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Study of liquid gallium as a function of pressure and temperature using synchrotron x-ray microtomography and x-ray diffraction

Renfeng Li,[1,2] Liangliang Li,[1,3] Tony Yu,[2] Luhong Wang,[1,a)] Jiaxuan Chen,[1,3] Yanbin Wang,[2] Zhonghou Cai,[3] Jiuhua Chen,[4,5] Mark L. Rivers,[2] and Haozhe Liu[1,4,a)]
[1]*Harbin Institute of Technology, Harbin 150080, China*
[2]*GeoSoilEnviroCARS, Center for Advanced Radiation Sources, The University of Chicago, Chicago, Illinois 60637, USA*
[3]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[4]*Center for High Pressure Science and Technology Advanced Research, Changchun 130015, China*
[5]*Center for the Study of Matter at Extreme Conditions, Florida International University, Miami, Florida 33199, USA*

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The volume change of liquid and solid gallium has been studied as a function of pressure and temperature up to 3.02 GPa at 300 K and up to 3.63 GPa at 330 K using synchrotron x-ray microtomography combined with energy dispersive x-ray diffraction techniques. Two sets of directly measured P-V data at 300 K and 330 K were obtained from 3D tomography reconstruction data, and the corresponding isothermal bulk moduli were determined as 23.6 (0.5) GPa and 24.6 (0.4) GPa, respectively. The existence of a liquid-liquid phase transition region is proposed based on the abnormal compressibility of Ga melt at about 2.44 GPa and 330 K conditions. © *2014 AIP Publishing LLC*.
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Liquid gallium exhibits unusual and unique physical properties. The low melting temperature (303 K) and high boiling temperature (2478 K) at ambient pressure display its wide stability range. Gallium has a rare water-ice type P-V-T phase diagram in which the density of Ga melt exceeds by about 3% that of the stable solid Ga phase I at ambient pressure. Moreover, liquid gallium, which is easily supercooled, can remain in a metastable liquid state for several months at ambient pressure.[1–5] A rich polymorphism and metastable modifications of Ga have been discovered in P-T domain. Ga phase I can undergo transitions to Ga II (*bcc*), Ga III (*bct*), Ga IV (*fcc*), Ga V (*hR6*), or liquid Ga depending on the P-T paths.[5–10] These uncommon properties of gallium could be related to the coexistence of metallic and covalent bonding.[3,11–16] The microstructure and compressibility of gallium melt has some similarity to high-pressure phases, therefore liquid-liquid transition in Ga melt under high P-T conditions has been suggested.[2,17–19]

There are a number of studies of liquid gallium under high pressure conditions, however, some fundamental properties such as the equation of state (EoS) of liquid Ga under extreme conditions remain unclear. Very recently, the advanced pair distribution function (PDF) method in which synchrotron high-energy x-ray total scattering data, combined with reverse Monte Carlo simulation, was used to study the microstructure and EoS of liquid gallium under high pressure conditions. However, the application of PDF method for amorphous or liquid samples under pressure conditions normally required a priori knowledge of their EoS. The density calculation from the reverse Monte Carlo simulation with the best mathematical fit to the measured structure factor data could cause big errors if it is calculated without knowing the EoS. For example, two independent groups reported controversial results on the EoS and density of Ga melt under pressure. Yu *et al*. reported that the density of liquid Ga is 6.46 g/cm^3 at ambient temperature under 0.8 GPa,[20] while Yagafarov *et al*. reported a value of 6.33 g/cm^3 at 0.8 GPa under 295 K using a similar method.[17] To shed light on this problem and gain insight into the density change of liquid gallium under pressure, we carried out synchrotron x-ray microtomography combined with XRD measurements on liquid and solid gallium in a pressure and temperature domain from 0 GPa to 3.02 GPa at 300 K, and 1.16 GPa to 3.63 GPa at 330 K, respectively. This study provides a directly measured EoS on gallium melt and solid in these P-T domains.

X-ray microtomography experiments under high pressure and high temperature were performed with the large volume press (LVP) at 13-BM-D of GSECARS, Advanced Photon Source (APS), Argonne National Laboratory. The apparatus consists of a 250-ton press with a rotational Drickamer cell that uses thrust bearings to allow full 180° rotation while under loads of up to 50 tons.[21] Fig. 1 shows the detailed configuration of the cell which was specifically designed for this Ga sample. The cell assembly parts are shown in Figs. 1(a)–1(c), while the entire cell assembly is shown in Fig. 1(d). A solid gallium sample with 99.9999% purity was heated to melt and then filled the Teflon sample container. The gold foil and MgO disk were used as pressure markers, while the graphite tube was used as heater.

