

Molar volumes of molten indium at high pressures measured in a diamond anvil cell

Guoyin Shen,^{a)} Nagayoshi Sata,^{b)} Mathew Newville, Mark L. Rivers,^{c)} and Stephen R. Sutton^{c)}

Consortium for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637

(Received 21 March 2002; accepted for publication 18 June 2002)

Molar volumes of molten indium have been measured in an isothermal compression up to 8.5 GPa at 710(3) K in an externally heated diamond anvil cell. The measurement is based on the x-ray diffraction and x-ray absorption of materials using a synchrotron monochromatic x-ray microbeam. The fit to the results with the Birch–Murnaghan equation of state gives parameters of $V_0 = 16.80 \text{ cm}^3$, $K_0 = 23.9(6) \text{ GPa}$, assuming that $K' = 4$. This method should be applicable for measuring molar volumes of liquids and other amorphous materials in the diamond anvil cell.

© 2002 American Institute of Physics. [DOI: 10.1063/1.1499737]

The liquid–liquid (LL) or the amorphous–amorphous (AA) phase transitions for a pure substance have been of interest recently in condensed matter physics.^{1–5} Experimental studies have suggested first-order LL or AA phase transitions, e.g., for molten phosphorus,⁴ supercooled water,³ densified porous silicon,⁵ and liquid carbon.⁶ A first-order phase transition should involve discontinuities in the first derivatives of free energy: volume and entropy. Therefore, molar volume is an appropriate order parameter for describing such LL or AA phase transitions. While the molar volume of crystalline phases can be determined by x-ray diffraction to ultrahigh pressures, molar volume measurements on melts and amorphous materials at high pressures are limited in a few systems^{4,7,8} using large volume presses. Recently, an effort has been made with the diamond anvil cell (DAC) for molar volume and structure measurements of high pressure fluids (water and argon) up to 1.1 GPa.⁹ In this letter, we introduce a method for measuring the molar volume of amorphous materials in a DAC and report the results on molten indium in an isothermal compression at 710 K up to the solidification pressure (8.5 GPa). Indium was chosen for the first experiment because of its relatively low melting temperatures and the absence of significant handling problems.

A rhenium gasket was preindented to about $50 \mu\text{m}$ in thickness with diamond anvils of $500 \mu\text{m}$ in culet diameter. Two holes with $100 \mu\text{m}$ diam were drilled at the positions equidistant from the center [Fig. 1(a)]. Indium powder (99.999%, Alfa Aesar) was loaded into one of the holes; the other hole was loaded with NaCl that serves as a thickness and absorption calibrant. Another NaCl chip ($\sim 5 \mu\text{m}$ in dimension) was put at the corner of the chamber with indium sample for the pressure measurement [Fig. 1(a)].

The x-ray diffraction and absorption measurements were performed at GeoSoilEnviroCARS, beamline 13-ID-D at the Advanced Photon Source (APS). The x-ray beam size was controlled by a slit system to $150 \times 150 \mu\text{m}$ and then focused

to a beam size of $5(\text{vertical}) \times 5(\text{horizontal}) \mu\text{m}$ at the full width at half maximum (FWHM) by Kirkpatrick–Baez (KB) mirrors.¹⁰ The x-ray intensity before and after the DAC was monitored by an ion chamber and a photodiode, respectively. The photodiode reading reflects the x-ray absorption of the sample and the DAC, while the reading from the ion chamber is used for normalization.

As shown in Fig. 1(b), x-ray transmission intensities of the sample (indium) and the calibrant (NaCl) can be precisely determined. According to the absorption law, the transmission intensity can be written as: $I_A = I_0 \exp(-\mu_{AP} l_A - \mu_{DP} l_D)$, where I_0 the normalized incident intensity, μ the mass absorption coefficient, ρ the density, l the thickness, subscript A representing NaCl, rhenium, and indium, and subscript D diamond anvils. Since the change of ρ_D and l_D is negligible and the change in $(\rho_D \cdot l_D)$ is even smaller, the absorption of diamond anvils can be considered to be constant throughout the experiment. Therefore, we can rewrite the equation as $I_A = I'_0 \exp(-\mu_{AP} l)$, where $I'_0 = I_0 \exp$

