Single-crystal elastic moduli $C_{ij}(P)$ and shear modulus $G(P)$ of solid argon up to 64 GPa from time-domain Brillouin scattering

A. Zerr[1]*, S. Raetz[2], M. Kuriakose[2], P. Djemia[1], S.M. Nikitin[2], N. Chigarev[1], A. Bulou[3], A. Lomonosov[4] and V.E. Gusev[2]*

[1]*LSPM, UPR-CNRS 3407, Université Paris 13, Avenu. J. B. Clément, 93430 Villetaneuse, France*
[2]*LAUM, UMR-CNRS 6613, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans, France*
[3]*IMMM, UMR-CNRS 6283, Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans, France*
[4]*Prokhorov General Physics Institute, Russian Academy of Sciences, 119991 Moscow, Russia*

Keywords: longitudinal sound velocity, elastic anisotropy, pair-wise atom interaction

*e-mail: zerr@lspm.cnrs.fr

Solid argon, crystallizing above 1.3 GPa in the face-centered cubic (fcc) structure, is considered as the archetype of a simple classical solid [1] due to a highly symmetric distribution of electron density in the atoms having completely filled electron shells. For this reason, its behavior at high pressures was intensively investigated, also by theory, aiming understanding of evolution of solids upon a strong density increase. Symmetric electron shells and cubic structure of solid argon imply elastic isotropy of its crystals which, however, was not confirmed experimentally. Accordingly, a significant and growing-with-compression contribution of non-central interaction between the Ar-atoms was hypothesized as an explanation. Also, solid argon (as well as other solidified noble gases such as neon or helium) is extremely compressible and produces a quasi-hydrostatic environment, as has been concluded on the basis of sharpness of its X-ray diffraction peaks measured up to ~8 GPa [2]. However, the degree of its hydrostaticity at higher pressures was a subject of recent controversial discussions [3,4]. Due to a strong change of its lattice parameter with pressure, solid argon was also suggested and used as an internal pressure standard [5-7].

In the present work, we have measured the maximal and minimal values of the product of the refractive index $n(P)$ with the longitudinal sound velocity $V_L(P)$, $n(P)\cdot V_L(P)$, in single crystals of solid argon up to 64 GPa (Figure 1). For solid argon having cubic structure, the maximal sound velocity corresponds to that along the ⟨111⟩ direction in a single crystal, $V_{L\langle 111\rangle}$, and the minimal sound velocity to that along the ⟨100⟩ direction, $V_{L\langle 100\rangle}$. The observed in this work strong deviation of $V_{L\langle 111\rangle}(P)$ from $V_{L\langle 100\rangle}(P)$ with pressure increase (Figure 1) indicated a strong elastic anisotropy of this solid, which deserves a special attention because, at the maximal pressure, the density of solid argon is more than twice higher than that just after its solidification at P=1.2 GPa [6]. It should be mentioned here that the detected strong elastic anisotropy of solid argon could not be falsified by the presence of the hcp phase, potentially coexisting with the main fcc phase at high pressures [8]. This is because our theoretical calculations showed that the hcp phase could not contribute to the measured-by-us strong deviation of the maximal and minimal $n(P)\cdot V_L(P)$ values (Figure 1).

In the present work we used the technique of time-domain Brillouin scattering (TDBS) [9] permiting 3D-scanning of the $n\cdot V_L$ distribution in transparent samples with sub-μm resolution along the DAC axis, in addition to the micrometric lateral resolution [10-12]. Important is to mention that the spatial resolution of the TDBS technique did not degrade with pressure. These capabilities of the TDBS technique permitted us to pitch on the extremes of the $n\cdot V_L$ values in the polycrystalline samples of fcc argon compressed in a DAC and to closely approach the $n\cdot V_{L\langle 111\rangle}$ and $n\cdot V_{L\langle 100\rangle}$ values up to the highest pressure of our work of 64 GPa (Figure 1). Calculation of the refractive index of the fcc argon as a function of pressure $n(P)$ was another part of the work which allowed to derive $V_L(P)$ values from the the products $n(P)\cdot V_L(P)$ obtained directly from the oscilating TDBS signals $S(t)$. To obtain the reliable axially resolved data, we applied the same demanding time-frequency analysis of the raw TDBS signals $S(t)$ as described in detail earlier [11].

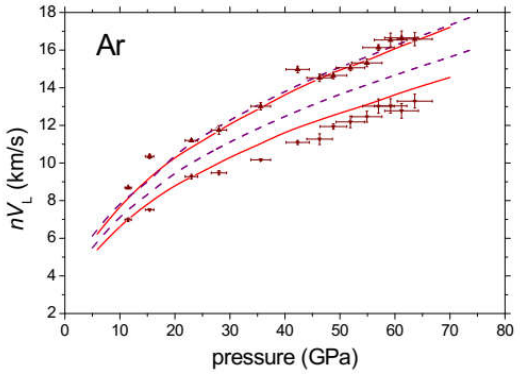

Figure 1. Our experimental and theoretical data on longitudinal sound velocities of solid argon at high pressures. The experimental datapoints in terms of the product $n\cdot V_L$, obtained using the TDBS technique, are represented by triangles pointing up and down corresponding to $n(P)\cdot V_{L\langle 111\rangle}(P)$ and $n(P)\cdot V_{L\langle 100\rangle}(P)$, respectively. They are compared with the same theoretically-calculated values for the fcc phase (solid red lines) and hcp phase (dashed violet lines)

