Brillouin scattering and x-ray diffraction of solid argon to 65 GPa and 700 K: shear strength of argon at HP/HT

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We performed simultaneous Brillouin scattering and x-ray diffraction measurements on solid argon at high pressures and high temperatures (HP/HT) in an externally heated diamond-anvil cell. From the measured acoustic velocities and densities, we derive the bulk elastic properties of solid argon up to 700 K at above 60 GPa. Our measured acoustic velocity results at room temperature are in agreement with previous Brillouin scattering results. However, the derived aggregate elastic moduli differ from previous studies. In particular, the shear modulus is significantly lower. Our HP/HT-data show that the bulk modulus is almost insensitive to an increase of temperature (within the P-T-range of our study), whereas the shear modulus G measurably decreases with increasing temperature. We find that \(G(P,T)\) can be described by a polynomial of the form: \(G(P,T) = 5.8(9) \text{ GPa} + 1.45(12)(P - P_0) - 0.007(2) \text{ GPa}^{1.8}(P - P_0)^2 - 0.01(3) \text{ GPaK}^{-1.8}(T - T_0) - 0.0006(2) \text{ KGPa}^{-1.8}(P - P_0)^*(T - T_0)\) (where the reference P/T-conditions are 4.3 GPa and 300 K). We use our results to estimate the shear strength of argon at HP/HT, which we find to be 0.8 GPa at 65 GPa, substantially lower than found in a previous study. Increasing temperature to 700 K reduces the shear strength to 0.5 GPa at 65 GPa. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4820578]

INTRODUCTION

The experimental study of noble gases is of great interest as it provides a valuable basis for the development and improvement of theoretical models, particularly many-body descriptions.1–4 In addition, argon is an important component of the Earth interior.5–7 Knowledge of the physical properties of argon at non-ambient conditions is also of significance in designing high-pressure experiments carried out in the diamond-anvil cell (DAC), where argon is frequently used as a pressure-transmitting medium.8 Several experimental2,4,12,13 and theoretical studies2,4,12,13 have reported the elastic properties of solid argon to high pressures, but the experimental results on their pressure-dependence are not in quantitative agreement.1,3 Furthermore, despite the longstanding interest in the HP/HT-elastic properties of solid argon, the high pressure measurements of the elastic properties of solid argon are still limited to room temperature, with the exception of relatively low pressures (<3.5 GPa).14,15 In this paper, we present simultaneously measured high-pressure high-temperature Brillouin scattering and synchrotron x-ray diffraction data (Fig. 1) on polycrystalline argon performed in an externally heated diamond-anvil cell.

MATERIALS AND METHODS

Simultaneous Brillouin scattering (acoustic velocity) and x-ray diffraction (density) measurements were performed at various P-T-conditions up to a maximum pressure of 65 GPa and a maximum temperature of 700 K. Gaseous argon, compressed to a pressure of 1.5–2 kbar, was loaded into the sample chamber of a BX-9016 DAC equipped with a resistive mini-heater. Diamonds with 300 μm or 400 μm-sized culets were employed. Rhenium was used as gasket material. The gaskets were pre-indent to a thickness of about 30 μm and sample chambers (150 or 200 μm diameter) were drilled with a pulsed IR laser. During the experiments, the temperature of the sample was determined with two different thermocouples—type K and type R/S—glued to opposing sides of one diamond close to its culet. The difference in temperature measurements between the two thermocouples was about 10 K at the highest pressure, indicating...
homogeneous heating. A small piece of gold foil was loaded into every sample chamber along with the argon and the sample pressure was determined from x-ray diffraction measurements of the unit cell parameter of gold by using its thermal equation of state.\textsuperscript{17} In addition to the combined Brillouin/x-ray measurements at GSECARS/APS, two sets of Brillouin measurements were performed at the German Research Center for Geosciences, in which case pressure was determined from ruby fluorescence using a calibration for (quasi-)hydrostatic conditions based on measurements performed in argon as pressure-transmitting medium.\textsuperscript{18}