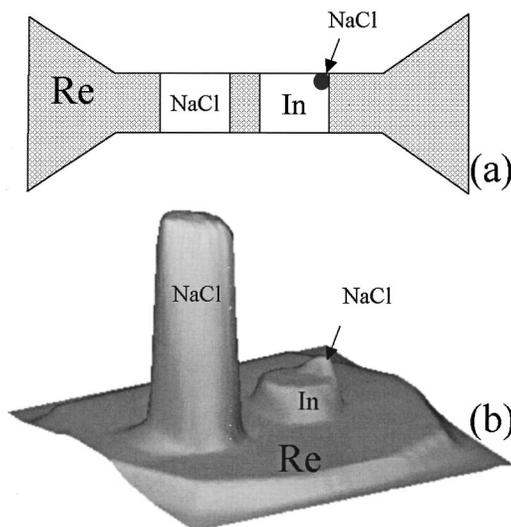


FIG. 1. (a) Dual hole configuration of a rhenium gasket between two diamond anvils. (b) X-ray transmission profile measured by a photodiode with a monochromatic x-ray beam at 29.200 keV. Profile was obtained by scanning the sample position in a step of $5 \mu\text{m}$ with x-ray beamsizes of $5 \times 5 \mu\text{m}$ at the FWHM.

^{a)}Electronic mail: shen@cars.uchicago.edu

^{b)}Also at: Department of Earth and Planetary Science, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan.

^{c)}Also at: Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637.

($-\mu_D \rho_D l_D$). If we assume that μ_A is the same for solids and liquids of the same substance and is independent of pressure and temperature, i.e., the monochromatic x-ray energy is far away (>1 keV) from any absorption edges, the thickness (l) can then be expressed by

$$l = \ln(I_{\text{NaCl}}/I_{\text{Re}}) / (\mu_{\text{Re}} \rho_{\text{Re}} - \mu_{\text{NaCl}} \rho_{\text{NaCl}}). \quad (1)$$

The quantities in the right side of Eq. (1) are either known values (μ) or measurable (ρ and I). The x-ray transmission (I) can be directly measured as shown in Fig. 1(b); the mass absorption coefficients (μ) at 29.200 keV are obtained from a report¹¹ by the National Bureau of Standards (NIST); the densities of NaCl and rhenium are obtained by x-ray diffraction measurements since these two materials were in crystalline states in the pressure–temperature range of this study. By assuming the same thickness across the indium and the calibrant, we obtain the density of indium to be

$$\rho_{\text{In}} = [\ln(I_{\text{NaCl}}/I_{\text{In}}) + \mu_{\text{NaCl}} \rho_{\text{NaCl}} l] / \mu_{\text{In}} l. \quad (2)$$

It should be noted that the distance between two diamond anvils is not always the same across the culet area. Especially at pressures over 30 GPa, deformation occurs with diamond anvils,¹² resulting in an uneven thickness across the sample chamber. Equations (1) and (2) should be then expressed as

$$l_{\text{Re}} = [\ln(I_{\text{NaCl}}/I_{\text{Re}}) + \mu_{\text{NaCl}} \rho_{\text{NaCl}} l_{\text{NaCl}}] / \mu_{\text{Re}} \rho_{\text{Re}}, \quad (3)$$

$$\rho_{\text{In}} = [\ln(I_{\text{NaCl}}/I_{\text{In}}) + \mu_{\text{NaCl}} \rho_{\text{NaCl}} l_{\text{NaCl}}] / \mu_{\text{In}} l_{\text{In}}. \quad (4)$$

where l_{NaCl} , l_{In} , and l_{Re} are the thicknesses of NaCl, indium, and rhenium, respectively. To the first-order approximation, we assume the same l_{NaCl} across the NaCl area (which is usually much less than the culet size), we can get l_{NaCl} by applying Eq. (1) and the average transmission of rhenium around the NaCl area. Uncertainties due to the averaging process are found to be less than 1.2%. A two-dimensional thickness profile can be obtained by applying Eq. (3) with the two-dimensional data of I_{Re} and ρ_{Re} across the anvil's culet area. Data of I_{Re} , as in Fig. 1(b), are measured by absorption and can be obtained in a reasonable time period of ~ 30 min, while the full profile of ρ_{Re} requires diffraction data from more than 5000 positions and could take a long time and much effort. In practice, because of the radial symmetrical configuration in the DAC experiment, data of ρ_{Re} along two lines perpendicular with each other across the center can be used to construct a reasonable radial symmetric profile of ρ_{Re} across the whole culet area. In the present study, the pressure range was below 10 GPa, and the anvil deformation was found to be negligible. The thickness at the sample area is the same as that at the calibrant (NaCl) area within experimental errors. Molar volumes were calculated from densities according to Eq. (2).

