PHYSICAL REVIEW B **81**, 132104 (2010)

Equation of state and refractive index of argon at high pressure by confocal microscopy

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(Received 12 March 2010; revised manuscript received 9 April 2010; published 27 April 2010)

Using confocal microscopy, we determined the high-pressure equation of state and refractive index of argon at 300 K, in the same experiment. The results show that, within the experimental uncertainty, the polarizability depends only on the density, and not on the phase (fluid or solid).

DOI: 10.1103/PhysRevB.81.132104 PACS number(s): 64.30.Jk, 07.35.+k, 62.50.−p, 78.15.+e

I. INTRODUCTION

The response of matter to extreme pressures is of fundamental interest to condensed matter physics, geology, and planetary science. Diamond anvil cells (DACs) have been used with great success in high-pressure investigations.[1] However, it is difficult to measure the volume of a sample contained in a DAC. While the area of the sample is easily observed through the diamond anvils, the metal gasket which contains the sample is not transparent, making thickness measurements challenging. While x-ray and neutron-diffraction techniques can measure the lattice volume of a solid sample to high precision, they do not measure the absolute volume and they cannot measure the molar volume of fluids. These experimental limitations have prevented researchers from obtaining accurate equation of state data for a range of fluids and amorphous solids.[2,3]

In the present work, we overcame the difficulties associated with measuring compressed fluids by using confocal microscopy. A confocal microscope illuminates the sample by a laser focused through the objective lens onto the point to be imaged.[4] Light originating from the focal point of the objective passes through the microscope to a pinhole located at the focus of the tube lens. The pinhole screens light originating from points other than the focus of the objective lens. This screening results in a significantly higher resolution than a conventional microscope,[5] by imaging one point at a time. The microscope scans the volume of the sample and assembles a three-dimensional (3D) image. Typically the scanning in the x and y directions is done by mirrors, keeping the z coordinate (which corresponds to the position of the objective lens) fixed. Thus the 3D image consists of a series of cross sections of the sample, each collected at a different position of the objective lens.

When scanning a DAC, light is reflected from the surfaces of the diamond anvils back through the pinhole. The reflected intensity varies as a function of focus position and is maximized when the objective is focused at a surface (Fig. 1). If the sample is optically homogeneous, there will be four peaks in the reflected intensity profile. The distance between the second and third peaks gives the thickness d of the sample divided by its refractive index n.[6,7] The refractive index can be determined from the ratio of the amplitudes of the first and second peaks.[8] Finally, the area is determined from the high-resolution image of the sample cross section. A major advantage of this technique is that volume, refractive index, and pressure are determined in a single experiment.

It should be noted that this technique was developed using thick samples (about 100 μm) under relatively low pressures (less than 10 GPa). Under these conditions the diamonds do not distort significantly. The technique is predicated on plane surfaces perpendicular to the optical axis and its effectiveness for less ideal conditions has not been evaluated.

In this work we measured the equation of state and refractive index of argon at 300 K. Argon is a model system that has been the subject of numerous experimental and theoretical investigations.[9–18] For weakly interacting systems, the dependence of refractive index on density is described by the Clausius-Mossotti relation

$$\frac{n^2-1}{n^2+2}=\alpha\rho, \tag{1}$$

where n is the refractive index, ρ the number density, and α the polarizability. The polarizability does depend on density and can be written[10,16,18,19]

$$\alpha=\alpha_0(1+A\rho+B\rho^2+C\rho^3+\cdots). \tag{2}$$

II. EXPERIMENT

Figure 2 shows a schematic of the experiment. We measured the refractive index and molar volume of argon at 300 K from about 0.3 GPa to about 5.5 GPa. Pressure was measured by ruby fluorescence[1,20,21] excited by green light from the confocal microscope's mercury lamp, collected in an 0.5-mm-diameter optical fiber. The ruby fluorescence spectrum was recorded by an Ocean Optics spectrometer.

The DAC we used is a Merrill-Basset design.[22] The diamond culets we used are 0.6 mm in diameter. We used a stainless steel gasket preindented to about 0.1 mm with a 0.29-mm hole drilled in the center. We inserted a small chip of ruby into the hole sealed the DAC, immersed in liquid argon. During the measurements, the temperature of the DAC was maintained at 300.0(5) K by a 100 W mica band heater wrapped around its circumference. The temperature was controlled by a proportional integral derivative (PID) controller with a platinum resistance temperature detector affixed to the backing plate of the DAC, close to one of the diamond anvils.