HP/H\textsubscript{T} synchrotron x-ray diffraction experiments were performed at APS-Beamline 13 BM-D using x-rays with an energy of 37 keV (0.3344 Å wavelength) and a focused x-ray spot of \(14 \times 4\) (V) \(\mu\text{m}^2\). The sample to detector distance was calibrated using a CeO\textsubscript{2} standard (NIST 674 a). Diffraction images were acquired on a MAR 345 image plate with exposure times ranging from 60 to 120 s. The program fit2d\textsuperscript{19} was used to convert the MAR-images to integrated diffraction patterns, which were then fit using the program MAUD.\textsuperscript{20}

The majority of in-situ Brillouin scattering experiments were performed using the on-line Brillouin system at Beamline 13 BM-D.\textsuperscript{21} Two additional sets of room temperature Brillouin measurements were performed at the German Research Center for Geosciences. Both systems use a solid-state laser (532 nm) as light source and a multipass tandem Fabry-Perot Interferometer\textsuperscript{22} along with a photomultiplier tube for signal detection. The measurements were performed in a symmetric forward-scattering geometry\textsuperscript{23} where the scattering angle was set to 50°, 60°, or 80°. Different phonon propagation directions were probed by translating the DAC or rotating it around its compression axis. Typical collection times for Brillouin spectra were between 10 and 30 min. The polarization of the incident and scattered laser was unconstrained, because of depolarization effects caused by the strained diamonds.

Experimental measurements were performed along two isotherms (300 K and 673 K) up to 65 GPa and along three (quasi-)isobars (5 GPa, 50.7 GPa, 61.7 GPa) up to 700 K to constrain the \(P-T\)-dependence of unit cell volumes and acoustic velocities. During temperature changes, the pressure in the sample chamber slightly changed as indicated by our in-situ pressure determination. However, pressure was constant throughout each individual measurement.

Pressure and temperature dependent unit cell volumes of argon were derived from the x-ray diffraction images. The data collected at 300 K and 700 (±25 K) were fitted to a third order isothermal Birch-Murnaghan Equations of State (EoS). For both fits, we fixed the reference pressure to 4.3 GPa. At this pressure the sample was a single-crystal, as shown by the x-ray diffraction images, and we could derive the complete elastic tensor from our Brillouin scattering measurements by using a full inversion procedure.\textsuperscript{24}

RESULTS AND DISCUSSION

X-ray diffraction images at 4.3 GPa indicate our sample material was a single-crystal at that pressure. Upon further pressure increase this single crystal transformed into a polycrystalline aggregate, which is consistent with previous observations.\textsuperscript{35,16} Our diffraction images collected at high-pressure indicate that the sample is a textured fine powder (Fig. 2(a)).

Figure 2 illustrates the effect of temperature and pressure on the compression behavior of argon. Our data indicate that a linear dependence of unit cell volumes with temperature at a given pressure adequately describes the measurements over the \(P-T\)-range studied here (Fig. 2(b)). Based on this observation, we derived a pressure dependent average (from 300 K to 700 K) volume thermal expansion coefficient \(\alpha\) from our data (Fig. 2(c)). At the highest experimental pressure, \(\alpha\) is about \(5\times10^{-5} \text{ K}^{-1}\). This value is almost two times larger than what is reported for diamond.

\begin{figure}[h]
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\caption{(a) Pressure dependence of the unit cell volume of fcc-argon along two different experimental isotherms. The curves are least-square fits of a third-order Birch-Murnaghan EoS (estimated uncertainties are smaller than the symbol sizes). A typical diffraction image of argon collected at 59.5 GPa and 673 K is shown as inset. (b) Temperature dependence of measured unit cell volume at constant pressure. The data can be well described by a linear dependence of unit cell volume on temperature, i.e., a \(T\)-independent volume thermal expansion coefficient. (c) The volume thermal expansion coefficient was derived from our x-ray diffraction data, the thermodynamic Grüneisen parameter is from Ross et al.\textsuperscript{9}}
\end{figure}
the value predicted at 300 K by a computational study.\textsuperscript{25} This discrepancy might be related to the assumption of a linear thermal expansion between 300 K and 700 K, which would lead to an overestimation of the thermal expansion coefficient at low temperatures, i.e., near 300 K, and an underestimation at high temperatures, i.e., near 700 K.

