a comparison between two raw diffraction spectra for fluid Rb contained in different cells at 100 °C. The X-ray windows of the two cells have different crystal orientations. The upper spectrum is that for fluid Rb in the cell with its crystal orientation of (110) plane appears at 82 keV, which disturbs the second diffraction peak from fluid Rb. The lower spectrum is that for fluid Rb in the cell with its crystal orientation of (123) being normal to the surface of the windows.
surface of the X-ray windows. There are no Bragg peaks from the cell in the lower spectrum. It is understood from the figure that control of crystal orientation of the X-ray windows is of crucial importance.

Fig. 8 shows raw spectra of energy-dispersive X-ray diffraction at scattering angle 2\( \theta \) of 4° from liquid to the supercritical regions. At 373 K the first maximum is located at 45 keV, which corresponds to the first peak of the structure factor \( S(Q) \) of liquid Rb. With increasing temperature (decreasing density), the intensity of the first maximum decreases and becomes broad. We deduced structure factor, \( S(Q) \) from raw spectra of scattered X-rays. Data analysis to obtain \( S(Q) \) from the raw spectrum requires several procedures such as the escape correction of the a pure Ge SSD, the determination of the energy spectrum of the incident X-ray beam, data correction to the effect of the absorption by the Mo cell, and compressed He gas, the Be windows, and the fluid Rb sample itself, and finally the Compton scattering of the sample and the cell. The procedure of data analysis appears in detail elsewhere [17].

Fig. 9(a) shows structure factor \( S(Q) \) at different 2\( \theta \) angles (4°, 7°, and 11.5°) at 373 K and 1 MPa. They are well overlapped to cover the \( Q \)-range from 1.2 to 7 Å\(^{-1} \) where the oscillatory of \( S(Q) \) is almost diminished. The \( S(Q) \)s at different 2\( \theta \) angles were merged to create a single \( S(Q) \) as shown in Fig. 9(b), which shows a reasonable agreement with the previous result [18]. By analyzing raw spectra over a wide temperatures and pressures up to the supercritical regions of Rb, 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.

Important feature to be noted is density dependence of the position of the first maximum of \( g(r) \), \( r_1 \), which corresponds to the average nearest neighbor distance. The value of \( r_1 \) is 4.85 Å at 373 K and is almost the same value as that of the solid state, which is consistent with the conventional view of liquid alkali metals that relatively little change in the local atomic arrangement occurs upon melting. The \( r_1 \) stays almost constant until 1.1 g cm\(^{-3} \), and then starts to decrease below 1.1 g cm\(^{-3} \). The \( r_1 \) gradually decreases with further density reduction and reaches to 4.4 Å near the density of 0.6 g cm\(^{-3} \). Finally, it shows a saturation around 4.2 Å below the density of 0.5 g cm\(^{-3} \).
The value of $r_1$ is close to the equilibrium bond length of isolated diatomic molecules of Rb (4.17 Å) [19], which suggests the existence of diatomic Rb molecules around this density.

To obtain the definite coordination number from the diffusive and broad $g(r)$ pattern of the liquid, we tried the method of integrating radial distribution function (RDF) defined as $4\pi r^2 n_0 g(r)$ up to the first minimum position of RDF, $r_m$ where $n_0$ denotes the average number density of Rb. The coordination number in the present work was derived by this method. At 373 K the coordination number is about 12. The coordination number decreases with decreasing density until 1.1 g cm$^{-3}$ and then shows a strong deviation from linear dependence within the density range between 1.1 and 0.5 g cm$^{-3}$ staying almost constant around 6–7 and then decreases to 4 with further density reducing. The density range where the coordination number shows a strong deviation from the linear decrease corresponds well to that where the value of $r_1$ starts to decrease.

