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1 3D characterization of individual grains of coexisting high-pressure H<sub>2</sub>O ice phases  
2 by time-domain Brillouin scattering

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16 Time-domain Brillouin scattering (TDBS) uses ultrashort laser pulses to (i) generate coher-  
17 ent acoustic pulses of picoseconds duration in a solid sample and (ii) follow their propaga-  
18 tion in order to image material inhomogeneities with the axial resolution that can be deeply  
19 sub-optical, to nm-scale, and the lateral one down to the optical diffraction limit (half the  
20 optical wavelength of the probe laser). TDBS permits highly resolved 3D-imaging of  
21 grains in polycrystalline transparent samples with unlimited lateral sizes and thicknesses  
22 of at least 10  $\mu\text{m}$  also when samples are orientationally textured and/or located in de-  
23 vices permitting access along one direction and from one side only. This optical technique  
24 presents, accordingly, clear advantages compared to any X-ray-based computed tomogra-  
25 phy (neither back-projection algorithm nor multiple viewpoints of the sample is needed)  
26 and classical spectroscopic methods. Here, we applied TDBS to the 3D-imaging of a  
27 sample of polycrystalline water ice containing two high-pressure phases. The imaging,  
28 accomplished via a simultaneous detection of quasi-longitudinal and quasi-shear waves,  
29 provided shape, coordinates, phase content and crystallographic orientation of resolved  
30 crystallites in a common coordinate system. Monitoring of acoustic pulses simultaneously  
31 propagating in two neighboring grains provided a new tool for the localisation of grain  
32 boundaries.

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## 33 I. INTRODUCTION

34 High-resolution imaging of the state and evolution of texture, phase and/or chemical composi-  
35 tion of polycrystalline solids upon any kind of action is a rapidly developing branch of scientific  
36 and industrial research, especially when texture strongly influences behavior and performance of  
37 the entire material or device. Examples of such devices or materials are electrodes of Li-ion bat-  
38 teries whose evolution upon charging/discharging may cause strong degradation of the battery  
39 capacity<sup>1</sup>; optoelectronic devices whose performance depends on homogeneity of the constituting  
40 material<sup>2</sup>; or rocks in the deep Earth where preferred orientations, shape, phase transitions, partial  
41 melting or change in distribution of the constituting minerals (mostly silicates and oxides) can  
42 initiate abrupt large-scale displacements leading to earthquakes<sup>3</sup>.

43 Until now, the most elaborated way to examine texture of polycrystalline solids, with the spa-  
44 tial resolution similar or better than the grain sizes, is X-ray microscopy because this radiation  
45 propagates through and interacts with sample and thus reveals texture, chemical, electronic and/or  
46 structural inhomogeneities in its interior. In order to perform such characterization at  $\mu\text{m}$ - to nm-  
47 scale, dozens of X-ray-based approaches have been developed. They can be distinguished not only  
48 with respect to the principal mechanism of the signal generation but also with the technique used  
49 for the signal detection and/or imaging<sup>2,4-6</sup>. Most techniques provide two-dimensional projec-  
50 tions of sample interiors which can be converted to three-dimensional (3D) images via computed  
51 tomography (CT) requiring collection of multiple projections upon rotation of samples by  $360^\circ$   
52 and, accordingly, an unhindered sample accessibility along at least two spatial directions. These  
53 techniques impose limitations on the shape of the entire sample which should have comparable di-  
54 mensions in all space directions and be preferably cylindrical. These two requirements are difficult  
55 to fulfill in examination of samples with a high aspect ratio, such as coatings on extended substrates  
56 or disk-shaped samples compressed to ultrahigh pressures in diamond anvil cells (DACs) where  
57 samples have typical dimensions of 50-400  $\mu\text{m}$  in diameter and of 10-50  $\mu\text{m}$  in thickness (*e.g.* in  
58 Refs. 7-9).

59 For examination of dense polycrystalline samples in general, but with a large diameter-to-  
60 height ratio or with a limited access in particular, a better solution than X-ray-based CT is to  
61 get local information, *i.e.* information from a limited volume in the sample usually named *voxel*  
62 (with sizes corresponding to the 3D-spatial resolution of the applied technique), directly from  
63 signals collected along a single direction. If such signals provide segmented information along

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64 this direction, a 3D image corresponding to the juxtaposition of voxels can then be obtained by  
65 moving the probed limited volume (voxel) along two other perpendicular directions. Such oppor-  
66 tunity/procedure is accessible via optical methods: strong focusing of laser light exciting Raman  
67 or classical frequency-domain Brillouin spectra permits extraction of 3D-resolved local informa-  
68 tion in the interior of transparent samples. However, in the absence of a control over the ther-  
69 mal phonons spatial localisation, the axial (*i.e.* along depth) resolution cannot be better than the  
70 Rayleigh distance of the focused radiation<sup>10,11</sup>. Thus, the dimensions of a voxel in that case are  
71 those of the 3D volume defined by the optical focal spot. Note that in our previous publication<sup>12</sup>,  
72 most of the achievements in 2D- and 3D-imaging at high pressures, reported at that time and  
73 including X-ray-based techniques and frequency-domain Brillouin scattering, were already re-  
74 viewed. While Raman spectroscopy is useful in only few special cases where samples contain  
75 compounds having distinct Raman spectra with strong lines, which is often not the case (e.g ice VI  
76 and VII, NaCl, MgO, Al<sub>2</sub>O<sub>3</sub>, etc.), the classical frequency-domain Brillouin scattering (FDBS)  
77 can provide, in principle, an integral/holistic information on the state and texture of a polycrys-  
78 talline transparent sample in 3D. This integral 3D information includes coordinates of each grain  
79 (if resolved) with respect to others—independently of their phase composition, the grain shapes,  
80 identification of the phase of particular grains, and crystallographic orientation of the identified  
81 grains with respect to a common coordinate system. Up to now, the record resolution, *i.e.* voxel  
82 dimensions, in FDBS has been reported in the confocal optical geometry:  $\sim 0.5 \times 0.5 \times 2 \mu\text{m}^3$ , yet  
83 at ambient conditions<sup>10,11</sup>. Using an oil-immersion objective lens, the resolution has even been  
84 recently enhanced<sup>13</sup> down to  $\sim 0.3 \times 0.3 \times 1.1 \mu\text{m}^3$ . However, maintaining such axial resolution  
85 by the application of the confocal optical FDBS microscopy for long working distances (around  
86 10 mm or even more) is technically demanding, if ever possible. Examples of experiments, where  
87 such distances are inevitable, are examination of samples compressed to ultrahigh pressures in a  
88 DAC, heated in an oven, or cooled in a cryostat. In common FDBS experiments on samples com-  
89 pressed in a DAC (which is possible thanks to the transparency of diamond anvils that squeeze  
90 samples) and similar measurements requiring long working distances, the FDBS spectra are col-  
91 lected from the volume, whose axial dimension is controlled either by the sample thickness or  
92 by the light penetration depth. In both cases, the FDBS technique does not provide any depth-  
93 resolved information for samples having thicknesses between 10-50  $\mu\text{m}$ , but provide information  
94 averaged along the complete thickness of the tested volume.

95 Another opto-acousto-optical technique, capable of providing down-to-nanometers axial res-

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96 olution, and not dependent on the working distance of the focusing optical element, was used  
97 in the present work. It is based on the interaction of light with a propagating coherent density  
98 perturbation (an acoustic pulse) caused by coherent non-thermal acoustic phonons. The lateral  
99 resolution, *i.e.* the lateral dimensions of voxels, of this technique is the same as for any other  
100 optical method, down to about half the wavelength of the used probe light radiation. The tech-  
101 nique had been pioneered for materials characterization at ambient conditions under the name  
102 of picosecond acoustic interferometry<sup>14,15</sup>, while currently the names of time-resolved or time-  
103 domain Brillouin scattering (TDBS) have become more common<sup>16</sup>. In this technique, based on  
104 the principles of pump-probe time-resolved experiments, pump laser pulses of the picoseconds-  
105 femtoseconds duration launch coherent acoustic pulses (CAPs) of picosecond duration in a solid  
106 transparent sample via one of the possible mechanisms of optoacoustic conversion<sup>17,18</sup>. The probe  
107 laser pulses of picoseconds-femtoseconds duration, launched with adjustable time delays after the  
108 pump pulses, are used to follow in time the propagation of the CAPs thanks to the probe light  
109 scattering by the CAPs via opto-acoustic (photoelastic) effect<sup>19,20</sup>. As the light scattering takes  
110 place only in the volume occupied by a CAP, the axial spatial resolution of the TDBS technique  
111 along the path of the CAP, *i.e.* the dimension of voxels along the CAP propagation direction, can  
112 be deeply sub-optical because typical width of a 10 ps duration CAP is shorter than 40 nm<sup>16,21–23</sup>  
113 and further shortens with diminishing duration of coherent acoustic pulses or of the strain gradient  
114 fronts inside them<sup>16</sup>. Thus, the axial resolution of the TDBS technique can outperform that of  
115 the FDBS microscopy, independently of the working distance between the sample and the objec-  
116 tive lens used to focus the pump and probe beams and to collect the scattered light. Application  
117 of the TDBS depth-profiling and imaging therefore provides opportunities and advantages earlier  
118 unavailable in the solid state research where the long working distances are inevitable. Examina-  
119 tion of samples compressed to ultrahigh pressures in a DAC is one of such cases we are dealing  
120 with below. The TDBS approach was introduced into high-pressure research quite recently<sup>24,25</sup>.  
121 It was applied for the depth-profiling of polycrystalline water ice and solid argon up to Megabar  
122 pressures<sup>12,26</sup>, revealing, in these densified granular assemblages, not only  $\mu\text{m}$ -sized textures at  
123 the sample surface as one could get using other approaches but also, and for the first time, sub- $\mu\text{m}$ -  
124 and  $\mu\text{m}$ -sized inhomogeneities along the sample axis, currently inaccessible in a DAC when using  
125 the FDBS technique as well as for the X-ray-based techniques. The TDBS technique was then  
126 applied for the measurement of pressure-dependencies of single crystal elastic moduli of cubic  
127  $\text{H}_2\text{O}$ -ice<sup>27</sup> and solid argon<sup>28</sup>, with a demonstrated better precision than by FDBS.

128 Although the above-mentioned experimental approaches<sup>12,26–28</sup> have already demonstrated ef-  
129 ficiency of the 2D TDBS-based imaging for qualitative and quantitative characterization of ma-  
130 terials elasticity and phase transitions, they were not sufficient for visualisation and examination  
131 of texture and its evolution in time, upon compression or any other action on a difficult-to-access  
132 sample (*e.g.* in an oven or a cryostat). To do so, 3D imaging of sample inhomogeneities is  
133 required. The 3D TDBS imaging has been first realised at ambient conditions in animal and bio-  
134 logical cells<sup>29,30</sup>, which are weakly inhomogeneous objects where regions having distinct elastic  
135 and/or optical parameters are separated by curved interfaces<sup>29–31</sup>. At ambient conditions, TDBS  
136 experiments on polycrystalline materials with large grain sizes were already reported, and it was  
137 found that the TDBS imaging inside individual grains is straightforward<sup>32–36</sup>. In particular, simul-  
138 taneous monitoring of the propagation of quasi-longitudinal acoustic (LA) and quasi-transverse  
139 acoustic (TA) pulses inside a grain by TDBS was demonstrated<sup>32,33</sup>. Taking advantage of this fea-  
140 ture, the TDBS technique provided opportunity to determine the orientation of an individual grain  
141 boundary in 2D geometry<sup>34</sup>. The first step to the 3D imaging of polycrystalline materials at am-  
142 bient conditions was undertaken in the recent work of Wang et al.<sup>35</sup> where the boundary between  
143 two adjacent grains and their relative crystallographic orientations were reconstructed in 3D space  
144 using the simultaneous TDBS imaging with LA and TA pulses. However, an integral/holistic 3D  
145 imaging of a polycrystalline sample (*e.g.*, H<sub>2</sub>O ice) containing, in addition to multiple grains, two  
146 different high-pressure phases (ice VI and ice VII) is here performed and presented for the first  
147 time. This particular case of a sample compressed in a DAC should be considered by the reader  
148 as an example of experiments with a sample inside a relatively heavy device providing access  
149 from only one side, which excludes the possibility to use X-ray-based approaches as well as the  
150 classical spectroscopic techniques for the high-resolution 3D imaging.