From our high-pressure x-ray diffraction measurements along the 300 K isotherm, we obtain the following best-fit parameters for unit cell volume $V$, bulk modulus $K$ and its pressure-derivative $K'$: $V_{4.3 \text{GPa}, 300 \text{K}} = 103.9$ ($\pm 1.6$) $\AA^3$, $K_{4.3 \text{GPa}, 300 \text{K}} = 23.3$ ($\pm 2$) GPa, $K'_{4.3 \text{GPa}, 300 \text{K}} = 4.77$ ($\pm 0.24$). In our analysis of the compression curve, we chose a pressure of 4.3 GPa as a reference. At this pressure, we could precisely constrain the bulk modulus using the elastic constants $c_{ij}$ determined from single-crystal Brillouin measurements ($c_{11} = 33.4$ ($\pm 0.8$), $c_{12} = 23.4$ ($\pm 0.8$), $c_{44} = 13.7$ ($\pm 0.4$)), which are in agreement with the previously published data of Shimizu et al.\textsuperscript{3} In the least-square fitting of the x-ray diffraction volumes, the bulk modulus at 4.3 GPa was then fixed to this value (corrected to isothermal conditions using the parameters reported in Fig. 2(c)). Within uncertainties, the EoS-parameters are in good agreement with previously reported experimental x-ray diffraction studies.\textsuperscript{9,11} At 700 ($\pm 25$) K, we find the isothermal bulk modulus at 4.3 GPa $K_{4.3 \text{GPa}, 700 \text{K}}$ and its pressure derivative $K'_{4.3 \text{GPa}, 700 \text{K}}$ to be 17.9 ($\pm 1.5$) GPa and 4.77 ($\pm 0.15$), respectively. We derive a value of 113.2 ($\pm 1.3$) $\AA^3$ for the unit cell volume of fcc-argon at 4.3 GPa and 700 K.

Except for the measurements performed at $P = 4.3$ GPa, our Brillouin scattering experiments were performed on polycrystalline aggregates as in previous studies.\textsuperscript{1,3,10} The spectra collected at high pressures are characterized by two spectral features related to average shear and compressional acoustic modes of polycrystalline argon. The velocities determined from the measured Brillouin frequency shifts are weighted averages of several crystallites with different crystallographic orientations and can only represent approximate average velocities. The intensity of the compressional acoustic mode was systematically much stronger than that from the shear mode (Fig. 3(a)), an observation consistent with previous findings.\textsuperscript{3,10,26} In addition to the overall weak intensity, the shear acoustic mode in polycrystalline samples can be strongly affected by elastic-optic coupling,\textsuperscript{27} which varies with the orientation of the individual crystallites, leading to a potential bias towards crystallographic directions with stronger coupling. In order to alleviate this potential bias, we based our data analysis on the compressional velocities that are characterized by a strong signal-to-noise ratio.

At each experimental condition in the HP/HT-experiments, the DAC was rotated/translated around its compression axis and at least 4 directions and/or positions were probed by Brillouin spectroscopy for better statistics. At each experimental condition, the maximum deviation of any individual velocity measurement from the average was smaller than 3%. We performed additional room temperature HP-Brillouin experiments at the German Research Center for Geosciences to verify that our measured average velocities are representative of the overall average. In these experiments, 18 and 24 different directions were probed at experimentally pressures of 31.4 GPa and 44.4 GPa, respectively. The maximum deviation of any measured compressional velocity from the average was 2.7% and 1.4% for both experimental pressures and the calculated standard deviations were $<=1\%$. These experiments show that the dependence of compressional acoustic velocities on the direction of measurement is small and that the observed texture does not cause a significant direction dependence of compressional velocities. We note that the results of Brillouin scattering measurements on polycrystalline samples are generally complicated by crystallite orientation effects and the effectiveness of elasto-optic coupling, which is related to the sample properties and the chosen polarization of incident and scattered light. In DAC experiments, a quantitative evaluation of the elasto-optic coupling effect on the measured acoustic velocities is particularly difficult, because of depolarization effects due to large strain in the diamond culets.

A previous study suggested the possibility of constraining single-crystal elastic constants by combining the texture information from x-ray diffraction with the small (but observed) direction dependence of the acoustic velocities.\textsuperscript{28} This approach requires a large number of measurements to resolve the small direction dependence of acoustic velocities. The present study, however, focuses on the high-temperature measurements and the number of possible measurements at HP/HT is limited due to the complex experimental setup.

