Is there a pressure-induced discontinuous volume change in liquid Cs?

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To verify the first-order liquid-liquid transition (LLT) in liquid Cs reported by Falconi *et al.* [Phys. Rev. Lett. **94**, 125507 (2005).], the pressure dependence of liquid density was measured up to 5 GPa by an x-ray absorption method. The results showed that the density continuously increases over the entire pressure region investigated, without showing the previously reported large volume jump ($\Delta V/V \sim 17\%$) at 3.9 GPa. No existence of the volume jump is also suggested from the slopes of the melting curve in the phase diagram. Although the electronic transition is one of the most promising candidates that may cause LLT, it is unlikely to occur in liquid Cs because of the gradual nature of the $6s$-$5d$ electron transfer.

First-order phase transitions between two crystalline states are quite common, whereas those between liquid states [i.e., a liquid-liquid transition (LLT)] are very rare. The investigation of the LLT is important for revealing the mechanism of transitions between phases with the same symmetry and the prerequisite conditions for them. Among many liquids, *elemental liquids*, i.e., liquids comprising a single element, have attracted considerable attention because this system does not have a degree of freedom with respect to the chemical composition, which prevents misinterpretation of the LLT caused by a change in the chemical composition of multicomponent systems. In 2000, a first-order LLT was discovered in liquid phosphorus [1], in which the local structure drastically changed at 1 GPa, accompanied by a large volume change of 40%. *In situ* high-pressure radiography also showed conclusive evidence of the first-order nature: the coexistence of low- and high-density liquids under the same pressure and temperature condition [2]. These phenomena have been successfully reproduced by theoretical calculations [3,4]. Inspired by the discovery, many studies have been conducted to find LLTs in other substances. Falconi *et al.* investigated the pressure evolution of the structure of liquid Cs and found that the density abruptly changes by 17% at 3.9 GPa [5]. A theoretical calculation by the same author [6] also revealed that the LLT is attributed to a change in electronic state ($6s$-$5d$ electron transfer). This has attracted considerable attention because it was the first example of a LLT caused by electron transfer, which will open the way to observe LLTs in many other liquid metals. However, the data which led to the discovery, i.e., the liquid density, were *indirectly* calculated from the structure factor $S(Q)$ and the volume of the crystalline phase before melting, thus there is still room for reconsideration. In this Rapid Communication, we investigate the existence of the LLT by *directly* measuring the liquid density using an *in situ* x-ray absorption method [7].

The principle of the x-ray absorption method is very simple. The density is calculated from a transmission profile of a liquid sample confined in a cylinder with known dimensions.

The experiments were conducted at beamline BL22XU at the SPring-8 synchrotron radiation facility. A multianvil press (SMAP180) was used to compress and heat the sample. The cell assembly used in the experiment is shown in Fig. 1. A fresh Cs sample (Nacalai tesque, purity > 99.9%) was placed in a teflon capsule together with a diamond cylinder with inner and outer diameters of 0.510 ± 0.005 and 1.010 ± 0.001 mm, respectively, and a height of 0.7 mm. The empty space below and above the cylinder was filled with the sample so that the sample could be continuously supplied into the cylinder under high-pressure conditions. This assembly was placed in a graphite tube heater embedded in a pressure-transmitting medium of boron-epoxy resin. All procedures were performed in a glove box to avoid oxidation of the sample. No deterioration of the sample during the experiments was confirmed by diffraction patterns. The sample was heated by supplying electric power to the heater. The temperature was estimated from the electric power based on the power-temperature relationship determined beforehand. The pressure was estimated from the lattice parameter of a pressure marker (NaCl) placed just above the teflon capsule, based on the equation of state by Decker [8]. The uncertainties of the determined pressure and temperature were less than 0.03 GPa and 10 °C, respectively. The density was measured along nearly the same pressure and temperature path as in the previous study (Fig. 2). For the absorption measurements, we used a monochromatic beam of 35 keV with a width of 0.05 mm and height of 0.05 mm. The intensities of the incident and transmitted beams were measured with a set of ion chambers. X-ray transmission profiles were obtained by scanning the sample across the beam. The density of the sample was calculated by fitting the transmission profiles with the following function,

$$\ln[I/I_0(x)] = A - (\mu_s/\rho_s)\rho_s l(x),$$
$$l(x) = 2\sqrt{r_0^2 - x^2} : (|x| < r_0)$$
$$= 0 : (|x| > r_0).$$