151 Extending several concepts developed recently in the TDBS experiments at ambient condi-  
152 tions, we succeeded to generate an integral 3D image of a polycrystalline sample in a DAC  
153 containing multiple differently oriented grains of two high-pressure phases of H<sub>2</sub>O ice. We  
154 were able to determine the position and shapes of grains constituting the sample in the complete  
155  $\sim 100 \times 100 \times 10 \mu\text{m}^3$  volume with the lateral resolution of 2.5  $\mu\text{m}$  and the axial resolution of  
156 1.2  $\mu\text{m}$  as well as orientation of their crystallographic axes with respect to a common system of  
157 coordinates. First experimental observation of coherent TA pulses in TDBS measurements at high  
158 pressures was crucial in obtaining the orientation of crystallographic axes of individual ice grains.  
159 Combining this observations with the signals generated by LA pulses, we could distinguish grains

160 of H<sub>2</sub>O ice VI from those of H<sub>2</sub>O ice VII coexisting at the pressure of our experiment, 2.15 GPa.  
161 In addition, we report on observation of particular TDBS signals, corresponding to the propaga-  
162 tion of LA pulses in two neighbor grains simultaneously, which provides an original opportunity  
163 to localize boundaries between grains. The main prerequisite of such experiments is the earlier  
164 determined densities, refractive indices and single crystal elastic moduli of both H<sub>2</sub>O-ice phases.  
165 In our opinion, 3D images collected using the TDBS-based approach can be considered as stan-  
166 dards for verification of the reliability of back-projection models used in the X-ray-based CT. This  
167 is because the 3D TDBS images are directly obtained from spatially 3D-resolved data requiring a  
168 minimal level of assumptions, as described below.

## 169 II. SAMPLE PREPARATION AND EXPERIMENTAL SET-UP

### 170 A. DAC and the sample

171 The high-pressure experiments on water ice were performed using a diamond anvil cell (DAC)  
172 of the Merrill-Bassett type<sup>37</sup>. We used diamond anvils with unbevelled culets having a diameter  
173 of  $\sim 500 \mu\text{m}$ . A hole of  $\sim 180 \mu\text{m}$  in diameter drilled in the center of a stainless steel gasket  
174 pre-indented to the thickness of  $\sim 60 \mu\text{m}$  represented the sample volume [Fig. 1(c)]. The latter  
175 was filled with bi-distilled water that solidified upon compression. The sample volume contained  
176 also a thin iron disk and few ruby grains of 1-5  $\mu\text{m}$  in size distributed in the space between the  
177 iron disk and the gasket wall. The iron disk served as the opto-acoustic generator for launching  
178 coherent acoustic pulses into the ice sample. It was obtained by a gentle compression of a small  
179 iron spherule between the diamond anvils, whose surfaces are parallel to each other, until the de-  
180 sired thickness was obtained. The disk was initially in contact with one of the anvils but lifted  
181 up on one side by a few microns when the sample volume was filled with water [Fig. 1(c)]. Note  
182 that the shape and the orientation of the iron generator presented in Fig. 1(c) are illustrative. The  
183 ruby grains were used to measure pressure using the calibrated shift of the R1 fluorescence line  
184 with compression<sup>38</sup>. Finally, the H<sub>2</sub>O ice sample was compressed to 2.15 GPa until the ice VI and  
185 ice VII phases were simultaneously present in the sample volume. The ruby fluorescence spectra  
186 were collected with an Ocean Optics USB4000 spectrometer. Within the instrument resolution,  
187 the pressure was found to be the same in all points around the sample. The collected spectra were  
188 fitted with the Gaussian-Lorentzian function to obtain position of the R1-line maximum. Corre-



189 responding pressure was calculated to be  $2.15 \pm 0.05$  GPa using the calibration for quasi-hydrostatic  
190 load conditions<sup>38</sup>.

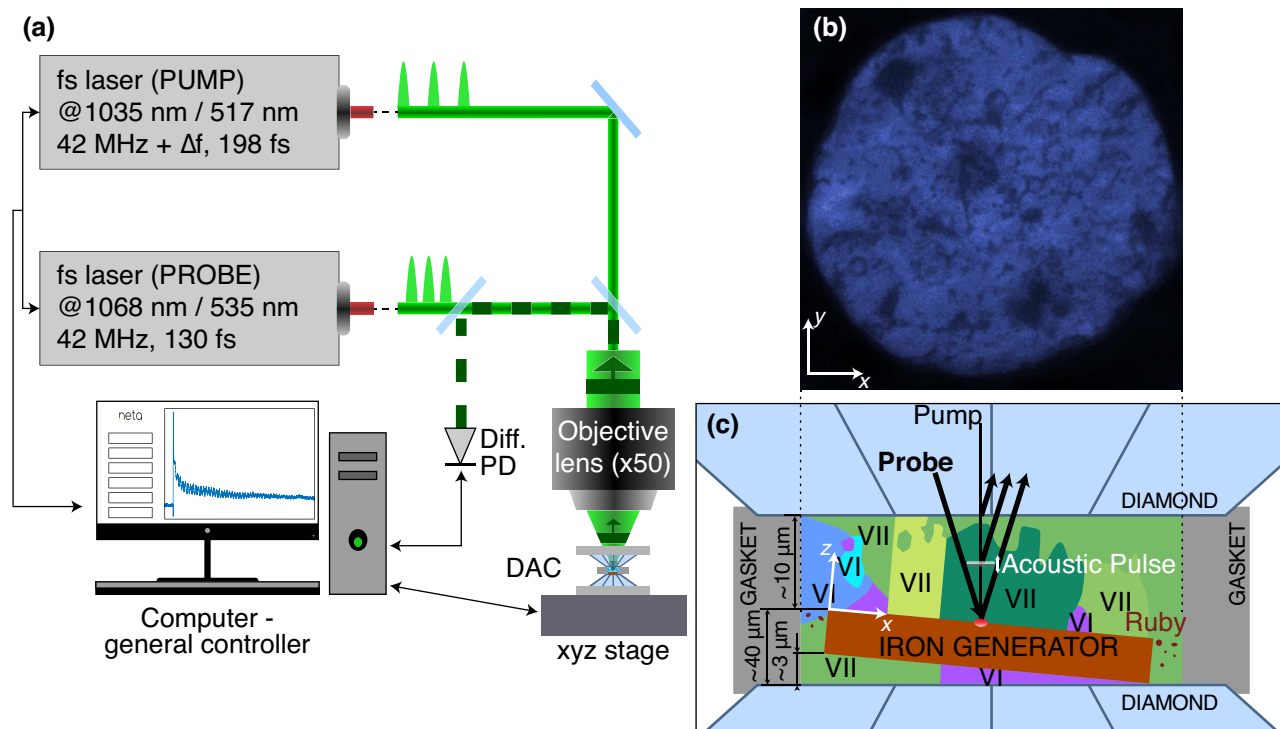


FIG. 1. (a) Experimental set-up of the picosecond acoustic microscope (JAX-M1, NETA, France) and (b) optical image of the  $\text{H}_2\text{O}$  ice polycrystal in the DAC between the diamond anvil and the iron optoacoustic transducer. (c) Magnified cross-sectional side view of the DAC. The results of the TDBS experiments (see Figs. 3 and 4) revealed the coexistence in the sample of two phases, ice VI (bluish) and ice VII (greenish). The disk-shape iron opto-acoustic generator inside the sample chamber has the diameter of about  $100 \mu\text{m}$ . It touches the lower diamond anvil at its right end. Even though the pump and probe laser paths are collinear in the experiment, the probe one is shown inclined for a better visualisation of its different reflections. The coordinate system used below is shown by white arrows in (b) and (c).

## 191 B. Pump/probe ASOPS set-up

192 The experimental set-up is a commercial picosecond acoustic microscope (JAX-M1, NETA,  
193 France)<sup>39</sup> based on asynchronous optical sampling (ASOPS) with pump and probe laser beams  
194 following the same path within the DAC, as shown schematically in Fig. 1(a). Two pulsed fiber  
195 lasers of optical wavelength of 1034.8 nm and 1068.4 nm, of pulse duration 198 fs and 130 fs,  
196 respectively, and with a repetition rate of 42 MHz are synchronised for asynchronous optical  
197 sampling<sup>40</sup>. The repetition rate of the follower laser cavity is slightly offset compared to that  
198 of the leader one. The used offset in our measurements of 500 Hz corresponds to a temporal sam-

219 pling of 0.28 ps. The two optical wavelengths obtained by frequency doubling of the fundamental  
220 radiations, 517 nm and 535 nm, were used as pump (follower cavity) and probe (leader cavity), re-  
221 spectively. The beams were normally incident and co-focused on the surface of the iron disk to the  
222 spot of approximately 1.25  $\mu\text{m}$  radius at the  $1/e^2$  level of the laser intensity. The averaged power  
223 of the pump laser was 7 mW and that of the probe laser 13 mW. Note that the chosen beam pow-  
224 ers have been set to maximize the ratio of the useful signal over noise: the probe power is nearly  
225 twice that of the pump in order to have a large enough reference and scattered probe light reaching  
226 the photodetector, which allows diminishing the number of averages and hence the overall time  
227 of the experiment. The sample analysed in this work was a water ice polycrystal compressed in  
228 a DAC to a pressure of 2.15 GPa, as presented in the previous section, with an embedded iron  
229 optoacoustic transducer for launching the CAPs<sup>41</sup>. The optical image of the H<sub>2</sub>O ice polycrystal  
230 in the DAC shown in Fig. 1(b) reveals some dark areas on the iron transducer corresponding to  
231 low local optical reflectivity of iron, that could be due to some degradation processes<sup>41</sup>. For the  
232 imaging experiments, the sample was mounted on a X-Y positioning stage equipped with step mo-  
233 tors ensuring the positioning precision of 0.16  $\mu\text{m}$ . For the below-presented images, the step was  
234 1.25  $\mu\text{m}$  along  $x$ - and  $y$ -axes [see Fig. 1(b)-(c) for the coordinate system]. As shown in Fig. 1(c),  
235 the origin of the  $z$ -axis is at the surface of the iron transducer.