FIG. 3. (a) Brillouin spectrum of argon measured at 62.6 GPa and 700 K. (b) Dependence of average compressional velocities on pressure along two isothersms. The solid curve represents the results of a previous study, corrected for a hydrostatic pressure scale. The grey curves represent the upper and lower bounds for the compressional velocities at 300 K as reported in the previous work.
Here, we assume that the average compressional velocities in our experiments are representative of the overall average in the sample. This also implies that, in our experiments, it is very unlikely that the maximum and minimum of measured velocities represent the overall “single-crystal” extrema. It is, therefore, not possible to extract reliable single-crystal elastic constants from our measured weighted average velocities (unless assuming elastic isotropy) as done in a previous HP-study at room temperature, where much larger deviations of acoustic velocities from the average were observed. This might be caused by a development of strong texture in that experiment. However, the previous study by Shimizu et al. was not supplemented by simultaneous high-pressure x-ray diffraction of the samples and consequently lacks any information about the crystals’ orientation distribution, complicating the evaluation of reliability of the inferred elastic constants.

In our data analysis, we averaged the compressional velocities measured at each given P-T-condition and assumed that the derived average represents the average velocity of a randomly oriented polycrystalline argon aggregate \( v_{p,\text{avg}} = ((4/3G + K_s)/\rho)^{0.5} \). This assumption is supported by the relatively small differences we observed between acoustic velocities along different directions at a given pressure. Despite the difference with respect to the range of observed velocities at a certain pressure, the average compressional velocities determined in this study agree well with the study by Shimizu et al., when corrected for differences caused by pressure calibration (Fig. 3(b)). Shimizu et al. determined pressure by ruby fluorescence using the pressure scale optimized for non-hydrostatic conditions, whereas we derive it by using the calibration for (quasi-)hydrostatic conditions (actually performed in argon pressure-medium) or, in most cases, by using an EoS of gold, which is well calibrated at high temperatures and suitable for the present study.

By combining our average compressional velocities with densities and bulk moduli derived from simultaneous x-ray diffraction, we extract the corresponding shear moduli. The adiabatic bulk modulus \( K_s \) was derived from the isothermal bulk modulus \( K_T \) by multiplying it by \((1 + \gamma(T))/T\), where \( \gamma \) and \( \gamma(T) \) denote the volumetric thermal expansion coefficient and the thermodynamic Grüneisen parameter, respectively. The pressure-dependent \( \gamma \) was calculated from our x-ray diffraction data; \( \gamma(P) \) was taken from the experimental work of Ross et al., which is also in agreement with more recent computational predictions (see Fig. 2(c) for employed values). With the experimental setup available at Beamline 13 BM-D, we have simultaneously measured pressure, sample density and sound wave velocities at each experimental P/T condition (Fig. 1).

The elastic moduli determined from our data at room temperature are plotted in Figure 4(a) along with previous results. Our data for the bulk moduli are higher than reported in the previous Brillouin study to 70 GPa. However, good agreement is found between our determination of isothermal bulk modulus, the values calculated from the EoS parameters of Errandonea et al. and computational results. The estimated uncertainty on our isothermal bulk modulus is 4% at the highest experimental pressure. The main uncertainty in our bulk modulus calculation at high-pressures arises from the uncertainty on the pressure derivative of the bulk modulus at the reference pressure. The adiabatic bulk modulus might additionally be affected by the uncertainty in thermal expansion coefficient. Substituting our \( \gamma \) by the values predicted in the computational study by Tretiakov and Scandolo lowers the adiabatic bulk modulus by 2% at 65 GPa (at room temperature). At this pressure, the maximum deviation in \( \gamma \) is observed between our experimentally determined value and the one predicted by computations (Fig. 2(c)). The uncertainties in the determined bulk modulus propagate into our derivation of the shear modulus, which we calculated from the measured average compressional velocities. The estimated uncertainties in the bulk modulus and the uncertainty in measured average compressional velocity (≈1%) lead to an overall estimated uncertainty in shear modulus of 14% (or ±9 GPa) at the highest pressure. However, even considering this uncertainty, we find a pronounced discrepancy between the shear modulus determined in our study and the results by Shimizu et al. This finding is in qualitative agreement with a recent Brillouin study to 30 GPa and computational data (Fig. 4(a)). However, our measured average compressional velocities are in agreement with the earlier study (when correcting for the different pressure calibrations). Consequently,
the difference in derived shear properties is mostly caused by the difference in density and bulk modulus, which we determined from x-ray diffraction at HP.