Here, A is a scale factor, (μ_s/ρ_s) is the mass absorption coefficient of Cs, ρ_s is the density of the sample, $l(x)$ is the pass length of the beam in the sample at position x distant
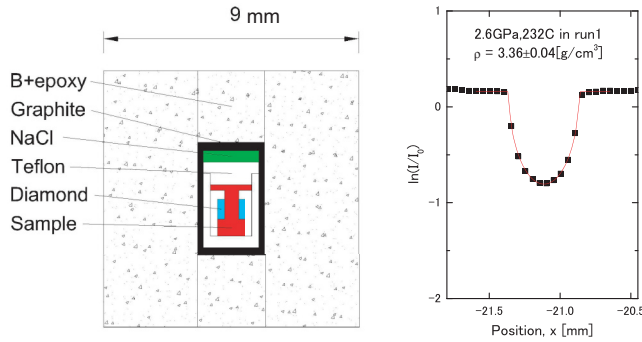
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FIG. 1. Left: A high-pressure cell assembly used in the density measurement. Right: A typical result for the fitting of the transmission profile. Black point: Observed. Red line: A result for the fitting.

from the center of the diamond cylinder, and r_0 is the inner radius of the cylinder. A typical result for the fitting is shown in Fig. 1 and the Supplemental Material [9]. The random and systematic errors of the determined density were less than 0.1 and 0.3 g/cm^3, respectively.

Figure 3 shows the pressure dependence of liquid density at two temperatures (232 and 350 °C). Here, the values of previous studies [5] are also shown. The experiments were conducted twice for each temperature. With increasing pressure, the density of the liquid gradually increased along the line for crystalline phases. In all experimental runs, no discontinuous change was observed at 3.9 GPa wherein a large density jump was previously reported [5]. This indicates that the liquid does not show LLT. When the values in the previous study are compared with my results, they are found to be markedly smaller than mine below 3.9 GPa, while they are close to mine above 3.9 GPa. The previously reported LLT seems to originate from the smaller values below 3.9 GPa and the abrupt increase at approximately 3.9 GPa.

To reveal the origin of the difference in the determined density, the methods used to estimate the density in the previous study [5] were examined. Generally, the measurement of liquid density at a high-pressure and high-temperature condition is
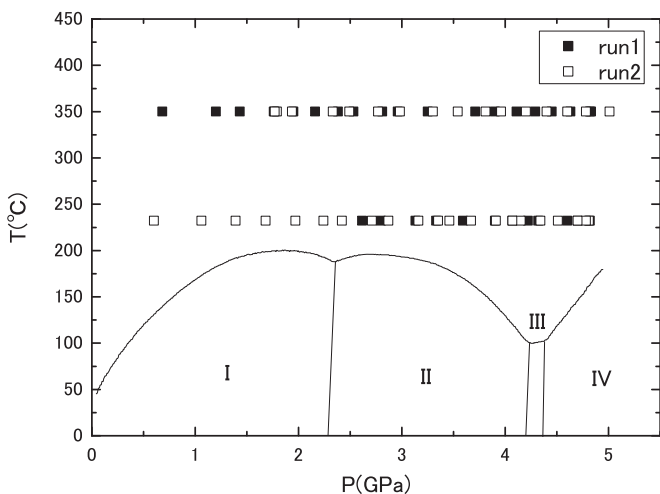