### 236 III. RESULTS

#### 237 A. Typical experimental signals

238 In the TDBS experiments, the probe light scattered by moving CAPs and the probe light re-  
239 flected by various stationary optical inhomogeneities of the sample interfere on a photodetector  
240 surface and thus produce a signal oscillating in time. In the considered experiments, the most im-  
241 portant stationary sources of the probe light reflection are (i) the metallic optoacoustic transducer  
242 where the pump and probe laser pulses are co-focused and (ii) the interface between the diamond  
243 anvil—providing optical access to the compressed sample—and the water ice [see Fig. 1(c)]. Het-  
244 erodyne detection in the TDBS technique is essentially interferometric and sensitive to the relative  
245 phase of the acoustically scattered and reflected probe light<sup>14,15</sup>. Because of a CAP propagation  
246 at its mode velocity, the phase of the light scattered by this CAP is continuously varying in time.  
247 The TDBS signal, due to the interferences on the photodetector of the acoustically-scattered probe

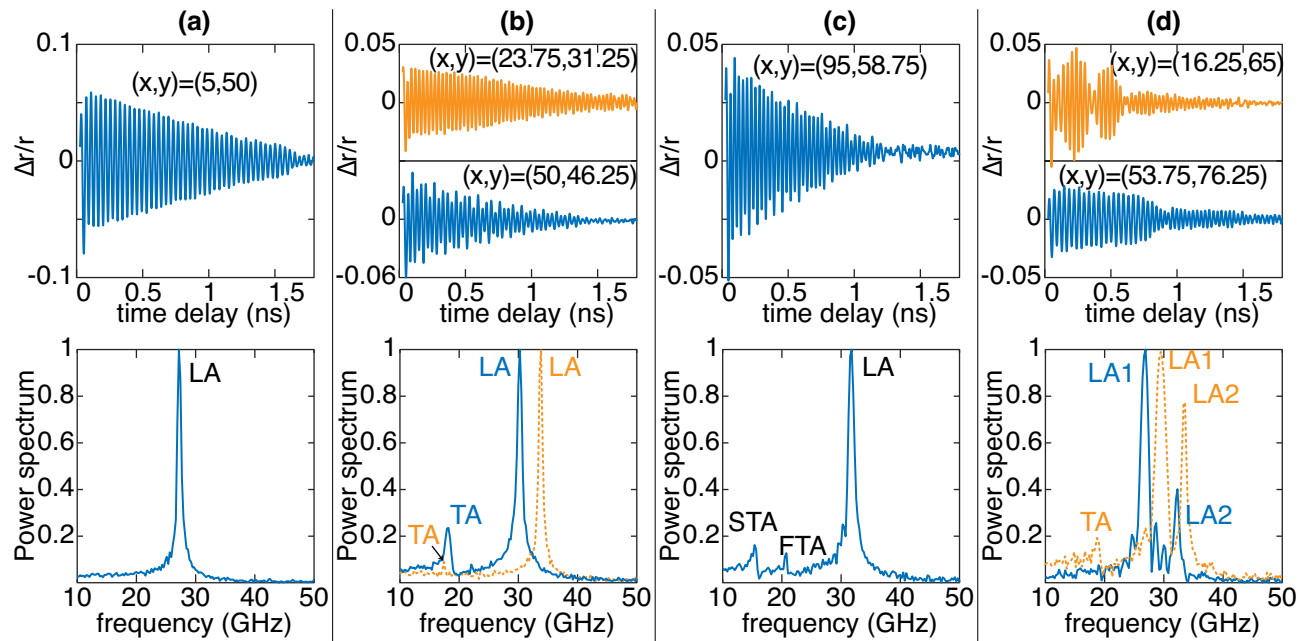


FIG. 2. Experimental acoustic contributions to transient reflectivity signals as a function of time delay (upper row) and their Fourier spectrum density (lower row) in four typical cases: (a) a single quasi-longitudinal acoustic (LA) mode, (b) a LA and one quasi-transverse acoustic (TA) modes with low (orange lines) and large (blue lines) relative shear amplitudes, (c) a LA and two TA modes, and (d) two LA modes propagating in two different grains “in parallel” (orange lines) and “in sequence” (blue lines). The coordinates  $x$  and  $y$  of the measurement points, which are indicated in the first row, correspond to the positioning (in  $\mu\text{m}$ ) of the ice sample in the coordinate system presented in Figs. 3 and 4.

228 light and the reflected one, is oscillating with extrema and zeros corresponding to the construc-  
 229 tive and destructive interferences, respectively. The oscillating TDBS signal, commonly called  
 230 the Brillouin oscillation (BO), contains the delay-time dependent information about variations of  
 231 optical, elastic, and photo-elastic properties in the sample along the CAPs propagation direction  
 232 which can be converted to the length/depth scale. The typical oscillating TDBS signals, obtained  
 233 for different lateral positions on the imaged area of the water ice sample, are presented in the first  
 234 row of Fig. 2. These signals are obtained from the raw transient reflectivity signals captured by a  
 235 photodetector followed by filtering, subtracting the thermal background and cutting of initial peaks  
 236 generally observed at the instants when the pump and probe laser pulses overlapped. First the sig-  
 237 nal is filtered with a 48th-order FIR bandpass filter with passband  $10 < f < 50$  GHz according  
 238 to the expected Brillouin frequencies from Tab. I. Then, the remaining-after-filtering background  
 239 was subtracted applying the local regression method LOESS from Matlab<sup>®</sup> using weighted linear  
 240 least squares and a 2nd degree polynomial model<sup>42</sup> with 319 points of span of the moving average  
 241 (*i.e.*, the window span for the moving average is about 0.15 ns). Because the fast non-oscillating

242 transients of optical reflectivity near the initial time are difficult to remove without influencing the  
243 high-frequency Brillouin oscillations (Brillouin peak), the first 25 ps of the remaining signal were  
244 cut. Therefore, the first tens of nanometres next to the iron generator are lost for the analyses. We  
245 applied a similar treatment to all signals presented in this paper before further processing.

246 The characteristic frequencies of the BOs in the TDBS signal (see Fig. 2) correspond to the  
247 frequencies of the Stokes/anti-Stokes frequency shifts of the scattered light in the FDBS technique,  
248 *i.e.*, to the Brillouin frequency (BF)<sup>19,20</sup>. In our experimental geometry, where the coherent CAPs  
249 and the probe light are propagating collinearly, the most efficient process of the photon-phonon  
250 interaction is the backward scattering of the probe light. In this case, the BFs ( $f_{B,\alpha}$ ) are related to  
251 the velocities ( $v_\alpha$ ) of the coherent acoustic phonons, where  $\alpha$  stands for the type of the acoustic  
252 mode (LA or one of the TA), by the following relation:

$$f_{B,\alpha} = \frac{2nv_\alpha}{\lambda_{\text{probe}}}, \quad (1)$$

253 where  $n$  is the refractive index of the transparent media at the wavelength in vacuum  $\lambda_{\text{probe}}$  of the  
254 probe laser pulses. The Fourier analysis of the BOs is therefore commonly the first step used to  
255 reveal the physical origins of variations of BF of each of the TDBS signals.

256 Fourier spectra of typical BOs detected in our sample are presented in the second row of Fig. 2.  
257 These spectra clearly indicate that the TDBS signals have contributions from different types of the  
258 CAPs in the different lateral positions of our sample. This was used in the following for 3D TDBS  
259 imaging. Near the pressure of 2.15 GPa, corresponding to the transition at room temperature  
260 from the lower-pressure phase VI to the higher-pressure phase VII of H<sub>2</sub>O ice<sup>41</sup>, the available  
261 data on the optical and elastic properties (see Table I) provide the opportunity to estimate the  
262 expected BFs in both phases of ice (see Appendix for detailed explanations of these estimations  
263 and their uncertainties). The comparison of the spectra presented in Fig. 2 with the results of  
264 these estimations, presented in the last row of Table I, indicated that not only LA modes but also  
265 TA modes are contributing to our detected TDBS signals. The latter is observed for the first time  
266 in high-pressure TDBS experiments. The BOs presented in Fig. 2(a)-(c) can be attributed to the  
268 Brillouin scattering by a single LA mode, by a LA and one TA modes, and by a LA and two TA  
269 modes, *i.e.* fast (FTA) and slow (STA), respectively. It is worth noting here that, potentially, in  
270 optically anisotropic ices, a single acoustic mode could produce up to three different BFs because  
271 of the birefringence phenomena giving rise to BS with optical mode conversion<sup>32,33</sup>. However,

| Phases of H <sub>2</sub> O ice<br>(Lattice system) |      | VI<br>(Tetragonal)   | VII<br>(Cubic)   |
|--|------|--|--|
| Density <sup>43,44</sup> (g cm <sup>-3</sup> )     |      | $\rho = 1.419$   | $\rho = 1.600$   |
| Elastic constants <sup>44,*</sup><br>(GPa)         |      | $C_{11} = 40.56$<br>$C_{12} = 13.75$<br>$C_{13} = 18.59$<br>$C_{33} = 34.43$<br>$C_{44} = 7.50$<br>$C_{66} = 6.39$ | $C_{11} = 37.61$<br>$C_{12} = 19.17$<br>$C_{44} = 21.59$ |
| Refractive index<br>@ 515 nm <sup>43,44</sup>      |      | $n = 1.468$  | $n = 1.521$  |
| Brillouin frequency<br>range (GHz)                 | LA:  | [26.71 – 29.37]  | [27.58 – 33.09]  |
|  | FTA: | [12.63 – 16.89]  | [16.46 – 20.90]  |
|  | STA: | [11.66 – 12.80]  | [13.66 – 20.90]  |

\* Our TDBS results for ice VII<sup>27</sup> agree reasonably well with those reported in Ref. 44

TABLE I. Properties of the high-pressure phases VI and VII of H<sub>2</sub>O ice near the pressure of 2.15 GPa and used to calculate the ranges of BFs for the LA, the fast TA (FTA) and the slow TA (STA) modes. The uncertainties in the estimated ranges of the Brillouin frequencies of different acoustic modes are discussed in the appendix.

272 the phase VII of H<sub>2</sub>O ice is cubic (and thus optically isotropic), while the birefringence of the  
273 hexagonal phase VI is too weak (less than 1%<sup>43</sup>) to be observed in our TDBS experiments.

274 The beating in the BO evidenced in Fig. 2(d) demonstrates that the LA pulses are propagating  
275 in two differently-oriented grains of ice. The orange lines correspond to their propagation in both  
276 grains simultaneously, *i.e.* “in parallel”. On the contrary, the blue lines correspond to the case  
277 when the LA pulses are propagating first in one grain and then in another one, *i.e.* “in sequence”.  
278 The BOs corresponding to the sequential TDBS in two different media, *i.e.* the TDBS imaging  
279 of the LA CAP transmission from one medium into another were already reported multiple times,  
280 for example for ice/diamond interface<sup>12</sup>, for the interface between ice VII and ice VI<sup>41</sup> and for  
281 SiO<sub>2</sub>/Si interface<sup>45,46</sup>. The sequential propagation of the LA CAPs in two different grains of a  
282 polycrystal was reported as well<sup>34</sup>. Note that there are also some reported observations of the  
283 simultaneous monitoring in two different media of two different LA CAPs propagating in the  
284 opposite directions: for example, the CAPs transmitted through and reflected from the interface  
285 between two media<sup>45</sup>. Here however, we report for the first time the TDBS monitoring of two LA  
286 CAPs propagating in parallel and in the same direction in two differently oriented ice grains along

287 their mutual interface. In the next subsection, it is revealed that all the TDBS signals of the type,  
288 highlighted in Fig. 2(d) with the orange colour, are detected in the vicinity of grain boundaries  
289 and are never detected in the grain volume. The latter suggests that the detection of these kind of  
290 TDBS signals could be fruitful for a fast localisation of grain boundaries, *in situ* and in real time.