The confocal microscope we used is a Zeiss LSM 510 Meta. We used a Zeiss Plan-Neofluar 10× objective with a numerical aperture of 0.26. A 514-nm-wavelength argon la-

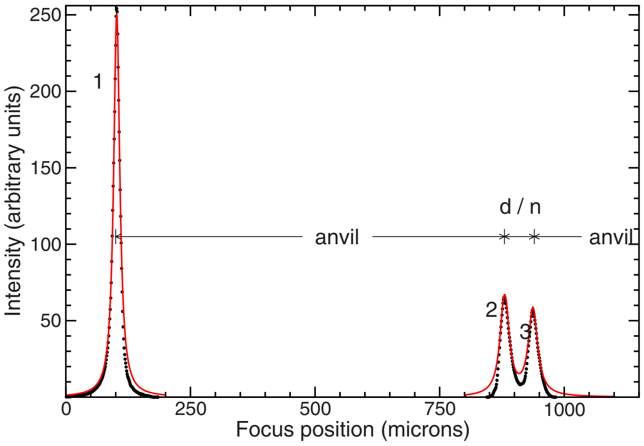

FIG. 1. (Color online) Reflected intensity profile, as measured by the confocal microscope (black dots) and as described by an exponential-Lorentzian function (Ref. 6) (lines). Scanning a DAC produces sharp peaks of reflected intensity corresponding to the objective lens being focused to an interface. The peak labeled 1 corresponds to the air-diamond interface, the peak labeled 2 to the diamond-sample interface, the peak labeled 3 to the sample-diamond interface. (The peak corresponding to the diamond-air interface is not shown but would be located at about 1800 μm.) The distance between adjacent peaks corresponds to the distance d between adjacent interfaces, divided by the refractive index n of the medium between them.

ser was for illumination, sent through an 80/20 beam splitter. The pinhole was set to a diameter of 2.5 Airy units, which for the wavelength we used is 174 μm. Using these settings, each pixel of the image has an area of 0.77 μm^2.

For each measurement, we scanned the DAC to produce an image stack. We used imaging software[23] to calculate the reflected intensity profile from the image stack by averaging the value of the pixels near the center of the sample. The sample area was determined by the number of pixels contained in the image of the cross section. From these measurements we calculated the refractive index and absolute volume of the argon sample as a function of pressure.[7]

III. RESULTS

We performed two experiments. Each began at the lowest pressure to which we could load the DAC (about 0.3 GPa) and ended at about 5.5 GPa, at which point we unloaded the cell. We observed the fluid-solid phase transition at 1.35(5) GPa, in good agreement with prior experiments.[24] Measured pressures are estimated to be uncertain to 0.02 GPa; it is possible to measure them more precisely than this, but unnecessary given the precision of the temperature control in this work.[20,21]

Because our confocal technique determines absolute volume, a method of estimating the mole number of the sample is necessary in order to convert the volume as a function of pressure into an equation of state. We did this by measuring absolute volumes well into the solid phase, up to about 5.5 GPa, and then fitting the absolute volumes to a published solid phase equation of state calculated from x-ray diffraction data (Fig. 3).

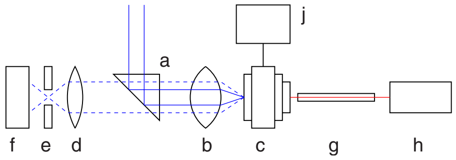

FIG. 2. (Color online) Schematic of experiment. A 514-nm argon laser (solid lines) passes through a beam splitter (a), through the objective lens (b), and into the DAC with heater (c). Reflected light (dashed lines) passes through the objective lens, the tube lens (d) and the pinhole (e) to the photomultiplier tube (f). A mercury lamp (not shown) shines through the objective lens and into the DAC, exciting ruby fluorescence (solid line) which passes through an optical fiber (g) and into a spectrometer (h). The DAC is maintained at constant temperature by a PID controller (j).

The x-ray equation of state is

$$P(V) = A_0 + A_1\frac{N}{V} + A_2\frac{N^2}{V^2} + A_3\frac{N^3}{V^3} \tag{3}$$

with $A_0 = 12.65$, $A_1 = -456.6$, $A_2 = 2394$, and $A_3 = 43350$, in the appropriate units.[11] (We verified this with our own measurements performed at beamline 12.2.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory.[25]) The mole number N was estimated to be 0.35(1) mmol in one experiment and 0.46(1) mmol in the other. The difference is due to differing diameters of the holes in the gaskets.