Using the envelope method and our theoretical $n(P)$ for the fcc phase we determined, with a high degree of confidence, pressure dependences of the fastest and

slowest longitudinal sound velocities in a single crystal of the fcc argon, $V_{L\langle 111\rangle}(P)$ and $V_{L\langle 100\rangle}(P)$, respectively. Then, using the earlier measured EOS, we derived the single crystal elastic moduli $C_{ij}(P)$ and the shear modulus in the Hill approximation $G_H(P)$ (Figure 2). We also estimated the transversal sound velocities $V_{T\langle 100\rangle}(P)$ and $V_{T\langle 110\rangle}(P)$ of the fcc argon up to 64 GPa. It was found that our $G_H(P)$ matches well $G(P)$ obtained directly from the averaged transversal sound velocities $V_{Tav}(P)$ measured earlier using the classical Brillouin light scattering technique [4] (Figure 2). This agreement mutually confirms reliability of the two experimental data-sets and supports the earlier finding that shear strength of the fcc argon at high pressures is very low [4]: At P~65 GPa, the shear strength of solid argon was estimated from the experimental data to be ~0.8 GPa which is significantly lower than the value proposed by Mao et al. [3] and similar to the shear strength of solid neon at the same pressure. Thus, at pressures below 70 GPa, both solidified noble gases are similarly soft and, accordingly, similarly suitable as pressure transmitting media providing quasi-hydrostatic load conditions.

Comparison of our experimental results with earlier calculations has shown that the theoretical many-body model based on the Buckingham (exp-6) pair potential [13] provides the best agreement. All other theoretical models, including the *ab-initio* approach we have used, couldn't predict our experimental $V_{L\langle 100\rangle}(P)$ and $V_{T\langle 110\rangle}(P)$. The magnitude of the Cauchy discrepancy (C_{12}-C_{44}-2P) for the fcc argon was found to increase much slower with pressure than could be concluded from the earlier experimental and theoretical works. Accordingly, the pair-wise interactions in solid argon also vanish only slowly with compression.

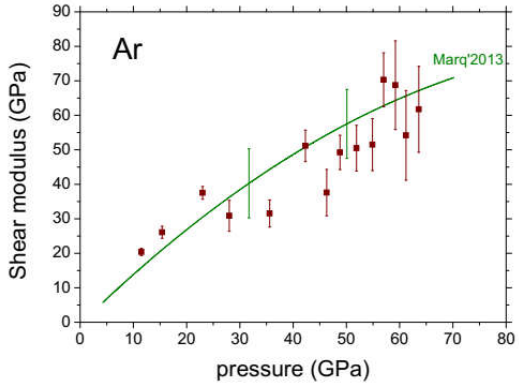

Figure 2. Pressure dependence of the shear modulus of polycrystalline fcc argon, $G_H(P)$, derived from our experimental $C_{ij}(P)$ using the Hill approximation (solid dark-red squares) in comparison with the earlier reported $G(P)$ (solid green line) obtained in the classical BLS experiments by Marquardt et al. [4] from the averaged $V_{Tav}(P)$. Vertical bars show experimental uncertainties for the both experimental data-sets

Acknowledgments: This work was supported by the French National Research Agency (ANR): project "LUDACism" (ANR-11-BS09-0010) and project "I2T2M" (ANR-18-CE42-0017). Technical support of R. Boehler is acknowledged.

[1] D.A. Young, *Phase diagrams of the elements* 1991, University of California Press, Berkeley.
[2] L.W. Finger, R.M. Hazen, G. Zou, H.K. Mao and P.M. Bell, *Applied Physics Letters* 1981, **39**, 892.
[3] H.K. Mao, J. Badro, J.F. Shu, R.J. Hemley and A.K. Singh, *Journal of Physics: Condensed Matter* 2006, **18**, S963.
[4] H. Marquardt, S. Speziale, A. Gleason, S. Sinogeikin, I. Kantor and V.B. Prakapenka, *Journal of Applied Physics* 2013, **114**, 093517.
[5] D.A. Dzivenko, A. Zerr, R. Boehler and R. Riedel, *Solid State Communications* 2006, **139**, 255.
[6] P. Richet, J.A. Xu and H.K. Mao, *Physics and Chemistry of Minerals* 1988, **16**, 207.
[7] A. Zerr, H. Reichmann, H. Euler and R. Boehler, *Physics and Chemistry of Minerals* 1993, **19**, 507.
[8] D. Errandonea, R. Boehler, S. Japel, M. Mezouar and L.R. Benedetti, *Physical Review B* 2006, **73**, 092106.
[9] V.E. Gusev and P. Ruello, *Applied Physics Reviews* 2018, **5**, 031101.
[10] M. Kuriakose et al., *Ultrasonics* 2016, **69**, 259.
[11] M. Kuriakose et al., *Physical Review B* 2017, **96**, 134122.
[12] S.M. Nikitin, N. Chigarev, V. Tournat, A. Bulou, D. Gasteau, B. Castagnede, A. Zerr and V.E. Gusev, *Scientific Reports* 2015, **5**, 9352.
[13] E. Pechenik, I. Kelson and G. Makov, *Physical Review B* 2008, **78**, 134109.