## 291 **B. 2D TDBS projections obtained with LA and TA coherent acoustic pulses and grain** 292 **identification**

293 The 2D TDBS projections in Fig. 3 highlight the contribution of the most prominent grains  
294 with a particular velocity of (a) LA mode or (b) one of the TA modes related to the orientation of  
295 those grains. The color maps in Fig. 3 represent indeed the dominant frequency content attributed  
296 to (a) LA modes and (b) TA modes of the first two nanoseconds of the TDBS signals observed in  
297 the polycrystalline ice sample covering a round disk-shaped iron optoacoustic transducer of about  
298 50  $\mu\text{m}$  radius [Fig. 1(b,c)]. The chosen time interval corresponds to the acoustic propagation time  
299 through about 10  $\mu\text{m}$  of the ice sample at a LA mode velocity. The TDBS signals are not observed  
300 in the locations indicated by white pixels due to poor signal-to-noise ratio. Note that the white  
301 pixel areas in Fig. 3(a) match the dark tones in the optical image of the sample [Fig. 1(b)]. It  
302 is important to note that while individual crystallites in the sample are not visible on the optical  
303 image, their presence is obvious in the 2D TDBS projection.

304 The black open squares in Fig. 3(a) depict pixels where a beating phenomenon of the kind “in  
305 parallel” (orange) in Fig. 2(d) has been observed. The automatic gathering of those pixels has  
306 been performed by tracking the signals that have two peaks in the spectrum density within the LA  
307 frequency range and that show at the same time a peak at the difference frequency in the spectrum  
308 density of its envelope. It is clearly visible from Fig. 3(a) that such signals are only found in  
309 locations in the vicinity of grain boundaries and never in a grain volume. We propose that this  
310 feature can be used for grain boundary imaging (see Discussion).

311 To obtain the map of TA modes [(Fig. 3(b)], we have extracted prominent frequency peaks in  
312 the 10 to 22 GHz frequency range, which excludes the LA modes (see Table I). The TA map is less  
313 complete than the LA one because TA modes have usually lower amplitudes in TDBS signals than  
314 LA modes, making them more difficult to detect/observe. Nevertheless, even TA modes with weak  
315 amplitudes are detected in the data with good signal-to-noise ratio as shown by the dashed orange  
316 curve of the spectrum density in Fig. 2(b). The white solid lines in Fig. 3(a) indicate areas where

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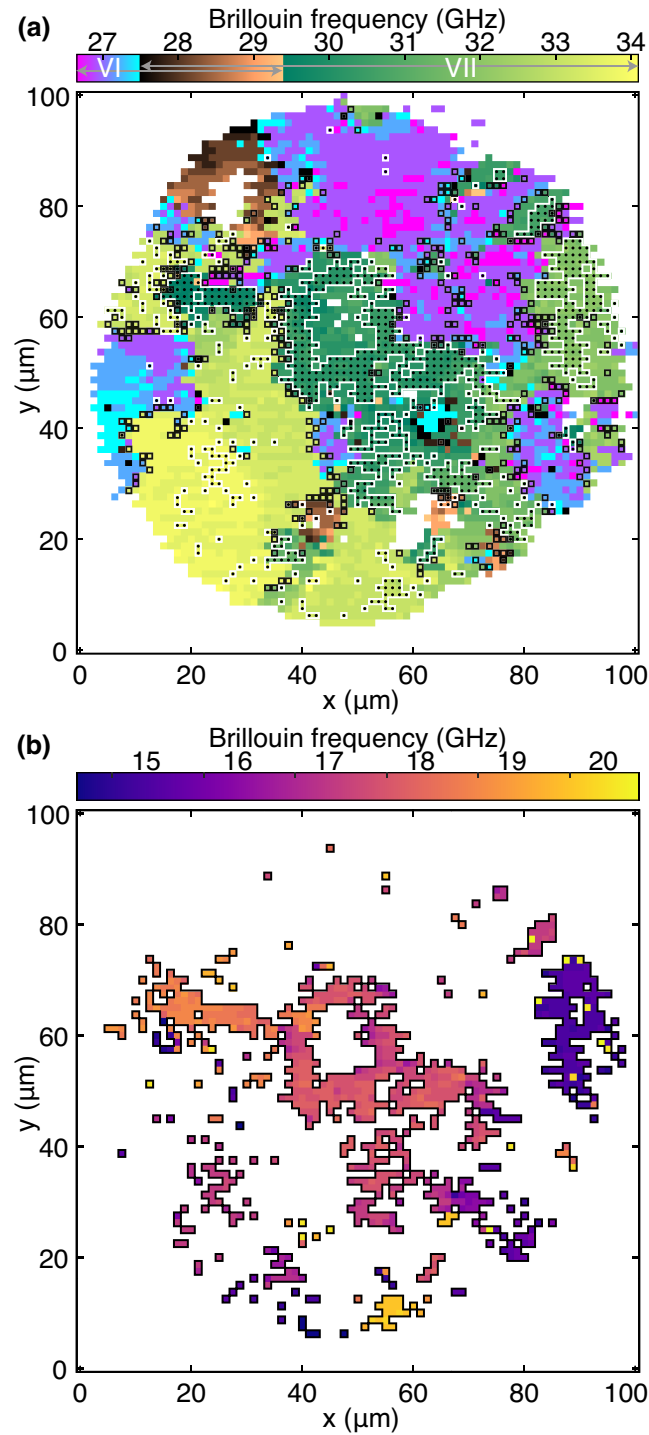


FIG. 3. Dominant frequency content attributed to (a) LA modes and (b) TA modes of the first two nanoseconds of the TDBS signals observed in the  $100 \times 100 \mu\text{m}^2$  area of the ice sample. The white solid lines in part (a) delimit areas where the TA modes shown in (b) have been detected. In (a), each pixel shown in (b) is marked with a central black dot. The black open square markers show the pixels where a beating phenomenon of the kind presented by the top (orange) signal in Fig. 2(d) has been observed.

317 the TA modes shown in Fig. 3(b) have been detected. Each pixel shown in Fig. 3(b) is marked

318 with a central black dot in Fig. 3(a). It is interesting to note that most of the detected TA modes are  
319 recorded in the voxels where the frequency content is higher than 29.4 GHz (greenish color scale),  
320 showing that the TA modes with decent amplitudes are all found in the phase VII of H<sub>2</sub>O ice, and  
321 mainly where the LA velocity is rather low (dark green) or high (light green). The lowest part of  
322 the color bar in Fig. 3(a), where the frequencies lower than 27.5 GHz are (magenta-to-cyan color  
323 scale), depicts the crystallites belonging to the phase VI of H<sub>2</sub>O ice. Interestingly, almost no TA  
324 modes are detected in these specific locations of the sample, which suggests that the monitoring  
325 of TA modes in the phase VI is, for the present state of the technique, very unlikely, not to say  
326 impossible (see next section). Note that in the center-right grain (around  $x \approx 90 \mu\text{m}$  and  $y \approx 60 \mu\text{m}$ )  
327 in Fig. 3(b) with the lowest TA frequencies, the color of some neighboring pixels is occasionally  
328 switching from dark violet, *i.e.* the lowest frequency of the color scale, to light yellow, *i.e.* the  
329 highest frequency of the color scale. This is because the figure represents the dominant frequency  
330 content in the TA frequency ranges and this particular grain contains two detectable TA modes.  
331 The amplitude of the slow (S) TA mode is usually higher than that of the fast (F) TA mode, except  
332 in some (light yellow) locations. The area where identification of the main ice phase remains  
333 unclear from the first analysis of the dominant frequency content of the LA signals, *i.e.*, where the  
334 frequency is greater than or equal to 27.5 GHz and lower than or equal to 29.4 GHz are depicted  
335 in a copper color in the scale in Fig. 3(a).

### 336 C. 3D TDBS imaging with LA coherent acoustic pulses

337 In order to obtain 3D images of the sample texture using the collected TDBS signals, we used  
338 a usual short-time Fourier transform. Fig. 4 represents the depth-resolved information of the ice  
339 sample texture recovered using the LA mode. Although the same imaging with TA coherent acous-  
340 tic pulses is possible, the detected TA modes are too sparse [see Fig.3(b)] to obtain an informative  
341 3D image. The latter is explained by very low power of both pump and probe lasers needed to  
342 preclude the non-thermal transformation of ice VII into ice VI (see below).

343 In Fig. 4, we estimate the dominant LA-mode-related frequency at different depths by calcu-  
344 lating the FFT of the acoustic signal sliced with a Hann window of 0.23 ns (about 7 oscillations  
345 of the LA mode), which gives an axial resolution of about 1.2  $\mu\text{m}$ . Using the temporal indication  
346 of the centre of the sliding window and the measured local velocities at the previous instants for  
347 the same acoustic mode, the time axis was transformed in the depth axis; the smaller the time, the



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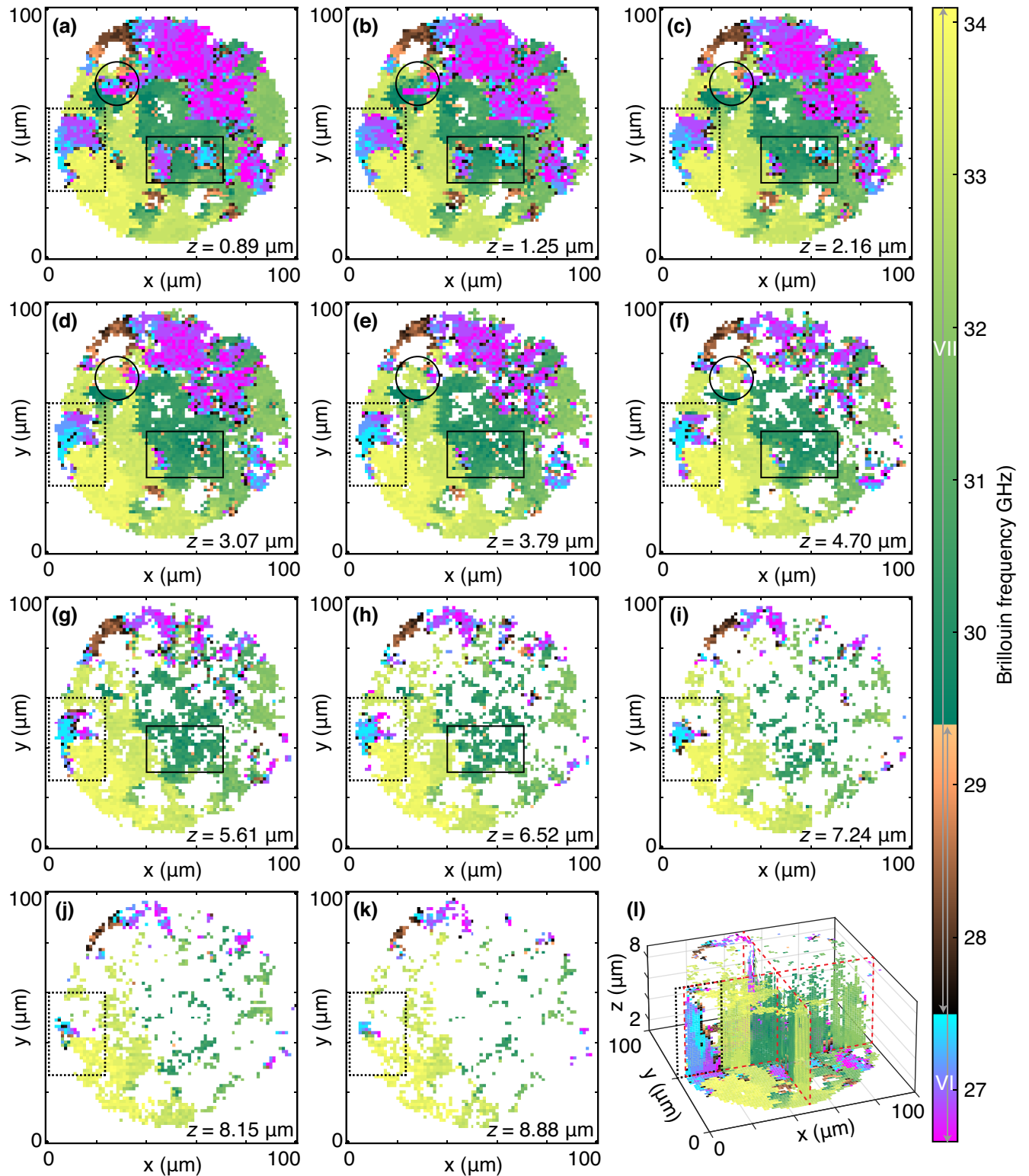