The sample was compressed and heated up to 3.63 GPa and 330 K, and the experimental data path in P-V diagram is shown in Fig. 2. Synchrotron energy dispersive x-ray diffraction (EDXRD) was employed to characterize the pressure from the known EoS of Au or MgO markers, and phases of the gallium sample in the LVP before and after performing tomographic measurements at each P-T point. After each diffraction pattern was taken, the white beam was switched to monochromic X-rays at 40 keV, which was optimized for tomographic imaging contrast for this specific sample and cell

[a)]Authors to whom correspondence should be addressed. Electronic addresses: luhong1@hit.edu.cn and haozhe@hit.edu.cn.

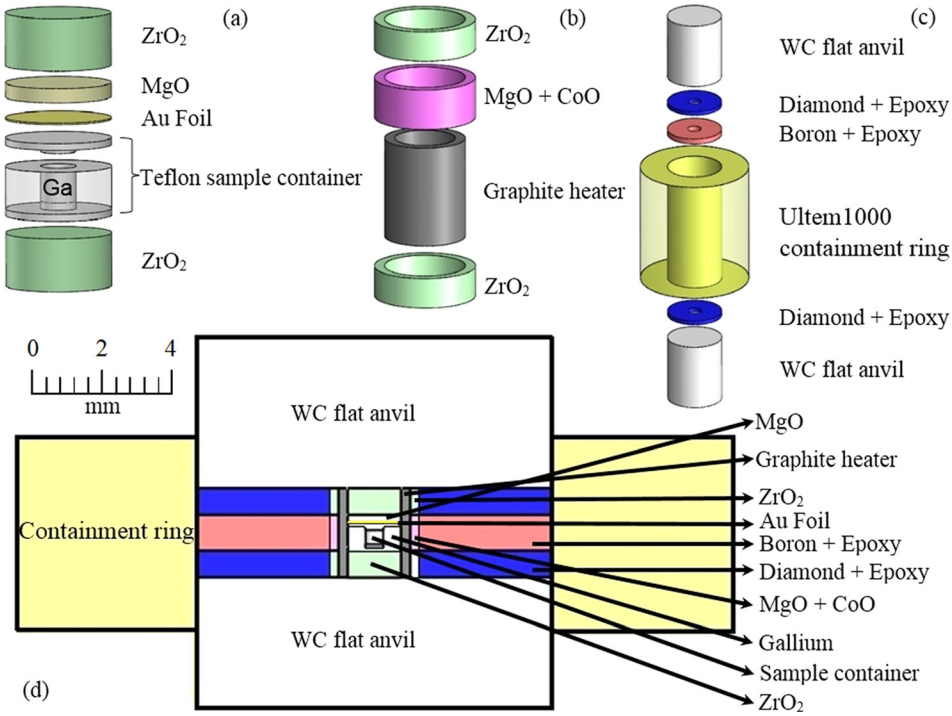

FIG. 1. Illustrations of Drickamer cell for the microtomography measurements. (a)–(c) The detailed cell assemblage. (d) Scaled view of section of Drickamer cell used in this study.

geometry. The transmitted x-ray radiographs were recorded using a LuAG scintillator, a 5× objective lens, and a CCD detector with an exposure time of 6 s. The cell was rotated using a step size of 0.5° from 0° to 180° with the rotation axis perpendicular to the direction of the incident beam, to obtain a series of radiography images. From this full set of radiographic images, 3D tomographic slices were reconstructed.[21,22] The uncertainty in pressure and temperature was estimated to be about 0.1 GPa and 5 K, respectively. Pressure values, which carried much smaller error bars from XRD data fitting process, were used in this paper.