Once the mole number for each experiment was calculated, the absolute volumes were converted to molar volumes, and the experiments combined to yield the fluid equation of state (Fig. 4). Fitting the fluid data to Eq. (3) yields $A_1 = 19.3(4)$, $A_2 = -1250(10)$, and $A_3 = 28900(200)$. A_0 was constrained to be zero, for convenience of fitting.

Our refractive-index measurements are shown as a function of pressure in Fig. 5. Refractive index does not depend directly on pressure; the dependence is largely on polarizability and density (via the Clausius-Mossotti relation).[11–18]

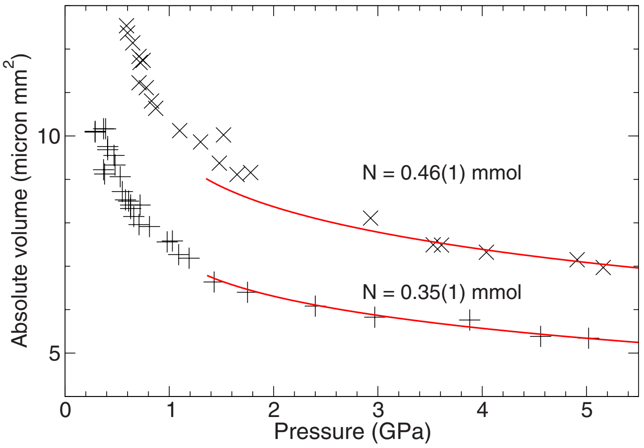

FIG. 3. (Color online) Absolute volume as a function of pressure. For each experiment the solid phase data ($P > 1.35$ GPa) are fitted to a published equation of state derived from x-ray diffraction data (Ref. 11) (solid lines), using mole number N as the sole fitting parameter.

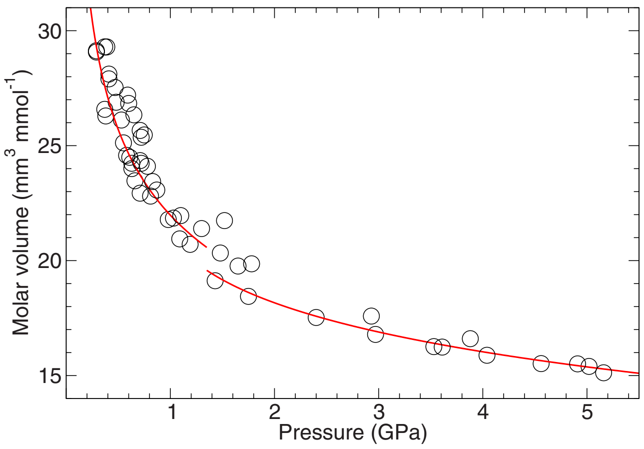

FIG. 4. (Color online) Equation of state. Each data set from Fig. 3 is divided by its mole number and plotted here as the equation of state. The fluid phase data ($P < 1.35$ GPa) are compared to a fluid equation of state compiled from the literature (Ref. 26) and the solid phase data are compared to the equation of state from x-ray diffraction (Ref. 11) (lines). Error bars are omitted for clarity. The uncertainty of the pressure measurement is estimated to be 0.02 GPa, and the uncertainty of the molar volume measurement is estimated to be 1 mm^3 mol^{-1}, from the scatter of the measurements about the fluid and solid fits.