FIG. 4. 3D TDDBS imaging of the polycrystalline  $\text{H}_2\text{O}$  ice sample. (a)-(k) The slices are shown at particular positions along the  $z$ -axis indicated in the right-bottom corner of each slice. In (a)-(f), the circles depict a volume zone composed of multiple small crystallites. In (a)-(h), the solid lines rectangles depict the zones where crystallites of the phase VI are seen between the optoacoustic transducer and the higher-located crystallites of the phase VII. In (a)-(l), the dotted lines rectangles depict zones with oblique boundaries between several crystallites of phase VI. (l) 3D representation of the complete probed volume with the first and last slices, (a) and (k) ( $xy$  planes), and the middle slices ( $yz$  and  $xz$  planes) at  $x = 50 \mu\text{m}$  and  $y = 50 \mu\text{m}$ , respectively (red dashed rectangles). The color map is common for all parts of Fig. 4 and is the same as in Fig. 3(a). It is important to note that for the sake of visibility of 3D textures, the vertical  $z$ -axis is expanded by 4 times when compared with the  $x$ - and  $y$ -axes.

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348 closer the probed voxel to the iron optoacoustic transducer. Note that this change of coordinates  
349 implies knowledge of the local refractive index. For the sake of simplicity, we have chosen here  
350 to attribute only one refractive index to a given pixel, even when it contains two phases. The at-  
351 tribution of the refractive index is based on the previous determination of the phases of each grain  
352 as discussed in Fig. 3(a). This means that we used the refractive index of the dominant phase. We  
353 are aware that this will engender some distortions of the grains, which we consider as minor in  
354 this analysis. For pixels with unattributed phases ( $f_{B,LA} \in [27.5, 29.4]$  GHz), the refractive index  
355 is chosen to be the average of that of phases VI and VII. The resulting 3D-imaging is shown in  
356 Fig. 4 where each panel, except the last one (l), is a slice of the polycrystalline H<sub>2</sub>O ice sample at  
357 a particular coordinate along the  $z$ -axis given in the right-bottom corner of each panel. In Fig. 4(l),  
358 a 3D representation of the complete probed volume is shown with the first and last slices, (a) and  
359 (k) ( $xy$  planes), and the vertical slices through the sample middle ( $yz$  and  $xz$  planes) at  $x = 50 \mu\text{m}$   
360 and  $y = 50 \mu\text{m}$ , respectively (red dashed rectangles). The rectangles (shown with solid and dotted  
361 lines) and the circle mark in Fig. 4 indicate the sample regions/volumes with some interesting  
362 changes in the bulk revealed by this 3D imaging that are discussed in the following.

363 From the analysis of the 2D projection in Fig. 3(a), the volume zone pointed out by the circle in  
364 Fig. 4(a)-(f) is expected to be composed of multiple small crystallites because it contains numerous  
365 TDBS signals with beatings. It can indeed be seen in Fig. 4 that close to the iron optoacoustic  
366 transducer, this zone is made of multiple and relatively small crystallites depicted by different  
367 colors. About half of the voxels within the circle depicted in the slice at  $z = 0.89 \mu\text{m}$  (Fig. 4(a))  
368 belong to ice VI crystallites. In the next slice at  $z = 1.25 \mu\text{m}$ , Fig. 4(b), it can be seen that  
369 in the place of the crystallites of phase VI with high LA velocity for that phase (cyan voxels,  
370  $f \approx 27.5$  GHz) the ice phase is now VII with low LA velocity for that phase (green voxels,  $f \approx$   
371  $31.1$  GHz). From that slice to the next one at  $z = 2.16 \mu\text{m}$ , Fig. 4(c), the voxel color slightly  
372 changes to lighter green, which could be tentatively attributed to a change from one phase VII  
373 crystallite to another having a deviating crystallographic orientation. Yet, the resolution along  
374  $z$  of about  $1.2 \mu\text{m}$  controlled by the width of the Hann window means that the frequency/color  
375 attributed to those voxels in the slice in Fig. 4(b) is indeed a weighted average of the frequency of  
376 the phase VI crystallite (close to the transducer) and that of the phase VII [higher in the DAC, see  
377 Fig. 1(c) for illustration]. An even more precise depth localisation of the boundary between the  
378 two could be done but requires a more sophisticated signal processing. The rectangles shown by  
379 solid lines [Fig. 4(a)-(h)] depict also the zones where crystallites of the phase VI are seen between

380 the optoacoustic transducer and the higher-located crystallites of the phase VII. Interestingly, the  
381 frequency (and color in Fig. 4) is not switching here from that of phase VI to that of phase VII  
382 at the same depth for all pixels. This is the clear sign of an oblique interface between the two  
383 grains composed of different phases of H<sub>2</sub>O ice. Last but not least, rectangles shown with dotted  
384 lines [Fig. 4(a)-(l)] surround other textural features demonstrating the 3D imaging capability of  
385 the TDBS technique. In this case, oblique boundaries between several crystallites of phase VI  
386 having different crystallographic orientations extend up to the ice/diamond interface. In Fig. 4(l),  
387 the inclined boundaries are clearly visible in the vertical slice (*xz* plane) at *y* = 50 μm.

## 388 IV. DISCUSSION

### 389 A. On the TDBS depth spatial resolution

390 In the 3D TDBS-ASOPS image shown in Fig. 4, shapes and coordinates of grains of both H<sub>2</sub>O  
391 ice phases, obtained using the LA modes only, were measured with the spatial resolution similar  
392 to that achieved in the most recent XRD-based CT measurements<sup>47,48</sup>. In our work, the axial  
393 resolution was 1.2 μm and the lateral one, defined by focusing of the laser beams to be 2.5 μm,  
394 was approximately twice larger than the lateral step of the scans. The XRD-based CT permits  
395 reconstruction of 3D-images of texture-free or weakly textured samples with the stated spatial  
396 resolution of 1 μm. However, the technically possible spatial resolution of the TDBS-ASOPS  
397 method is much higher<sup>16,31</sup>. The lateral resolution, limited by the wavelength of the used lasers,  
398 can be improved to half the probe optical wavelength, down to 150 nm if UV-blue light lasers are  
399 used. The axial resolution of < 170 nm with our probe laser can be achieved if both LA mode and  
400 TA modes are used because it is only limited by the probed acoustic wavelength  $\lambda_B = \frac{\lambda_{\text{probe}}}{2n}$ . In our  
401 present 3D imaging, the axial resolution was controlled by the application of the time-frequency  
402 analysis technique known as the short-time Fourier transform requiring a balance between the  
403 frequency- and temporal (and thus axial) resolution. We had to keep the frequency resolution,  
404 which permits recognizing of grains having different crystallographic orientation, high enough to  
405 be able to differentiate frequency changes in the interval of the LA Brillouin frequencies of phase  
406 VI spanning only over 2.7 GHz (see Table I and Fig. 4). For this reason, the temporal size of  
407 the Hann window was 0.23 ns, which is theoretically even a bit small since the 3 dB bandwidth  
408 of such a window function is 3.2 GHz. In addition, one should not forget that a polycrystalline

409 aggregate under pressure in a DAC is usually subjected to stress inhomogeneity/nonhydrostaticity,  
410 which could lead to an induced optical anisotropy within the DAC and therefore could influence  
411 the obtained 3D images if not accounted for. This effect in our case is negligible. Indeed, we  
412 estimated a uniaxial stress component parallel to the load axis of the DAC of 30 MPa, from the  
413 measured 0.15 GPa difference in pressure between the center and the edge of the sample. In the  
414 case where the uniaxial stress component was estimated to be 1 GPa for a 4 GPa difference in  
415 pressure over 45  $\mu\text{m}$ , we have already reported that the induced optical anisotropy in that case is  
416 negligible<sup>12</sup>.

## 417 B. On the TDBS depth of imaging

418 The TDBS imaging theoretically allows imaging of transparent samples to the depths exceeding  
419 100  $\mu\text{m}$  but it can be limited by several factors such as (i) the coherence length of the probe laser  
420 pulses,  $L_{\text{coherence}}^{\text{probe}}$ , in the medium under evaluation, (ii) the diffraction length,  $L_R$ , of the probe laser  
421 radiation and of the coherent acoustic waves, as well as (iii) by the absorption of the acoustic pulses  
422 and probe light. For further details on depth of the TDBS imaging, we refer interested readers to  
423 the review article on advances in applications of TDBS for nanoscale imaging (Ref. 16) and ref-  
424 erences cited therein. We estimated the coherence length in our measurements using the equation  
425  $L_{\text{coherence}}^{\text{probe}} \equiv c_0 \tau_{\text{probe}} / (2n) \approx 15 \mu\text{m}$ , where  $c_0$  denotes the speed of light in vacuum,  $\tau_{\text{probe}} \approx 150$  fs  
426 the duration of the laser pulses of our TDBS-ASOPS set-up, and  $n \approx 1.5$  the refractive index of ice  
427 at  $P = 2.15$  GPa for  $\lambda = 515$  nm<sup>43,44</sup> (close to our probe wavelength  $\lambda_{\text{probe}} \cong 535$  nm). The main  
428 limiting parameter was, obviously,  $\tau_{\text{probe}}$  because, currently, only for this type of lasers (*i.e.*, fs  
429 lasers) the needed cavities synchronisation of the pump and probe lasers for ASOPS is available.  
430 Because of the strict relation between  $\lambda_{\text{probe}}$  in the medium and the wavelength of the coherent  
431 acoustic phonon at the Brillouin frequency, *i.e.*  $\lambda_B = \frac{\lambda_{\text{probe}}}{2n}$ , the Rayleigh range (*i.e.*, the diffraction  
432 length) of both the probe light beam and the coherent acoustic beam at Brillouin frequency, can be  
433 described by the formula:  $L_R \equiv \frac{\pi a^2}{(\lambda_{\text{probe}}/n)}$ , where  $a$  is the radius at  $1/e^2$  level of the intensity distri-  
434 bution in the probe or in the pump laser beams. Because focusing of the pump laser beam controls  
435 the radius of the photo-generated CAPs and the pump and probe laser beams were co-focused,  
436 in our experiments, to the same spot with  $a \approx 1.25 \mu\text{m}$ , we obtained  $L_R \approx 14.3 \mu\text{m}$ , very similar  
437 to  $L_{\text{coherence}}^{\text{probe}}$ . However, the signal amplitude drops by  $e^2$  times at the coherence length, while it  
438 decreases by only  $\sqrt{2}$  times at the Rayleigh range. Accordingly, the influence of the diffraction