Some typical EDXRD patterns collected at 300 K and 330 K are shown in Fig. 3. Besides the Bragg peaks from the Ga sample, diffraction peaks from the graphite heater, pressure markers, and other materials in cell environment are

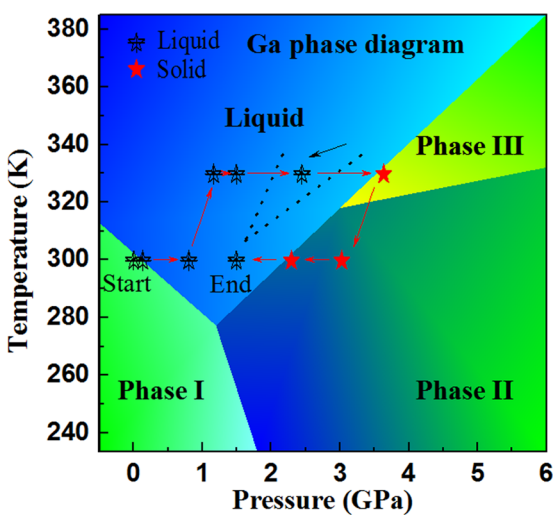

FIG. 2. Pressure-temperature paths for gallium in X-ray microtomography and EDXRD experiments. Phase diagram of gallium is cited from Ref. 6. The dotted lines outline a possible liquid-liquid transition region.

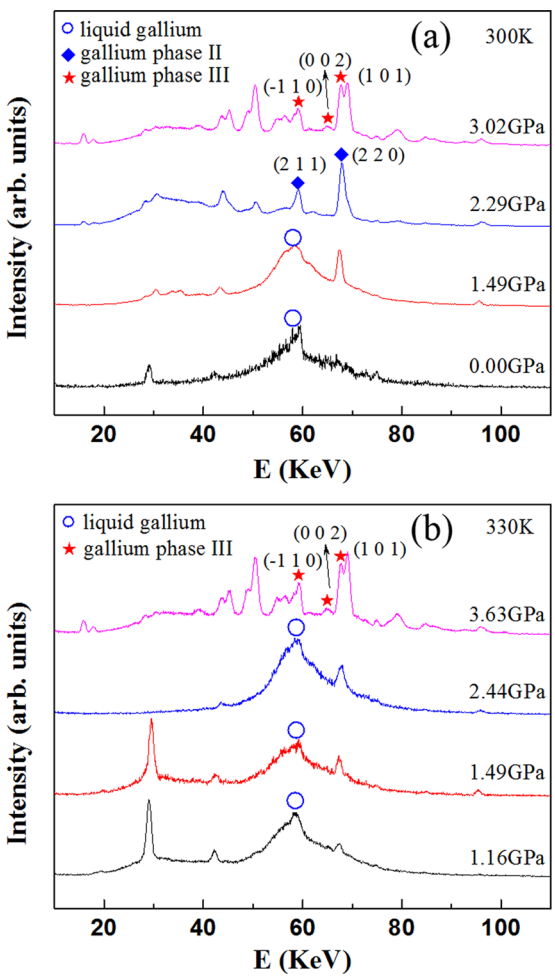

FIG. 3. Selected typical EDXRD patterns of Ga as a function of pressure at (a) 300 K and (b) 330 K.

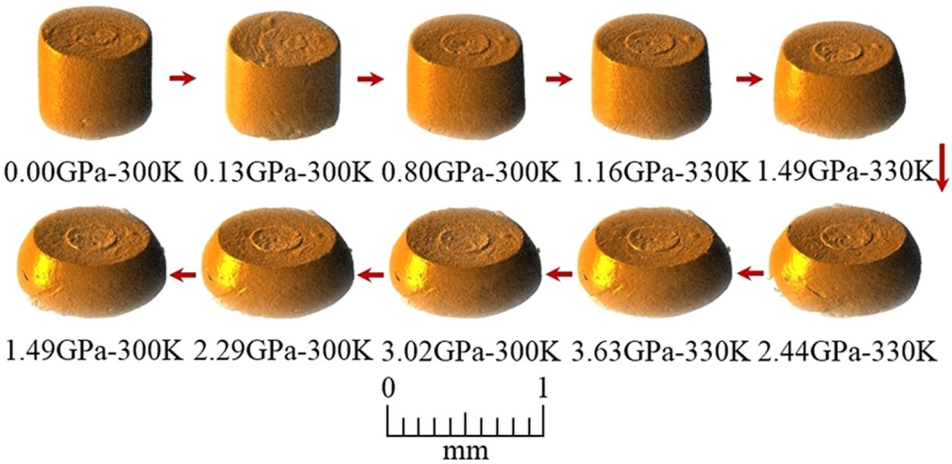

FIG. 4. Reconstructed 3D images for the gallium as a function of pressure and temperature. The order follows experimental P-T path in Fig. 2.