FIG. 2. Previously reported phase diagram of Cs [15] and the experimental PT conditions of this study.
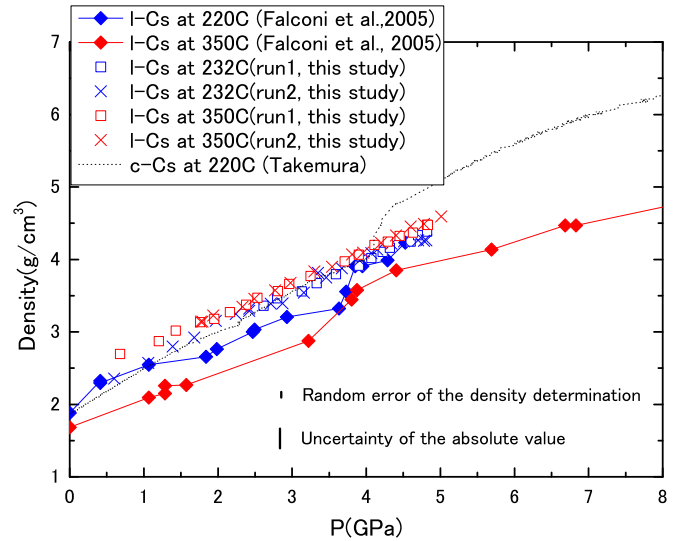

FIG. 3. Pressure dependence of density of liquid Cs at 232 and 350 °C. The values of the previous study [5] and those of the crystalline phases [26,27] are also shown together.

difficult. Therefore, the density is often estimated by indirect methods. Falconi *et al.* tried to calculate the density from the position of the first peak in $S(Q)$, assuming the uniform contraction model, i.e., the microscopic length linearly decreases with macroscopic scale [10]. This model is applicable only when the liquid contracts uniformly without changing its shape of $S(Q)$. In their study, no significant change of the profile was observed on compression to 3.9 GPa, thus the liquid density below 3.9 GPa was calculated based on this model. However, upon further compression, they found a significant change in the profile of $S(Q)$, and then they unavoidably used another method above 3.9 GPa: The density was calculated from the volume of the crystal phase before melting and the volume change on melting using the Clausius-Clapeyron relation ($dT/dP = \Delta V_{melt}/\Delta S_{melt}$, where ΔV_{melt} and ΔS_{melt} are the volume and entropy jump, respectively, on melting). The methods employed below and above 3.9 GPa are different and will have different systematic errors, therefore, it is natural that the determined density shows a gap at 3.9 GPa, which is most likely the cause of the apparent density jump at 3.9 GPa. Furthermore, the assumption used to calculate the density below 3.9 GPa is found to be inappropriate for liquid Cs when the electronic states change under pressure, as will be discussed later.

In the study of Falconi *et al.*, the density below 3.9 GPa was estimated from the position of the first peak in the structure factor $S(Q)$ assuming the uniform contraction model. In the context of the hard sphere model [11], this corresponds to a contraction in which the hard sphere diameter σ linearly decreases with the cube root of specific volume $V^{1/3}$. In this case, the packing fraction $\eta = \frac{1}{6}\pi\rho\sigma^3$ remains constant regardless of pressure (ρ is the number density and is the inverse of the specific volume). If a liquid follows the uniform contraction model, the position of the first peak in $S(Q)$ shifts with volume following the relationship $(Q_P/Q_0)^{-1} = (V_P/V_0)^{1/3}$ (the suffix represents the values at high-pressure and zero-pressure states, respectively) and the height of the first peaks remains constant. This model is often used to
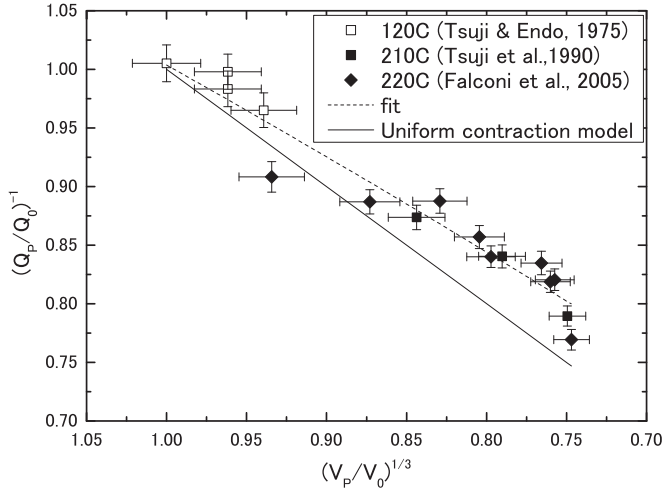
FIG. 4. The relationship between $(V_P/V_0)^{1/3}$ and $(Q_P/Q_0)^{-1}$. The solid line represents the relationship expected for the uniform contraction model. The dotted line is only to guide the eyes. The procedure to obtain each value is described in the text.
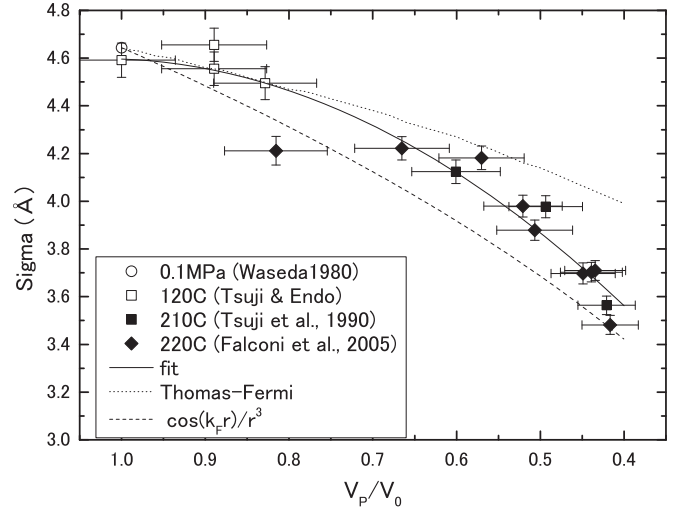