439  $(\sim 1/[1 + (v_{LA}t/L_R)^2]^{1/2})$  on the depth of imaging was negligible in our experiments. We have  
440 confirmed this consideration experimentally. In some lateral positions, the gaps between the op-  
441 toacoustic transducer and the diamond anvil were filled by single crystals as followed from the  
442 observed Brillouin oscillations within the complete gaps (see Fig. 1(c) and Supplementary infor-  
443 mation). In one of these positions, the quasi-longitudinal acoustic wave with  $f_B = 26.85$  GHz and  
444  $v_{LA} \approx 4881$  m s<sup>-1</sup> propagated from the optoacoustic transducer to the diamond anvil in 2.15 ns,  
445 thus providing the distance of 10.5  $\mu$ m. We note that, during the propagation, the Brillouin os-  
446 cillation amplitude decreased by only 75%. We fitted the observed Brillouin amplitude decay by  
447 accounting for (i) the Gaussian temporal decay related to the coherence length of the probe laser  
448 pulses and (ii) the additional exponential temporal decay that could be potentially caused by un-  
449 known absorption of CAPs using the model signal  $A \exp(-\alpha t) \exp[-2(t/\tau)^2] \cos(2\pi f_{B,LA}t + \phi)$ .  
450 Here,  $A$  is the amplitude,  $\alpha$  the acoustic absorption coefficient,  $\tau$  the coherence time of the probe  
451 laser pulses and  $\phi$  the phase of the signal (see Supplementary information for details). The optical  
452 absorption of the probe green light was not considered because it is known to be negligible at the  
453 evaluated coherence length. The fit result demonstrated that the contribution of the acoustic ab-  
454 sorption in the observed decay of the Brillouin amplitude is negligible too and that the decay of the  
455 TDBS signal in single crystals of ice is controlled by the coherence length because we obtained the  
456 fitted values of  $L_{\text{coherence}}^{\text{probe}} \approx 13$   $\mu$ m and  $\tau_{\text{probe}} \approx 125$  fs, consistent with the experimental pulse du-  
457 ration of the probe laser. Thus, the depth of imaging was limited in our experiments by the sample  
458 thickness. We note that application of lasers with pulses in ps-range, presently not commercially  
459 available for ASOPS although achievable from fs-lasers-based ASOPS systems with prisms or  
460 optical gratings, will allow a significant extension of the 3D-imaging depth of the TDBS-ASOPS  
461 method (not needed in our case) without any degradation of other imaging characteristics.

### 462 C. Comparison of the TDBS and X-ray imaging methods

463 As mentioned in the introduction, the most elaborated way to examine texture of polycrystalline  
464 solids, with the spatial resolution similar or better than the grain sizes, is X-ray microscopy. Yet,  
465 most of the techniques based on the X-ray CT provide only partial information related to sam-  
466 ple texture or composition such as distinct absorption coefficients, refractive indices<sup>6</sup>, or electron  
467 densities [*e.g.* in Ref. 48] of the constituting grains. For this reason, they are of limited interest  
468 for examination of texture of densified pore-free samples composed of light elements and/or of

469 only one compound. However, they permit examination of individual particles with a very high  
470 reconstruction resolution of  $< 0.1 \mu\text{m}$ . Similarly, coherent X-ray diffraction allows 3D imag-  
471 ing of morphology and strains in isolated deformed crystals with the reconstruction resolution of  
472  $< 30 \text{ nm}$  (e.g., Refs.<sup>49,50</sup>) as well as visualisation of twinning and dislocation dynamics in an indi-  
473 vidual nanoparticle using a particular Bragg reflection<sup>50,51</sup>. Yet, the particle itself and its position  
474 in the sample with respect to other particles (or a common system of coordinates) should be deter-  
475 mined using another technique<sup>51</sup>. Dark field X-ray microscopy also permits 3D mapping, with the  
476 spatial resolution approaching  $0.3 \mu\text{m}$ , of subgrains or even domains in individual particles having  
477 sizes around  $10 \mu\text{m}$ <sup>12,47,52</sup>. Once again, the particle positions in the sample interior had to be de-  
478 termined using other techniques: either 3D X-ray Diffraction or Diffraction Contrast Tomography  
479 whose spatial reconstruction resolution was specified as  $1 \mu\text{m}$ <sup>12,47,52</sup>. The differential-aperture X-  
480 ray microscopy provides 3D images without CT reconstruction with the resolution of  $\leq 1 \mu\text{m}$ <sup>53</sup>.  
481 It requires, however, the rare polychromatic synchrotron X-ray microbeams to probe local crys-  
482 tal orientations and strains. Unfortunately, measurements for samples in devices with a limited  
483 access, *e.g.*, a DAC, were not yet published. In a polycrystalline pore-free sample, the latter tech-  
484 niques based on X-ray diffraction (XRD) are providing the most comprehensive 3D imaging of  
485 the position, shape and orientation of grains with respect to each other and/or with respect to a  
486 common coordinate system. Due to the nature of the XRD, these approaches permit distinguish-  
487 ing differently oriented particles of the same compound as well as particles of different phases of  
488 the same compound provided the particles are crystalline and their structures are known under the  
489 temperature and/or pressure conditions of the measurements.

490 While X-ray-based CT techniques are widely used for 3D imaging of polycrystalline solids,  
491 thorough discussions of quality and reliability of the 3D-images obtained with  $\mu\text{m}$ - or even sub-  
492  $\mu\text{m}$  resolution are surprisingly underrepresented [*e.g.* Ref. 54]. The main source of uncertainties  
493 comes, obviously, from the procedure used to reconstruct a 3D image of a sample from the 2D pro-  
494 jections collected upon its rotation. Here, the criteria applied to evaluate the image-reconstruction  
495 reliability, *e.g.* modulation transfer function, signal-to-noise ratio, or detection effectiveness, are  
496 of outstanding importance. A simple test of several X-ray-based 3D-scanners, consisting in deter-  
497 mining the known ratio of microbeads of two monodisperse sizes of  $10 \mu\text{m}$  and  $20 \mu\text{m}$ , showed  
498 variations of almost one order of magnitude between the tested devices<sup>54</sup>. It was also reported that,  
499 by the use of the XRD-based CT and unhindered sample accessibility along two spatial directions,  
500 the reconstructed 3D-images exhibit “spotty” aspects as a consequence of the noncontinuous inten-

501 sity of the Debye–Scherrer rings<sup>55</sup>. The authors attributed this artifacts either to grain preferential  
502 orientations present in the examined cold-compressed sample or to large grain sizes relative to  
503 the beam size. Further difficulties can arise during *in-situ* measurements due to (i) use of intense  
504 focused X-ray beams altering the material texture or even melting caused by heating, (ii) incom-  
505 plete solid-angle region accessible for X-rays when samples are located in tools or devices such as  
506 a DAC<sup>56</sup>, a high-temperature oven or a cryostat, further aggravated by (iii) insufficient accuracy  
507 of displacement and rotation of such relatively heavy devices<sup>12,54</sup>. According to earlier works,  
508 the device/tool weight and an incomplete solid-angle region do not permit localization of grains  
509 with the accuracy better than 5-10  $\mu\text{m}$ , thus strongly degrading the spatial resolution expected  
510 with X-ray-based imaging in more favorable experimental conditions<sup>57–59</sup>. Even when using the  
511 technically-primitive methods based on the X-ray absorption-contrast imaging (ACI) and phase-  
512 contrast imaging (PCI), the obtained 3D-images of entire samples, not to mention of grains inside  
513 the sample, did “not represent the absolute shape of the sample”<sup>56</sup>.

514 Contrasting with the above-discussed limitations of X-ray methods, optical methods and espe-  
515 cially the TDBS one, as demonstrated here, are better suited for getting local information directly  
516 from signals collected at a long-working distance and along a single direction: the rotation of  
517 relatively heavy devices are not needed anymore, partial access to samples is not an issue any-  
518 more. Providing that densities, refractive indices and single crystal elastic moduli of a tested  
519 (polycrystalline) sample are known from previous measurements, that could also involved TDBS  
520 measurements<sup>27,28</sup>, the reconstruction of the 3D images from TDBS signals does require a minimal  
521 level of assumptions and could therefore be used for verification of the reliability of X-ray-based  
522 CT 3D imaging, at least where samples are located in devices with a limited access.

#### 523 **D. On the TDBS imaging with TA modes**

524 Even though the TA modes showed up too sparsely to provide a qualitative 3D image as it has  
525 been done in Fig. 4 with the LA mode, the TA modes [Fig. 3(b)] are of a great importance and com-  
526 plementary to the LA mode because they allow identification of unknown grains and estimation of  
527 a set of possible crystallographic orientations of each recognized crystallite. The latter was done  
528 by scanning all propagation directions of the CAPs accompanied by the calculation of Brillouin  
529 frequencies of the corresponding LA and TA modes until they matched the measured Brillouin fre-  
530 quencies simultaneously. In some cases, the TA modes were the only way to distinguish two grains

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531 having different orientations but the same LA velocity. Accordingly, the stronger the anisotropy  
532 of the TA modes, the stronger the contrast in the TA-mode-based images, which can even exceed  
533 that in LA-mode-based images and thus provides additional insight on the sample state<sup>35</sup>. So, in  
534 our measurement, the detection or not of a TA mode, together with the LA-mode-based 3D image,  
535 permitted identification of the H<sub>2</sub>O-ice phase composing recognized grains.

536 For this aim, the below-described analysis of efficiency of generation of CAPs, and of each in-  
537 dividual acoustic mode contributing to them, was performed. In TDBS measurements, generation  
538 of the LA and both TA modes in a sample (*e.g.* H<sub>2</sub>O ice) occurs due to the mode conversion of the  
539 plane LA mode thermo-elastically generated in the isotropic optoacoustic transducer absorbing  
540 the pump laser pulses<sup>60–62</sup>. Thermo-elastic generation of CAPs directly in a transparent sample  
541 (*e.g.* H<sub>2</sub>O ice) via heat transfer from the light absorbing transducer to the sample material is es-  
542 timated to be negligible. If the interface between the optoacoustic transducer and the H<sub>2</sub>O ice is  
543 flat and perfect, the elastic forces (stresses) and the mechanical displacements across the interface  
544 are continuous. In such case, the generation efficiency of each acoustic mode in the H<sub>2</sub>O ice is  
545 directly proportional to the efficiency of the mode conversion, *i.e.*, transfer of the acoustic energy  
546 from the excited mode(s) in the transducer to each acoustic mode in the sample<sup>60–62</sup>. The transfer  
547 efficiency, depending on the particular orientation of each particular H<sub>2</sub>O-ice crystallite relative  
548 to the interface, could be obtained by calculating the acoustic transmission coefficients, from an  
549 isotropic medium (the transducer) to an anisotropic medium (an arbitrary-oriented crystallite of the  
550 polycrystalline H<sub>2</sub>O ice). We considered the particular case of a plane LA wave transmitted and  
551 mode-converted, at the interface, to a plane LA and two plane TA modes, respectively. Because  
552 the lateral size of the focused pump-laser spot was one order of magnitude larger than the probed  
553 acoustic wavelength, this transmission/conversion problem could be solved as one-dimensional  
554 where plane acoustic modes propagated normally through the interface. Changing relative orien-  
555 tation of the principal axis of an ice crystallite with respect to the normal to the interface we derived  
556 the transmission coefficients and thus the generation efficiency of each acoustic mode. Finally, to  
557 reveal reasons of a TA mode absence/presence in our TDBS signals, we assumed that detection  
558 of different acoustic modes predominantly takes place via the interaction of the probe light with  
559 the longitudinal, *i.e.*, the  $z$  strain component, of the acoustic modes. Details on the derivation of  
560 the generation efficiency can be found in Refs. 61 and 62, or else in any textbook dealing with the  
561 reflection and transmission coefficients of plane waves at an interface between two (anisotropic)  
562 solids<sup>63,64</sup>.