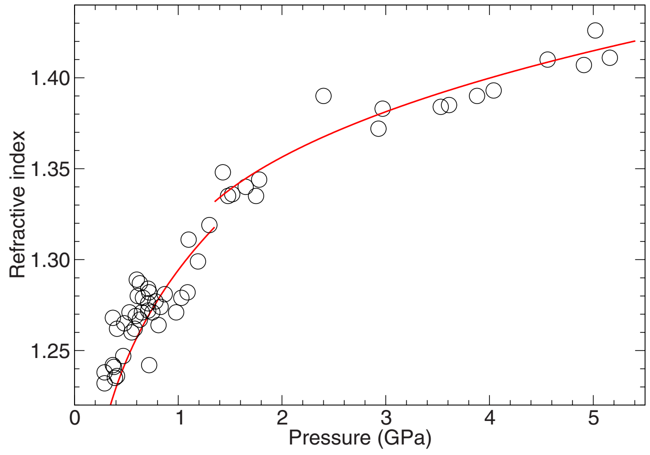

FIG. 5. (Color online) Refractive index as a function of pressure as measured by the confocal technique (circles). The solid line is the refractive index calculated from density via the Clausius-Mossotti relation and the equations of state for fluid and solid argon [Eq. (3)]. Error bars are omitted for clarity. The uncertainty of the pressure measurement is estimated to be 0.02 GPa and the uncertainty of the refractive index to be 0.01.

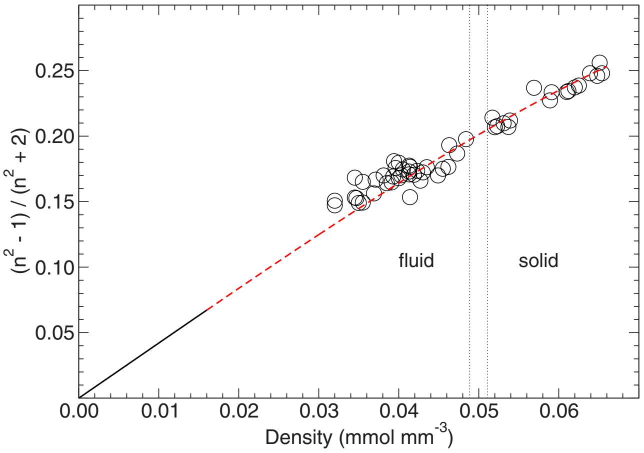

FIG. 6. (Color online) Plot of the Clausius-Mossotti relation. The relation was determined by interferometry (Ref. 18) to third order in density, for pressures up to 40 MPa (solid black line). Confocal data from this work (circles) extend the relation up to 5.5 GPa and we estimate the fourth-order coefficient to be $-350(80)$ mm^{12} mmol^{-4}. Dashed line: Fit from the literature (Ref. 18) with added fourth-order coefficient from this work. Error bars are omitted for clarity. The uncertainty of the pressure measurement is estimated to be 0.02 GPa and the uncertainty of the quantity $(n^2-1)/(n^2+2)$ is estimated to be 0.07.

Many experiments show that polarizability is not independent of density.[10] Our results for polarizability (Fig. 6) show good agreement with the low-pressure results. The dependence of polarizability on density was determined to high precision, to third order, for pressures up to 0.04 GPa in interference experiments.[18] Expanding the Clausius-Mossotti relation in density gives

$$\frac{n^2-1}{n^2+2} = a\rho + b\rho^2 + c\rho^3 + d\rho^4 + \cdots . \tag{4}$$

Averaging the results of the interference experiments yields, in the appropriate units, $a=4.1960(3)$, $b=1.74(3)$, and $c=-85.9(7)$. The confocal data from this work yields an estimate of $d=-350(80)$ and extends the range of the fit to 5.5 GPa. More importantly, as shown in Fig. 6, the polarizability is independent of phase. This observation indicates that long-range order plays *no significant role* in the optical response of argon, in the range of densities studied here.

IV. CONCLUSION

In summary, we measured the molar volume and refractive index (at 514 nm) of fluid and solid argon under high pressure. From these measurements, we determined that refractive index depends only on the density, within experimental uncertainty. The confocal technique provides direct measurements of refractive index, volume, and pressure, opening up the possibility of studying a diverse range of fluids and disordered solids. In further research we plan to incorporate measurements of Fabry-Perot interference into the confocal technique. Fabry-Perot measurements give the product of refractive index n and sample thickness d; this would complement the measurement of d/n yielded by the reflected intensity profile and would improve the accuracy of the technique.

ACKNOWLEDGMENTS

We would like to thank Michael Knoblauch, Chris Davitt, and Valerie Lynch-Holm (Franceschi Microscopy and Imaging Center) at WSU for assistance with the confocal microscope; Yogendra Gupta, Choong-Shik Yoo, Zbiegnew Dreger, and Mike Winey (Institute for Shock Physics) for helpful discussions; Simon Clark at ALS for assistance with the x-ray diffraction experiments, and Kirill Zhuravlev for processing the argon XRD data. This work was funded by the NSF and DOE. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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