Below the sample's melting points, molar volumes can be determined by x-ray diffraction. This gives us a good opportunity to cross check the results of the present method based on absorption. At 3.4 GPa and 448 K, where the indium was at a crystalline state, we obtained a molar volume of 14.976(31) cm^3 from the x-ray diffraction measurement, and of 14.87(21) cm^3 from the absorption measurement, where the standard errors were estimated by the uncertainties in molar volume measurements by x-ray diffraction and in

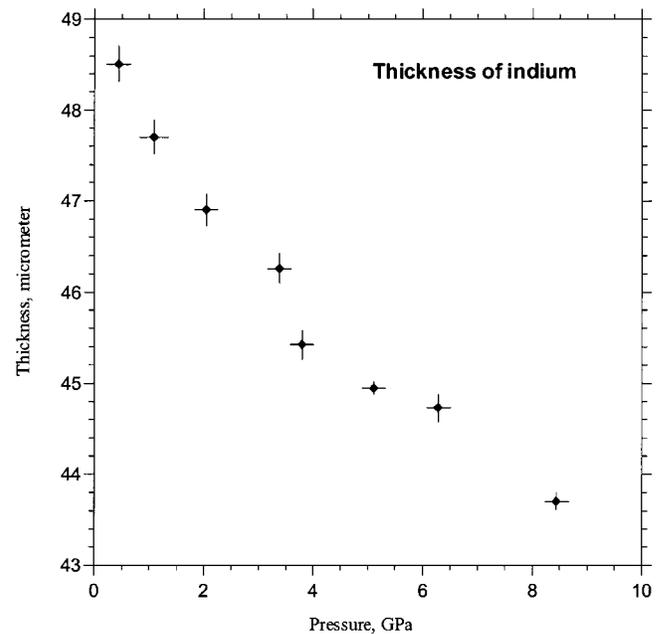


FIG. 2. Thickness of indium sample as a function of pressure in the diamond anvil cell at 710(3) K. Pressures were determined by the x-ray diffraction on the NaCl piece located at the corner of the indium sample chamber (Fig. 1). Thickness was measured according to Eq. (1). Error bars are mainly from uncertainties in the transmission measurements.

x-ray transmission intensities. The relative error ($\Delta V/V$) by the absorption method is 1.4% compared to that of 0.2% by diffraction. The molar volume difference between the two methods is 0.106 cm^3 , which is within the standard error of 0.21 cm^3 by the absorption method. We found that the main source of errors with the absorption method is in the measurement of transmission intensities. A proper choice of monochromatic x-ray energy and materials (gasket, calibrant) should help to have an optimal intensity contrast [$2 < \ln(I_0/I) < 4$] among materials involved.

From Eqs. (1)–(4), the sample thickness can be obtained together with molar volumes of crystalline and noncrystalline materials. The method introduced here could be applicable to other DAC measurements where the thickness of the sample is an important experimental parameter, e.g., ultrasonic interferometry,¹³ refractive index,¹⁴ and conduction measurements. Figure 2 shows the measured thickness in an isothermal compression at 710(3) K. The thickness decreases almost linearly with pressure in this pressure range. Typical error in thickness is ~ 0.2 μm , which is estimated from uncertainties in x-ray transmission intensities and in densities of crystalline materials by x-ray diffraction. The accuracy of the thickness measurement should be tied to the accuracy of absorption coefficients used in this study.¹¹ Calibration for absolute values is possible for crystalline materials with a known thickness and a molar volume measured by x-ray diffraction. In this study, we verified the absorption coefficient of rhenium at 29.200 keV. A rhenium gasket with measured thickness of 44(1) μm was placed at the sample position. X-ray intensities with and without the gasket were measured to be 7047(58) and 77592(32), respectively, resulting in a thickness of 44.8(2) using the literature data ($\mu_{\text{Re}} = 25.484 \text{ cm}^2/\text{g}$).¹¹ Since the agreement between two measurements is within experimental errors, the literature data of absorption coefficients¹¹ were used without correction. This