563 Using the known mechanical properties of both phases of H<sub>2</sub>O ice (Tab. I) and those of the  
564 cast iron (isotropic) reported to be  $\rho_{\text{Fe}} = 7.87 \text{ g cm}^{-3}$ ,  $C_{11}^{\text{Fe}} = 279 \text{ GPa}$ , and  $C_{44}^{\text{Fe}} = 82 \text{ GPa}$ , the  
565 generation (transmission and mode conversion) efficiencies of each acoustic mode are calculated  
566 for both H<sub>2</sub>O ice phases (Fig. 5). The efficiency values are plotted in Fig. 5 as a function of  
567 the orientation of the  $z$ -axis (the normal to the iron/ice interface, *i.e.*, the propagation direction)  
568 relative to the principal axes of ice crystals. The results are presented separately for different  
569 modes: for the LA mode in Figs. 5(a) and 5(d), for the FTA mode in Figs. 5(b) and 5(e), and  
570 for the STA mode in Figs. 5(c) and 5(f). For each acoustic mode transmitted in ice, with (TA) or  
571 without (LA) mode conversion, the transmission/mode conversion coefficient (Fig. 5) is defined  
572 as the ratio of the  $z$  strain component of the transmitted mode to the  $z$  strain component of the  
573 LA mode generated in iron and incident on the iron/ice interface. The results in Fig. 5 indicate  
574 that, for any crystallographic direction of any of the ice phases, the efficiency of generation of the  
575 LA mode is one-to-two orders of magnitude larger than for any of the two TA modes. We note  
576 also that the generation efficiency of the STA mode in phase VII is one order of magnitude larger  
577 than that of any other TA mode, which therefore partly explains why TA modes have not been  
578 observed for the phase VI and why mostly a single TA mode has been observed for the phase VII.  
579 According to our calculations, it is very probable that, in all grains of ice VII where only one TA  
580 mode was recognized, we dealt with the STA mode. As a result, a careful analysis of voxels with  
581 unidentified phases [copper colour scale in Fig. 3(a)] permitted attributing, with a high degree of  
582 confidence, the two center-bottom grains to the ice VII because the black dots denote the detection  
583 of TA modes in the related TDBS signals. In contrast, the top-left voxels in Fig. 3(a) are attributed  
584 to the ice VI because no TA modes could be recognized in the TDBS signals. This attribution  
585 is supported by the analysis of the whole  $xy$  cross-sections because the center-bottom grains are  
586 surrounded by the phase VII whereas the top-left one is surrounded by the phase VI.

588 Knowledge of the Brillouin frequencies of the LA modes permitted estimation of crystallo-  
589 graphic directions of all recognized crystallites with respect to the CAP propagation direction and  
590 thus with respect to other crystallites in a common system of coordinates. Moreover, the crystal-  
591 lographic directions corresponding to the highest and the lowest LA-mode frequencies in crystals  
592 of each of the two phases could be recognized with the accuracy of the frequency measurement.  
593 For example, for the cubic phase VII of H<sub>2</sub>O ice, the frequency of the LA mode along  $\langle 111 \rangle$  is  
594 the highest while that along  $\langle 100 \rangle$  is the lowest (e.g. Ref. 27). However, we were able to provide  
595 more detailed information on crystallographic orientations of particular crystallites if they showed

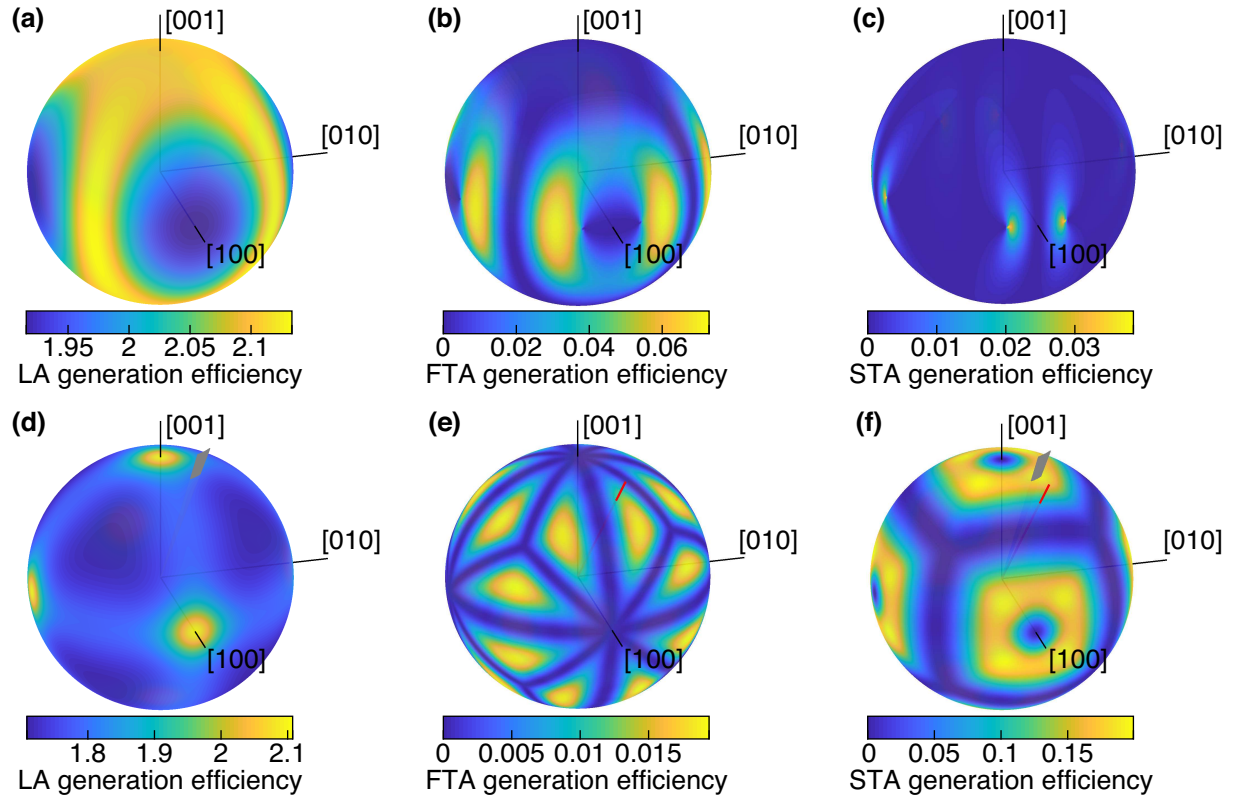


FIG. 5. Generation efficiency of each acoustic mode for (top) the phase VI and (bottom) the phase VII of  $\text{H}_2\text{O}$  ice along the principal axes of the crystals as a function of the orientation of the normal to the iron/ice interface relative to the ice crystal principal axes. The results are presented separately for different modes: in (a,d) for the LA mode, in (b,e) for the FTA mode, and in (c,f) for the STA mode.

596 both TA modes, in addition to the LA mode: For example, we consider such a crystallite of the  
 597 phase VII located, in Fig. 2(b), at  $x \approx 90 \mu\text{m}$  and  $y \approx 60 \mu\text{m}$ . It was pointed out above that the  
 598 dominant TA frequency was usually the lowest of the two TA modes, *i.e.*, the STA mode, which is  
 599 consistent with our frequency calculations using the  $C_{ij}$ -values summarised in Table I. Knowing  
 600 that in the considered crystallite the measured Brillouin frequencies are  $\sim 31.8 \text{ GHz}$ ,  $\sim 20.8 \text{ GHz}$ ,  
 601 and  $\sim 15.4 \text{ GHz}$ , the CAP propagation direction was found to form an angle  $\varphi$  of  $17^\circ$ - $18^\circ$  and an  
 602 angle  $\theta$  of  $32^\circ$ - $33^\circ$ , where  $\varphi$  and  $\theta$  are the proper Euler angles of intrinsic rotations about moving  
 603 axes  $e_Z$ - $e'_X$ - $e''_Z$ <sup>65</sup>. Of course, all symmetry-equivalent crystallographic directions are also possible.  
 604 If we consider this direction in Fig. 5(e)-(f) (red thick line) then we recognize that it corresponds  
 605 to a direction in which the FTA mode has a generation efficiency of about 0.01 (half of the highest  
 606 possible efficiency) and that of the STA mode is of about 0.085, which explains the ease in the si-  
 607 multaneous detection of these two modes. If only one TA mode is measured, as in the centre of the  
 608 sample occupied by the phase VII, it is likely that this mode is the slow one and the orientation of

609 the  $z$ -axis in the crystal principal axes is not unique anymore but defines a part of an arc ( $\theta = 20^\circ$ ,  
610  $\varphi \in [26^\circ, 45^\circ]$ ) shown in grey in Fig. 5(d,f). This is the case for the TDBS signal collected for  
611 the voxel with the coordinates  $(x, y, z) = (50, 46.25, 1.25) \mu\text{m}$  in Fig. 2(b). As already mentioned  
612 above, detection of the LA mode alone, as is the case for the TDBS signals attributed to  $\text{H}_2\text{O}$  ice  
613 VI, permits only a rough estimation of orientations of the crystallites if the detected frequencies  
614 are not the extremes. However, detection of the LA mode and of one of the TA modes, whose type,  
615 *i.e.*, STA or FTA, is known (here from the analysis of the generation efficiency) allows bracketing  
616 the range of orientations to limits which could already be of interest for the comparison with mi-  
617 cromechanical models describing behaviour of polycrystalline materials and their evolution upon  
618 external action, *e.g.*, nonhydrostatic compression. It is worth noting here that the determination of  
619 the propagation direction in a crystallite does not mean the complete orientation of the crystallite  
620 relative to other crystallites, because the crystallite could be arbitrary rotated around the  $z$  axis  
621 (interface normal). A complete orientation of crystallites could be obtained by performing TDBS  
622 measurements with different polarisations of the probe light<sup>36</sup>, which will be a subject of the future  
623 work.

