Structural study of expanded fluid cesium

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Abstract. We have performed x-ray diffraction and small-angle x-ray scattering measurements for expanded fluid cesium from the triple point up to supercritical regions. The experimental results show that the nearest neighbor distance starts to decrease and the density fluctuation increases below the density around 1.3 g cm$^{-3}$. These structural features suggest that clustering occurs in the metallic fluid accompanying spatial atomic-density fluctuations. The density range where such inhomogeneity of the atomic arrangement appears corresponds to the region where the compressibility of the interacting electron gas has been predicted to become negative, which suggests that the observed structural changes are those induced by the instability of the electron gas.

1. Introduction

Liquid alkali metals in the vicinity of the triple point behave as a simple monatomic metallic liquid, whereas alkali metal vapors are insulating and consist of monomers and dimers in equilibrium. These facts tell us that fluid alkali metals finally experience a metal-insulator (M-I) transition with volume expansion[1]. The conductivity measurements have revealed that fluid alkali metals show a departure from the NFE character very early in metallic liquid range ($\sim 3\rho_c$) and suggest that the electrons in the fluid are in highly correlated state as the density of the fluid decreases [2].

It is of quite an interest to investigate how these electronic transition is correlated with the structural properties. Several diffraction measurements have been carried out for expanded fluid alkali metals. Winter et al. [3] measured the neutron diffraction for fluid Cs up to the critical region. They reported that the local structure of expanded fluid Cs 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.

We have so far carried out x-ray diffraction measurements for expanded fluid Rb and observed that the peak position of the pair distribution function decreases and the density fluctuation of ionic system starts to increase in spite of the fact that the mean interatomic distance increases[7]. The density range where such structural change appreas corresponds to the region where the negative compressibility of the electron gas has been predicted [4-6], which indicates that these structural changes might be driven by the instability of the electron gas [7]. In order to investigate structural features particular to low-density fluid alkali metals and clarify such point of view, we have measured x-ray diffraction and small angle x-ray scattering of expanded fluid Cs.
2. Experimental
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 molybdenum (Mo), which is resistant to highly corrosive nature of alkali fluids [8]. High-temperature and high-pressure experiments were performed using an internally heated high-pressure vessel made of super-high-tension steel. The vessel is pressurized by He gas of high-purity grade (99.9999%). The details of the experimental setup are described elsewhere [9].

X-ray diffraction measurements for fluid Cs 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 0.2×0.2 mm² were used as an incident beam on the sample and scattered x-rays were detected with a pure Ge solid-state detector (SSD). The measurements were carried out over a wide range of temperature and pressure 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.

SAXS measurements were carried out on the beamline BL04B2 at SPring-8. 38 keV x-rays monochromatized using flat Si(111) were collimated to 0.2×0.2 mm² by the horizontal and vertical slits located in the optical hutch and then incident on the sample. The scattered x-rays were detected using an imaging plate with a camera length of about 2960 mm. A vacuum path was mounted between the sample stage and the imaging plate to reduce background from the air. By combining the Mo cell with high-pressure and high-temperature apparatus, we have succeed to perform x-ray diffraction and small-angle x-ray scattering measurements from the triple point up to the supercritical regions using synchrotron radiation at SPring-8 in Japan.

3. Results and Discussion
The structure factor $S(Q)$ for fluid Cs is plotted at different temperatures, pressures and densities in Fig. 1. With increasing temperature and decreasing density, both intensities of the first and second maxima decrease. However, the overall oscillatory structure persists even in the high-temperature region of up to 1873 K. As seen in the figure, the second peak of $S(Q)$, which is not completely blurred out, shifts to a relatively higher $Q$ region.

The pair distribution function $g(R)$ is deduced from the Fourier transform of $S(Q)$ and shown in Fig. 2. The peak height of the first maximum of $g(R)$ progressively decreases, whereas that of the second maximum approaches one. A noticeable feature of $g(R)$ is that the position of the first maximum starts to shift to a low $R$ below a density of 1.3 g cm$^{-3}$.