Increasing the temperature to 700 K has only a minor effect on the bulk modulus, in agreement with a computational study using molecular dynamics and classical potentials.\(^{25}\)

The shear modulus, however, decreases with increasing temperature (Fig. 4(b)), by about 25–30% in the studied pressure and temperature (Fig. 4(b)), by about 25–30% in the studied pressure range. We find that the shear modulus as function of P and T, at conditions of $4.3 < P < 65$ GPa and $300 < T < 700$ K, can be described by a polynomial of the form:\(^{30}\) $G(P,T) = G_0 + (\partial G/\partial P)_0(P - P_0) + (\partial^2 G/\partial P^2)_0(P - P_0)^2 + (\partial G/\partial T)_0(T - T_0) + (\partial^2 G/\partial P \partial T)_0(P - P_0)(T - T_0)$, where the zero values refer to 4.3 GPa and 300 K. The derived parameters are $G_0 = 5.8 \pm 0.9$ GPa, $\partial G/\partial P)_0 = 1.45 \pm 0.12$, $(\partial^2 G/\partial P^2)_0 = -0.007 \pm 0.002 \text{ GPa}^{-1}$, $(\partial G/\partial T)_0 = -0.01 \pm 0.003 \text{ GPa/K}$, $(\partial^2 G/\partial P \partial T)_0 = -0.0006 \pm 0.00002 \text{ K}^{-1}$. Note that this equation is only applicable at P-T-conditions where argon is solid (see also Fig. 3(b)).

Following the approach used in a very recent Brillouin scattering study of solid argon,\(^{10}\) we use our results for $G(P,T)$ together with the room temperature high-pressure differential strains measured in argon by an earlier radial x-ray diffraction study\(^{11}\) to estimate the shear strength of solid argon at HP/H\(_T\) (Fig. 5). The following relation was employed: $t = 6G(Q)/2 \tau$, where $t$ represents the uniaxial stress component, $(Q)$ refers to the average differential strain and $\tau$ represents a lower bound of the shear strength.\(^{31,33}\)

Our findings qualitatively support the conclusion by Chen et al.\(^{10}\) that the shear strength of argon at high pressures is significantly lower than reported by Mao et al.\(^{31}\) (who used the HP shear moduli determined in an early Brillouin scattering study\(^{1}\) as input parameters). The shear strength we derive at 65 GPa is 0.8 GPa. Increasing temperature further decreases the shear strength of argon by $\sim 30\%$ for $\Delta T$ of 400 K at 65 GPa. In addition, it is most likely that the differential strains in argon are reduced upon temperature increase, but experimental data are absent. Based on this expectation, the shear strength of argon might even be lower at HP/H\(_T\) than shown in Fig. 5. Our findings suggest that thermally annealed argon might allow for generating quasi-hydrostatic conditions comparable to the ones expected in neon\(^{34,35}\) (Fig. 5), at least in the pressure range up to 65 GPa.

**CONCLUSION**

We report data on the bulk elastic properties of solid fcc-argon at HP/H\(_T\). Our room temperature velocity data are in agreement with previous data, but the derived elastic moduli differ significantly, particularly the shear modulus. The combination of simultaneous Brillouin scattering and synchrotron x-ray diffraction allows for a direct analysis of the derived acoustic velocities in terms of density and elastic moduli. We find that the bulk modulus is only slightly affected by a temperature increase from 300 K to 700 K, whereas the shear modulus is visibly reduced. We use our data to estimate the shear strength of argon at HP/H\(_T\). Based on our findings, argon might be a competitive candidate pressure-transmitting medium for HP/H\(_T\)-experiments up to at least 65 GPa, particularly in laser-heating experiments, where its low thermal conductivity and chemical inertness are ideal to insulate the heated sample from the diamond anvils. At very high pressures, however, the shear strength of argon might substantially exceed the one of neon, which was shown to increase linearly with increasing pressure.\(^{34}\)

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