FIG. 5. Volume dependence of the hard sphere diameter σ. The solid line is only to guide the eyes. Those expected for the two theoretical models [10] are also shown by the dashed and dotted lines.

estimate the liquid density at high pressures, however, the applicability is strongly dependent on the species of liquid. To check the applicability of this model to liquid Cs, the $(Q_P/Q_0)^{-1} - (V_P/V_0)^{1/3}$ relationship is plotted in Fig. 4. Here, the position of the first peak in $S(Q)$ was obtained by fitting $S(Q)$ in Refs. [5,12–14] (up to 4.4 GPa) by a Gaussian function. In the fitting, only the top part of the first peak [i.e., the Q region where $S(Q)$ is higher than the 90% of the maximum] was used to avoid uncertainty caused by asymmetry of the peak. The plot shows that the contraction behavior of liquid Cs significantly deviates from the uniform contraction model. The maximum deviation of the $(V_P/V_0)^{1/3}$ value is approximately 8%, which causes a density error of 24%. This value is much larger than the volume jump (17%) previously reported at 3.9 GPa. These results indicate that the density of liquid Cs cannot be estimated from the position of the first peak in $S(Q)$ and that the smaller density below 3.9 GPa in the previous study would originate from an inappropriate use of the model.

No existence of the LLT is supported by the phase diagram because a volume jump in the liquid phase is, if present, reflected as a kink in the melting curve. Figure 2 shows the previously reported phase diagram of Cs up to 5 GPa [15]. The LLT is located at approximately 3.7–3.9 GPa regardless of temperature in the study of Falconi *et al.* [5] and the phase boundary of LLT generally becomes steeper at low temperatures [16], thus the phase boundary between two liquid states would hit the melting curve of Cs-II at that pressure when it is extended toward lower temperatures. The phase diagram that was thoroughly investigated by Kennedy *et al.* [17] and Jayaraman *et al.* [15], however, shows no anomaly near 3.7–3.9 GPa. The absence of the LLT is more quantitatively proven by calculation of the melting slope expected for the previously reported density jump. In the thermodynamics, the difference in the slope of the melting curve below and above the LLT pressure can be expressed as

$$\Delta(dT/dP) = (dT/dP)_{\text{cryst}-\text{HDL}} - (dT/dP)_{\text{cryst}-\text{LDL}}$$