The density variation of the position of the first maximum, $R_1$, is shown in Fig. 3 (a). $R_1$ corresponds to the nearest-neighbor distance. It is located at approximately 5.3 Å at 313 K. It slightly decreases with decreasing density and stays almost constant until it reaches around 1.3 g cm$^{-3}$, but it starts to decrease with further density decrease.

Figure 3(b) shows the density variation in coordination number $N_1$ which is derived by integrating the radial distribution function defined by $4\pi R^2 n_0 g(R)$ ($n_0$: number density) up to the first-minimum position. $N_1$ decreases substantially and almost linearly with decreasing density from 1.8 to 1.3 g cm$^{-3}$ and then shows a deviation from a linear dependence.

In Fig.4, the density dependence of the SAXS intensity of fluid Cs is shown. Around the density of 1.3 g cm$^{-3}$, the $I(Q)$ at a low $Q$ less than 0.4 Å$^{-1}$ starts to increase with decreasing $Q$, which indicates the appearance of density fluctuation.

While many implications have been given for the importance of the effect of electron-electron correlation in expanded fluid alkali metals, it is still not sufficiently understood how the effect manifests itself in the structural properties. One of the possible routes to understand this is to regard expanded alkali metals as the realization of the three-dimensional dilute electron gas. In this sense, it is very meaningful that the local structural parameter $(R_1, N_1)$ is scaled by expansion parameter $r_s$ (the Wigner-Seitz radius in units of the Bohr radius). The parameter
Figure 1. Structure factors \( S(Q) \) for expanded fluid cesium at various temperatures and pressures. Temperature, pressure and density are indicated on the upper right-hand side of each data set. The dots represent the experimental data and the full curves show the Fourier transforms of \( g(R) \) in Figure 2.

Figure 2. Pair distribution function \( g(R) \) of fluid cesium derived from Fourier transform of \( S(Q) \). The broken line denotes the peak position of the first maximum of \( g(R) \) at 313 K. Temperature, pressure and density are indicated on the upper right-hand side of each curve.

\( r_s \) is the same order of magnitude as the ratio of the interaction energy of electrons to their average kinetic energy. However, in real metals, the effect of core polarization due to the ions reduces the strength of the effective interaction among electrons. Kukkonen et al. pointed out that an ionic background can be viewed as a uniform and polarizable background by taking core polarizability to be a constant. Thus, \( r_s \) for the electron gas in metals should be scaled with \( r_s^* = r_s/\epsilon_B \) rather than with \( r_s \), where \( \epsilon_B \) is the dielectric constant of the polarizable background defined by \( \epsilon_B = 1 + 4\pi \alpha \) (\( \alpha \): ionic polarizability, \( n \): the number density of ions) [10]. This corrected \( r_s^* \) is shown on the upper horizontal axis of Fig. 3(a).

As seen in the figure, the \( r_s^* \) value where \( R_1 \) starts to decrease and the coordination number shows a deviation from linear decrease is located between 5 ∼ 5.5. Note that the value agrees well with the critical value of \( r_s^* = 5.25 \) beyond which the static electron dielectric function (DF), \( \varepsilon(q, 0) \), of electron gas in jellium becomes negative [4-6]. Dolgov et al.[11] pointed out a negative sign of the static DF of the electron gas appears only if the exchange and correlation effects are taken into account and is theoretically admissible. The negative electron DF generates an attractive Coulomb interaction among test charges with the same sign[12].

Therefore, the structural features of expanded fluid Cs such as local contraction and the appearance of the density fluctuation in the metallic state below 1.3 g cm\(^{-3}\) might be caused by the enhancement in the attractive interaction among the ions and interpreted as the emergence of such an inhomogeneous state induced by the negative sign of the DF of the electron gas.
Figure 3. Density variation of local structure of fluid Cs, (a): the nearest interatomic distance $R_1$, (b): the coordination number $N_1$. The corresponding scale of $r^*_s$ is shown on the upper axis of the graph of $R_1$.

Figure 4. Density variation of the SAXS intensity of expanded fluid Cs with decreasing density.

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