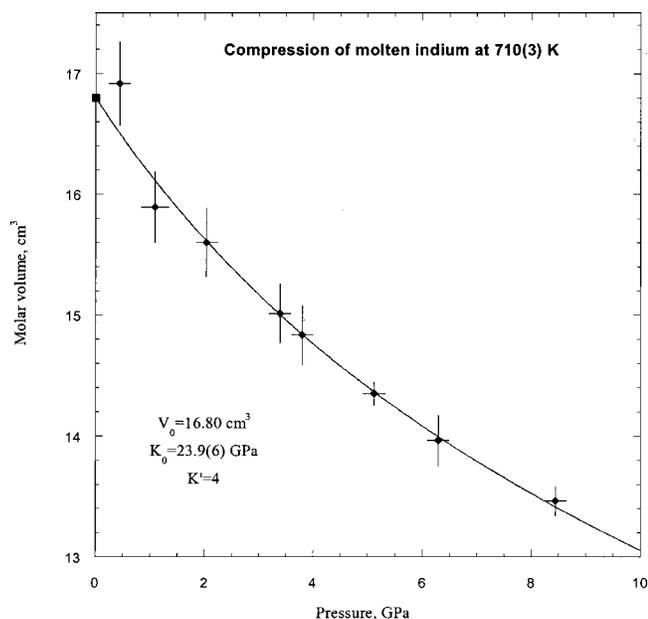


FIG. 3. Molar volumes of molten indium at 710(3) K at high pressures. The line is the fit with the third-order Birch–Murnaghan equation of state with the parameters shown. Our high-pressure data are consistent with the room pressure value (solid square) from Ref. 18.

is also supported by the fact that the molar volume difference between the x-ray diffraction method and the absorption method was found to be within the standard errors by the absorption method.

As the indium sample melts at high temperatures, no clear change in molar volume was found before and after melting. Instead, pressures were found to increase upon melting by a noticeable amount (e.g., by 0.5 GPa at ~ 3.2 GPa). This means that the volume of the sample chamber in the DAC is nearly constant. The increase in molar volume upon melting causes the increase in pressure. A similar phenomenon was found in a recent study of helium melting,¹⁵ where a sudden increase in pressure was used to signify melting. This shows that pressures should be internally monitored when there involves a phase transition. With the data of both pressures and molar volumes, it is possible to identify a first-order LL or AA phase transition that should involve a discontinuity in an isothermal pressure–volume relation.

Melting of indium at high pressure has been studied with the use of the x-ray diffuse scattering to identify melting.¹⁶ Analysis on the diffuse scattering from melts shows that at 710(3) K the coordination number at the nearest neighbor increases from 10.1(4) at 1 GPa to 12.1(5) at 6.3 GPa.¹⁷ The temperature dependence of molar volumes of molten indium at room pressure was measured by the sessile-drop method,¹⁸ which gives the molar volume of indium at 710 K to be 16.80 cm^3 . Figure 3 shows our data on molar volumes of molten indium in an isothermal compression at 710(3) K. If we fit our data with the Birch–Murnaghan equation of state, it gives $V_0 = 16.86 \text{ cm}^3$, $K = 23.2(6) \text{ GPa}$ assuming that $K' = 4$. The fitted V_0 is in excellent agreement with that by the sessile-drop method,¹⁸ confirming the validity of this method. By fixing V_0 to be 16.8 cm^3 , the fit to the Birch–Murnaghan equation of state resulted in a bulk modulus of $23.9(6) \text{ GPa}$ with $K' = 4$. From the compression data at 300

K for crystalline indium,^{19,20} both the bulk modulus and its pressure derivative are larger than those for molten indium. Clearly, the melt is more compressible than that of the corresponding solid, a result consistent with the coordination number increase as pressure increases.¹⁷