$$= \Delta V_{\text{LDL}-\text{HDL}} / \Delta S_{\text{melt}}.$$

Here, $(dT/dP)_{\text{cryst}-\text{HDL}}$ and $(dT/dP)_{\text{cryst}-\text{LDL}}$ are the slope of the melting curve from Cs-II to high- and low-density liquids, respectively. $\Delta V_{\text{LDL}-\text{HDL}}$ is the volume difference of the two liquid states. ΔS_{melt} is the entropy change on melting and is assumed to be common for both liquids. By using values taken from the literature ($\Delta V_{\text{LDL}-\text{HDL}} = 7.0$ cm^3/mol [5], $\Delta S_{\text{melt}} = 2.92$ cal/mol K [15]), the expected difference in the slope of the melting curve is calculated to be $\Delta(dT/dP) = 1 \times 10^4$ K/GPa. This implies that either or both melting curves need to be steep near 3.7–3.9 GPa if a LLT accompanied by a density change of 17% were to occur. Even if the transition pressure is slightly shifted toward a higher pressure beyond the II-III or III-IV boundary in the crystalline phases, the absence of the LLT is also confirmed in a similar way [the maximum volume difference is found to be less than a few percent, taking the slope of the melting curve into consideration (see Supplemental Material [9])]. This indicates that the previously reported large volume jump in a liquid state [5] is inconsistent with the phase diagram. The nonexistence of the LLT is also suggested from a high-pressure inelastic x-ray scattering study [18], in which no anomaly was observed in the microscopic dynamics near 3.9 GPa, even though a large change was expected because the density strongly affects the microscopic dynamics. All these findings suggest that the LLT of Cs does not exist.

If the 6s-5d transfer suddenly occurs at a certain pressure, it may cause the LLT. To check this possibility, the pressure evolution of the electronic state in the liquid is examined. Resistivity measurements [15,19] showed that the increase in the resistivity, which reflects the electronic transfer from the 6s to the more localized 5d state, continuously occurs over a wide pressure region up to 4.5 GPa. The gradual change in the electronic state is also supported from the results of the present study. Figure 5 shows the volume dependence of the hard sphere diameter σ obtained by coupling the liquid density determined in this study and σ determined by fitting $S(Q)$ in Refs. [5,12–14] with a hard sphere model [11]. The figure also shows the dependence expected for the two theoretical models with different screened potentials [10]: (i) When the screening

of a point ion is described by the Tomas-Fermi model, σ changes with $V^{1/6}$; and (ii) when the potential is described by $\cos(2k_F r)/r^3$ and therefore the core diameter σ inversely changes with the Fermi momentum k_F, σ changes with $V^{1/3}$ (this results in the uniform contraction model). The obtained σ initially decreases along the line for the Thomas-Fermi model, but it starts to deviate near $V_P/V_0 = 0.8$ ($P \sim 0.5$ GPa). At higher pressures, the *rate* of the decrease becomes larger than that expected for both models, indicating that the electron starts to transfer from the $6s$ to the more localized $5d$ state. These findings suggest that the s-d transfer smoothly occurs over a wide pressure region in liquid Cs. This shows a marked contrast to the s-d transfer in the crystalline state, in which the transfer rapidly occurs at Cs-II to Cs-III or Cs-IV transitions [20] although it has already started at low pressures [20–23].

The LLT in elemental liquids has been observed or proposed in many substances such as liquid C, Si, P, Bi, S, and Se [24]. All these substances have directional bonding in low-pressure liquid, and the transitions are accompanied by a change in the symmetry of their local structure. From this viewpoint, they are similar to crystalline transitions wherein the symmetry changes at the transition, rather than the liquid-gas transition where

the symmetry does not change even on a microscopic scale. In contrast, the LLT caused by electronic transfer would be similar to the latter case. Although its existence in liquid Cs is denied in this study, theoretical calculations suggest that liquids with an isotropic interatomic potential can show an LLT if the interatomic potential has an attractive part and two characteristic repulsive distances [25]. This situation may be realized in liquid metals where the potential oscillates as a result of the Fermi cutoff. Therefore, an LLT without a change in local symmetry may be observed in other liquid metals in the future.

By using the x-ray absorption method, the present study clarified the nonexistence of the LLT of Cs, which has been claimed by an indirect density estimation. The method to estimate the liquid density from the position of the first peak in $S(Q)$ assuming the uniform contraction model is often used. The present study provides instructive caution; the contraction behavior of a liquid itself is a subject of liquid state physics, so that this method should be used taking the limit of the approximation into consideration.

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