visible but were not indexed in these figures to avoid confusion. From these XRD experiments, pressure values were calculated from diffraction peaks of Au or MgO markers, and the melting and solidification of the gallium sample were determined. From the XRD patterns in Fig. 3(a), we can confirm that the starting Ga sample under ambient conditions was undercooled liquid after it was heated in loading process to reaching its full density. The melting of Ga could be identified from the appearance of a broad scattering peak at around 58 KeV for Ga melt, and the disappearance of the narrow diffraction peaks for solid Ga in EDXRD signals. Previous studies revealed that the metastable region could exist in the gallium phase diagram depending on the dynamics of P-T treatment paths. In this high-pressure high-temperature experiment, the liquid and solid boundaries did follow the stable phase diagram of Ga (as shown in Fig. 2) from the EDXRD data. It is noted that Ga phase III was observed in its metastable region (at about 300 K and 3.02 GPa conditions) along with Ga phase II. This kind of metastable behavior of solid Ga is consistent with the results of previous high-pressure high-temperature experiments.[4]

The scattering patterns of gallium melt are very broad due to the lack of long-range order. Unlike a crystalline sample whose specific density can be evaluated from its XRD data, densities of liquid or amorphous materials are traditionally difficult to determine under high-pressure and high-temperature conditions. The synchrotron high-pressure X-ray microtomography technique is an advanced method for EoS measurements for liquids and amorphous materials under extreme conditions. Some long standing puzzles in amorphous systems have been solved in previous high pressure tomography studies.[23]

Data reconstruction was performed using the fast Fourier transform based Gridrec software modified at GSECARS.[21] After 3D tomography reconstruction, ImageJ software was used to analyze the 3D volume data.[24] Fig. 4 shows a series of reconstructed 3D images of the gallium sample as a function of pressure and temperature. The relative volume change with pressure and temperature, for liquid Ga and solid Ga, can be precisely calculated. The P-V data of Ga at 300 K and 330 K are presented in the inset of Figs. 5(a) and 5(b) using several microtomography analysis filter settings. It is clear that the effects of filtering methods on relative volume V/V_0 are very small (up to 0.19%). The mean filter method was used in the EoS data for gallium at 300 K and 330 K as shown in Figs. 5(a) and 5(b), respectively.

At room temperature, the isothermal bulk modulus B_0 of Ga melt is determined to be 23.6 (0.5) GPa by fitting to the second order Birch-Murnaghan EoS (blue solid curve in Fig. 5(a)). For comparison, several sets of EoS data for Ga melt from previous reports are also plotted in Fig. 5(a). The values of the bulk modulus B_0 in these previous studies are between

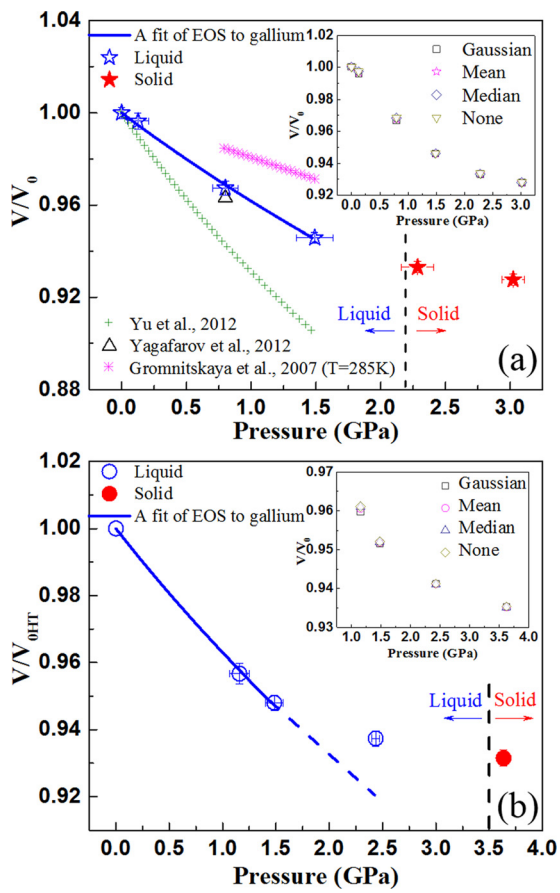

FIG. 5. Relative volume V/V_0 of the gallium as a function of pressure determined by microtomography measurement at (a) 300 K and (b) 330 K. Error bars reflect uncertainties in relative volume based on threshold determination and in pressure from fitting of the diffraction peaks of gold. The blue open star illustrates liquid gallium, while red solid one illustrates solid gallium in this study. The blue solid line shows an EoS fitting to the liquid data using the second order Birch-Murnaghan EoS.