It is quite evident that our observation is different from those of the previous observations [10,11] in which microscopic structural variation is essentially similar to that of rare-gas liquids. The shortening of $r_1$ is seemingly consistent with the appearance of diatomic molecules as suggested by the inelastic neutron scattering measurements [20]. However, the observed structural features within the density range from 1.1 to 0.5 g cm$^{-3}$ cannot be simply interpreted as such a physical picture that the amount of diatomic molecules in the fluid increases with decreasing fluid density [21]. The coordination number shows strong retention at the corresponding density with volume expansion. The feature is in contrast to the formation of the diatomic molecules in the fluid which prefers the expansion. The feature is in contrast to the formation of the diatomic molecules in the fluid which prefers the metallic state.

4. Summary

We have succeeded to measure X-ray diffraction for expanded fluid Rb up to the supercritical region using synchrotron radiation at SPring-8. A sample cell made of molybdenum, which is resistant to highly corrosive nature of hot alkali metals, has been developed and makes it possible to perform stable and precise structural experiments for expanded fluid Rb. Observed structural features reveal a new characteristic density range where the expansion causes the nearest neighbor separation shorten while the coordination number shows retention. The features suggest significant clustering emerges accompanying density fluctuation.

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References

[1] C.T. Ewing, J.P. Stone, J.R. Spann, R.R. Miller, J. Phys. Chem. 71 (1967) 473.
[2] F. Hensel, W.W. Warren Jr., Fluid Metals; Liquid–Vapor Transition of Metals, Princeton University Press, Princeton, NJ, 1999.
[3] H.P. Pfeifer, W. Freyland, F. Hensel, Ber. Bunsenges. Phys. Chem. 83 (1979) 204.
[4] S. Jungst, B. Knuth, F. Hensel, Phys. Rev. Lett. 55 (1985) 2160.
[5] G. Franz, W. Freyland, F. Hensel, J. Phys. Colloq. C8 (1980) 70.
[6] W. Freyland, Comments Solid State Phys. 10 (1981) 1.
[7] W. Freyland, Phys. Rev. B20 (1979) 5104.
[8] W. Freyland, J. Phys. Colloq. C8 (1980) 74.
[9] W.W. Warren Jr., G.F. Bremmert, Phys. Rev. B39 (1989) 4038.
[10] G. Franz, W. Freyland, W. Gläser, F. Hensel, E. Schneider, J. Phys. Colloq. C8 (1980) 194.
[11] R. Winter, F. Hensel, T. Bodensteiner, W. Gläser, Ber. Bunsenges. Phys. Chem. 91 (1987) 1327.
[12] S. Hosokawa, W.-C. Pilgrim, F. Hensel, J.-L. Hazemann, D. Raoux, M. Mezouar, T. Le Bihan, D. Häusermann, J. Non-Cryst. Solids 250–252 (1999) 159.
[13] K. Tamura, M. Inui, J. Phys.: Condens. Matter 13 (2001) R337.
[14] K. Okamoto, M. Mori, T. Fujii, Y. Hiraoka, in: H. Bildstein, H.M. Ortner (Eds.), Proceedings of the 12th International Plansee Seminar ‘89, Reutte, Tirol, Austria, 1989, p. 171.
[15] Y. Hiraoka, T. Fujii, in: H. Bildstein, H.M. Ortner (Eds.), Proceedings of the 12th International Plansee Seminar ‘89, Reutte, Tirol, Austria, 1989, p. 265.
[16] R.W. Ohse (Ed.), Handbook of Thermodynamics and Transport Properties of Alkali Metals, Blackwell Scientific Publications, Oxford, 1985, p. 508.
[17] K. Tamura, M. Inui, S. Hosokawa, Rev. Sci. Instrum. 70 (1999) 144.
[18] Y. Waseda, The Structure of Non-Crystalline Materials; Liquids and Amorphous Solids, McGraw Hill, New York, 1980.
[19] M. Urban, A.J. Sadlej, J. Chem. Phys. 103 (1995) 9692.
[20] W.-C. Pilgrim, M. Ross, L.H. Yang, F. Hensel, Phys. Rev. Lett. 78 (1997) 3685.
[21] R. Redner, W.W. Warren Jr., Phys. Rev. B48 (1993) 14892.