In conclusion, we have introduced a method for measuring molar volumes of melts and other noncrystalline materials in a diamond anvil cell. With a dual hole configuration (Fig. 1), a sample can be loaded equidistantly from the center with a selected material that serves as a thickness and absorption calibrant. Molar volumes were measured by the contrast of transmission intensities among the sample, the calibrant, and the gasket with a monochromatic x-ray microbeam. Data of molten indium have been obtained in an isothermal compression at 710(3) K up to the solidification pressure of 8.5 GPa in an externally heated diamond anvil cell. The current method provides data on the pressure–volume–temperature equation of state for amorphous materials and should be applicable to studies of melts and liquids including the first-order LL or AA phase transitions recently suggested.^{1–5} The method also allows for measurements of long-sought pressure–volume–temperature equations of state of melts for materials (e.g., liquid iron, silicate melts) inside the Earth and other planets.

This work is supported by NSF-EAR 0001149. GSE-CARS sector is supported by the NSF (Earth Science Instrumentation and Facilities Program) and DOE (Geoscience Program).

- ¹ S. Aasland and P. F. McMillan, *Nature (London)* **369**, 633 (1994).
- ² P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, *Science* **275**, 322 (1997).
- ³ O. Mishima, L. D. Calvert, and E. Whalley, *Nature (London)* **314**, 76 (1985); O. Mishima and H. E. Stanley, *ibid.* **396**, 329 (1998).
- ⁴ Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata, and K.-I. Funakoshi, *Nature (London)* **403**, 170 (2000).
- ⁵ S. K. Deb, M. Wilding, M. Somayazulu, and P. F. McMillan, *Nature (London)* **414**, 528 (2001).
- ⁶ M. Togaya, *Phys. Rev. Lett.* **79**, 2474 (1997).
- ⁷ Y. Katayama, K. Tsuji, O. Shimomura, T. Kikegawa, M. Mezouar, D. Martinez-Garcia, J. M. Besson, D. Hausermann, and M. Hanfland, *J. Synchrotron Radiat.* **5**, 1023 (1998); Y. Katayama, *High Press. Res.* **14**, 383 (1996).
- ⁸ C. Sanloup, F. Guyot, P. Gillet, G. Fiquet, R. J. Hemley, M. Mezouar, and I. Martinez, *Geophys. Res. Lett.* **27**, 811 (2000).
- ⁹ J. H. Eggert, G. Wenk, P. Loubeyre, and M. Mezouar, *Phys. Rev. B* **65**, 174 (2002).
- ¹⁰ P. Eng, M. L. Rivers, B. X. Yang, and W. Schildkamp, *Proc. SPIE* **2516**, 41 (1995).
- ¹¹ M. J. Berger and J. H. Hubbell, National Bureau of Standards, (1987); at the energy of 29.200 keV, $\mu_{\text{NaCl}} = 1.888 \text{ cm}^2/\text{g}$, $\mu_{\text{Re}} = 25.484 \text{ cm}^2/\text{g}$, $\mu_{\text{In}} = 42.312 \text{ cm}^2/\text{g}$.
- ¹² R. J. Hemley, H. K. Mao, G. Shen, J. Badro, P. Gillet, M. Hanfland, and D. Häusermann, *Science* **276**, 1242 (1997).
- ¹³ W. A. Bassett, H.-J. Reichmann, R. J. Angel, H. Spetzler, and J. R. Smyth, *Am. Mineral.* **85**, 283 (2000).
- ¹⁴ C. S. Zha, R. J. Hemley, H. K. Mao, T. S. Duffy, and C. Meade, *Phys. Rev. B* **50**, 13105 (1994).
- ¹⁵ F. Datchi, P. Loubeyre, and R. LeToullec, *Phys. Rev. B* **61**, 6535 (2000).
- ¹⁶ G. Shen, N. Sata, M. L. Rivers, and S. R. Sutton, *Appl. Phys. Lett.* **78**, 3208 (2001).
- ¹⁷ G. Shen, N. Sata, N. Taberlet, M. Newville, M. L. Rivers, and S. R. Sutton, *J. Phys. Condens. Matter* (in press).
- ¹⁸ M. A. McClelland and J. S. Sze, *Surf. Sci.* **330**, 313 (1995).
- ¹⁹ K. Takemura, *Phys. Rev. B* **44**, 545 (1991).
- ²⁰ O. Schulte and W. B. Holzapfel, *Phys. Rev. B* **48**, 767 (1993).