50 (3) GPa (with $B_0' = 1$) determined by Gromnitskaya *et al.* from ultrasonic measurements at 285 K,[1,2] and $B_0 = 12.1$ (6) GPa calculated by Yu *et al.* from reverse Monte Carlo simulations combined with experimental scattering data.[20] Even considering the well-known trade-off effect of small B_0' on B_0, the difference on the EoS of Ga melt is quite huge in these previous reports. It is clear that the relative volume change in this study is close to that of one data set calculated by Yagafarov *et al.* at 0.8 GPa and 295 K,[17] which is very different from the results of Yu *et al.*, using a similar method, i.e., reverse Monte Carlo simulations combined with fitting the experimental structure factor of Ga melt under pressure. The present direct measurement of the EoS of Ga melt upon compression at room temperature, therefore, gives a fundamental justification for the controversial results of density from these two previous PDF studies.[17,20] Furthermore, we suggest that special care is needed when fitting the EoS of amorphous materials or liquid systems when the PDF method is used at high-pressure conditions, since the methodology of PDF alone cannot be guaranteed to produce a physically meaningful EoS. A measured EoS is always needed as guideline to avoid large uncertainties from Monte Carlo fitting. Otherwise, the microstructure information for non-crystalline systems from PDF analysis without measured EoS as input, such as $g(r)$ and coordination number change under pressure, could cause unexpected bias and become misleading.

In case of 330 K compression, the relative volume $V_{0,HT}/V_0$ is determined based on previous work,[25] where $V_{0,HT}$ is the volume of liquid gallium at 330 K and V_0 is the one at 300 K under ambient pressure. Then relative volume $V/V_{0,HT}$ was plotted in Fig. 5(b) based on the tomographic measurement. Using the 3 data points from 0 GPa to 1.49 GPa to fit to the second order Birch-Murnaghan EoS, the isothermal bulk modulus $B_{0,330K}$ is determined as 24.6 (0.4) GPa. This $B_{0,330K}$ should have relatively bigger uncertainty due to the limited number of data points, and this caused its slightly higher than the B_0 of Ga melt at room temperature. It is interesting to note that the slope of relative volume change is clearly different when pressure is extended up to 2.44 GPa at 330 K as shown in Fig. 5(b). At this pressure range, Ga melt becomes much less compressible compared with the compressibility trend from lower pressure region. This observation suggests that there is a potential liquid-liquid transition region at about 330 K around 2.44 GPa, in which the Ga melt seems more like solid Ga phase III. Therefore, a zone indicated with dotted lines is outlined in Fig. 2 for this possible transition zone. If we carefully check the EDXRD data and analysis for Ga melt from a recent high P-T experiment,[26] the data points at 4.20 GPa/340 K and 4.30 GPa/450 K did show a different trend compared to the higher temperature data point at about 4.20 GPa.

Combining the relative volumes of the gallium determined in this work with a starting reference density, the densities for liquid and solid gallium can be calculated. It is noted that starting sample was liquid at 300 K under ambient pressure in this work. Density of 6.097 g/cm^3 cited form previous work[25] was used as the starting reference density point. The density of liquid gallium was determined as 6.303 g/cm^3 at 300 K under 0.8 GPa, which is close to the previous reported value by Yagafarov *et al.*[17] Moreover, at 300 K under 3 GPa, the density of the solid gallium is 6.572 g/cm^3 which is consistent with the calculation from present EDXRD measurement for gallium phase III, and also close to the previously reported density of 6.57 g/cm^3 measured at 298 K under 2.8 GPa.[6] These agreements demonstrate that relative volume measurements from tomography imaging method under pressure indeed provide reliable EoS for Ga melt and solid.

In this work, gallium under pressure has been studied using *in situ* synchrotron x-ray microtomography combined with EDXRD techniques, and its volume change as a function of pressure and temperature were obtained. The bulk moduli of Ga melt were determined as 23.6 (0.5) GPa at 300 K and 24.6 (0.4) GPa at 330 K, respectively. The density values of gallium are in good agreement with previous works. In the region around 330 K and 2.44 GPa, a liquid-liquid transition is proposed based on the abnormal compressibility of melt at this zone. The present work demonstrated that this direct volume measurement for non-crystalline systems under pressure using microtomography techniques could provide fundamental insight, and offer crucial EoS for related PDF research.

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