#### 624 **E. On the use of the detected TDBS signals with beatings**

625 The above-mentioned observation of particular TDBS signals, corresponding to the simulta-  
626 neous propagation of LA pulses in two adjacent crystallites [see black open squares in Fig. 3(a)]  
627 provides an original opportunity to localize the boundaries between them. If the interest is focused  
628 on imaging of grain boundaries, such signals can be used to 3D-map the boundaries and to follow  
629 their movement in real time while performing sample deformation. To do so, a feedback signal  
630 could indeed be designed out of the observation of beatings to control the displacement stage. This  
631 procedure will limit the number of measurement points and thus accelerate the imaging procedure  
632 of grain boundaries drastically.

#### 633 **F. On the data collection rate**

634 Last but not least, the here-presented 3D image was collected during 110 hours because we kept  
635 powers of both lasers very low (below 10 mW). However, the image collection can be accelerated  
636 by 2 orders of magnitude, if both lasers are used at the full power of  $\sim 100$  mW. The low laser

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637 powers were used in order to exclude possible progress of the transition from ice VII to ice VI  
638 observed to occur when one spot in the sample is illuminated for long time<sup>41</sup>. We remind, that  
639 this phase transition is not initiated by thermal heating (the estimated stationary and transient  
640 temperature rises did not exceed 3 °C) but by electrons photo-generated in the conduction band of  
641 diamond<sup>41</sup>. Because our 3D image (Fig. 4) contains about 58500 voxels (lateral step of 1.2 μm  
642 and axial of ~ 1.2 μm), we estimated the data collection rate of the presented TDBS-ASOPS  
643 measurement to be ~ 0.15 voxel/s. If the 3D imaging is performed on a sample containing only  
644 one phase and far from the phase transition boundary, the full laser powers can be used and the  
645 duration of collection of a similar 3D image will drop to ~ 65 minutes, which corresponds to the  
646 data collection rate of ~ 15 voxel/s. For comparison, an XRD-based CT examination (at the ESRF,  
647 one of the most powerful synchrotron radiation sources) of a sample with lateral and axial sizes of  
648 ~ 1 mm and the spatial resolution of ~ 27 μm (~ 32000 voxels) required 8 hours (or ~ 1 voxel/s)  
649 but the obtained 3D image still contained artefacts<sup>55</sup>. According to the authors of this work, the  
650 artefacts were caused by orientational texture and big grain sizes of the examined material. Such  
651 effect makes the XRD-based CT less suitable for the 3D-imaging of texture of polycrystalline  
652 solids, one of the main purposes of such imaging measurements. The artefacts caused by a sample  
653 texture are not possible in 3D-images obtained using the TDBS-ASOPS technique because the  
654 signals are collected directly from each voxel and the data treatment is nearly free of assumption.  
655 High laser powers can be used for examination of condensed matter in a DAC because the samples  
656 inside are thin and the diamond anvils are a very efficient heat sink, especially when pressure  
657 increases in the Mbar range and above. Despite of the immense pressure difference from 2 GPa to  
658 100 GPa, both lateral and axial resolution of the TDBS-ASOPS technique does not degrade<sup>12,27,28</sup>.  
659 The higher pump and probe laser powers result then in stronger TDBS signals and thus a more  
660 efficient detection of TA modes in the Mbar range promising a more detailed 3D-imaging of texture  
661 of transparent polycrystalline samples at extreme conditions of high pressures and, eventually,  
662 high-temperatures to several thousands °C if combined with laser heating (e.g. Ref. 66). We  
663 emphasize that a DAC is only one example of devices with a limited access. It can be extended to  
664 cryostats, very high-temperature ovens (well above 1000 °C), and reactors of different types.

665 **V. CONCLUSIONS**

666 We reported on advances in applications of the time-domain Brillouin scattering (TDBS) tech-  
667 nique for 3D imaging of transparent polycrystalline samples located in a device with a limited  
668 access, along only one spatial direction and from one side only. The applied TDBS-ASOPS set-  
669 up provided a comprehensive, reliable high-resolution *in-situ* 3D visualisation of microstructure  
670 of a transparent polycrystalline sample of H<sub>2</sub>O ice compressed in a diamond anvil cell (DAC) to  
671 2.15 GPa where two phases, ice VI and ice VII, coexist. The approach permits, in general, 3D  
672 images of samples with infinite lateral sizes and thicknesses of at least 10  $\mu\text{m}$  in their entirety.  
673 The latter means that the TDBS-ASOPS provides shapes and relative coordinates of all grains (if  
674 resolved) with respect to each other or a common coordinate system, independent of their phase  
675 composition with, in our experiments, the lateral resolution of 2.5  $\mu\text{m}$  and the axial one of 1.2  $\mu\text{m}$ ,  
676 identification of phase of each particular grain, as well as crystallographic orientation of the iden-  
677 tified grains with respect to a common coordinate system. The here-reported resolution of the  
678 TDBS-ASOPS technique can be further improved down to the optical diffraction limit in the lat-  
679 eral direction, say down to 150 nm, if a blue-UV probe laser is used and the sample is transparent  
680 for these wavelengths, and to sub-optical dimension in the axial direction, theoretically down to  
681 the nanometers length of the coherent acoustic pulse or of the strain front in it<sup>16</sup>. The 3D images,  
682 obtained using the TDBS technique, are reliable because the information is recovered directly for  
683 each image voxel using minimal level of assumptions. Accuracy of the recovered information  
684 (*e.g.*, crystallite orientations) depends only on the quality and content of the TDBS signals and the  
685 degree of elastic anisotropy of the examined crystalline material that can be measured in advance  
686 using the same technique (see Refs. 27 and 28).

687 In the here-presented 3D imaging experiments, we observed, for the first time at high pressures  
688 in a DAC, TDBS signals containing contribution of quasi-shear coherent acoustic pulses (CAPs).  
689 We demonstrated some examples of fruitful application of the TDBS imaging with several acous-  
690 tic modes simultaneously. We revealed the possibility to localize positions of grain boundaries in a  
691 transparent polycrystal by the identification of specific TDBS signals that are due to the simultane-  
692 ous propagation of an acoustic pulse in two adjacent grains. Overall, our reported results are a big  
693 step towards the perspective of full 3D characterization of sample texture at extreme conditions  
694 (high pressures and/or temperatures) and its evolution on further compression, temperature change  
695 or any other type of action. Such characterization is of special interest for different branches of

696 research at extreme conditions. It will make possible *in-situ* examination of texture of minerals  
697 present in the deep Earth and its evolution upon nonhydrostatic compression with the detailedness  
698 presently not accessible by other techniques. Such information will permit conclusion about the  
699 nature of seismic anisotropies observed in the Earth's mantle. Also, it could help to quantitatively  
700 investigate (i) kinetics of phase transitions and chemical reactions at high pressures and/or high or  
701 low temperatures as well as (ii) relations between the crystallographic orientations of crystallites  
702 of the forming phase and of those of the parent phase. Obviously, further improvement of the sig-  
703 nal treatment and resolution of the 3D TDBS imaging permitting recovery of quantitative values of  
704 shear sound velocities in the same time as longitudinal sound velocities and within the full imaged  
705 volume will further extend the horizons of investigation of solids at extreme conditions. We be-  
706 lieve that 3D images collected using the TDBS-ASOPS technique can be used for the verification  
707 of 3D images obtained using the X-ray-based CT, especially for samples located in devices with a  
708 limited access.

#### 709 **SUPPLEMENTARY MATERIAL**

710 See supplementary material for the details about the distribution of the Brillouin frequency for  
711 phases VI and VII of H<sub>2</sub>O ice, the detailed discussion on the coherence length of the probe laser  
712 pulses, and the micro-Raman spectrometry of the water ice sample.

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718 NETA who provided insight and expertise that greatly assisted the research.

#### 719 **DATA AVAILABILITY**

720 The data that support the findings of this study are available from the corresponding author  
721 upon reasonable request.

722 **APPENDIX: ESTIMATION OF THE EXPECTED BRILLOUIN FREQUENCIES IN**  
723 **BOTH PHASES VI AND VII OF WATER ICE AT 2.15 GPa**

724 At the room temperature and the pressure of 2.15 GPa, both phases VI and VII of H<sub>2</sub>O ice  
725 are coexisting (phase transition)<sup>43,44,67–69</sup>. We give here details on the way the Brillouin frequen-  
726 cies have been estimated for both phases. The goal was to have at hand estimated values of the  
727 expected Brillouin frequencies for the subsequent analysis of the experimental data. The error of  
728 the estimates is overall not very small, especially because of the drastic change of properties the  
729 sample material can exhibit at the phase transition. We do believe though that the below presented  
730 strategy of extrapolation allows the 3D characterization of individual ice grains at high-pressure  
731 and in two-phase region with an acceptable correctness.

732 The densities, reported in the first row of Tab. I, are deduced by interpolating the same data  
733 than the ones used in Fig. 3 of Ref. 43 plotting the density of the various H<sub>2</sub>O forms as a function  
734 of pressure. Uncertainties in the densities in Ref. 43 (also used in Ref. 44, wherefrom the elastic  
735 constants were taken) are negligible in comparison with uncertainties of the elastic moduli. The  
736 elastic constants are deduced by fitting and extrapolating to a pressure of 2.15 GPa the results  
737 presented in Figs. 4 and 5 of Ref. 44. Thus, the accuracy of  $\sim \pm 2\%$ , reported in Ref. 44 for  
738 the ratios of the elastic moduli and the density, results in  $\sim \pm 2\%$  accuracy in the moduli and in  
739  $\sim \pm 1\%$  accuracy in velocities of the acoustic modes<sup>44</sup>. The refractive index of ice was evaluated  
740 in Ref. 44 (Fig. 3) with the accuracy of  $\sim \pm 2\%$ .

741 To calculate the Brillouin frequency ranges, the density and the elastic constants are used to  
742 solve the Christoffel equation for all possible propagation directions to get the minimal and maxi-  
743 mal possible velocities for each acoustic mode in each phase of H<sub>2</sub>O ice. Then Eq. (1) is used to get  
744 the minimal and maximal possible Brillouin frequencies in each case. Since the acoustic velocities  
745 are known in any propagation direction of the CAPs, so do the Brillouin frequencies. Combining  
746 the uncertainties in velocities and in the refractive indices, we could conclude that maximal and  
747 minimal Brillouin frequencies in Table I and Fig. S1 (see Supplementary information) are deter-  
748 mined with the uncertainties of  $\sim \pm 3\%$ . The uncertainty of the Brillouin frequencies confining  
749 the overlap interval of the LA Brillouin frequencies in ices VI and VII, *i.e.* [27.5, 29.4] GHz, can  
750 be scaled respectively. Thus, the overlap interval shrinks but does not disappear ([27.5, 29.4] GHz  
751  $\Rightarrow$  [28.3, 28.5] GHz).

752 **AUTHOR CONTRIBUTIONS STATEMENT**

753 A.Z., V.E.G., S.R., N.C. and A.B. designed the research, N.C. and A.Z. prepared the sample,  
754 S.S., E.D.L.S, S.R., N.C. and A.B contributed to the experiments, S.R., T.T., S.S., E.D.L.S and  
755 V.T. contributed to signal processing, V.E.G., S.R., T.T. and S.S. developed the theoretical esti-  
756 mates, S.R., V.E.G., A.Z., S.S., N.C., A.B. and V.T. analysed and interpreted the experimental  
757 observations, S.R., V.E.G. and A.Z. wrote the manuscript. All authors reviewed the manuscript.

758 **ADDITIONAL INFORMATION**

759 The authors declare no competing interests.

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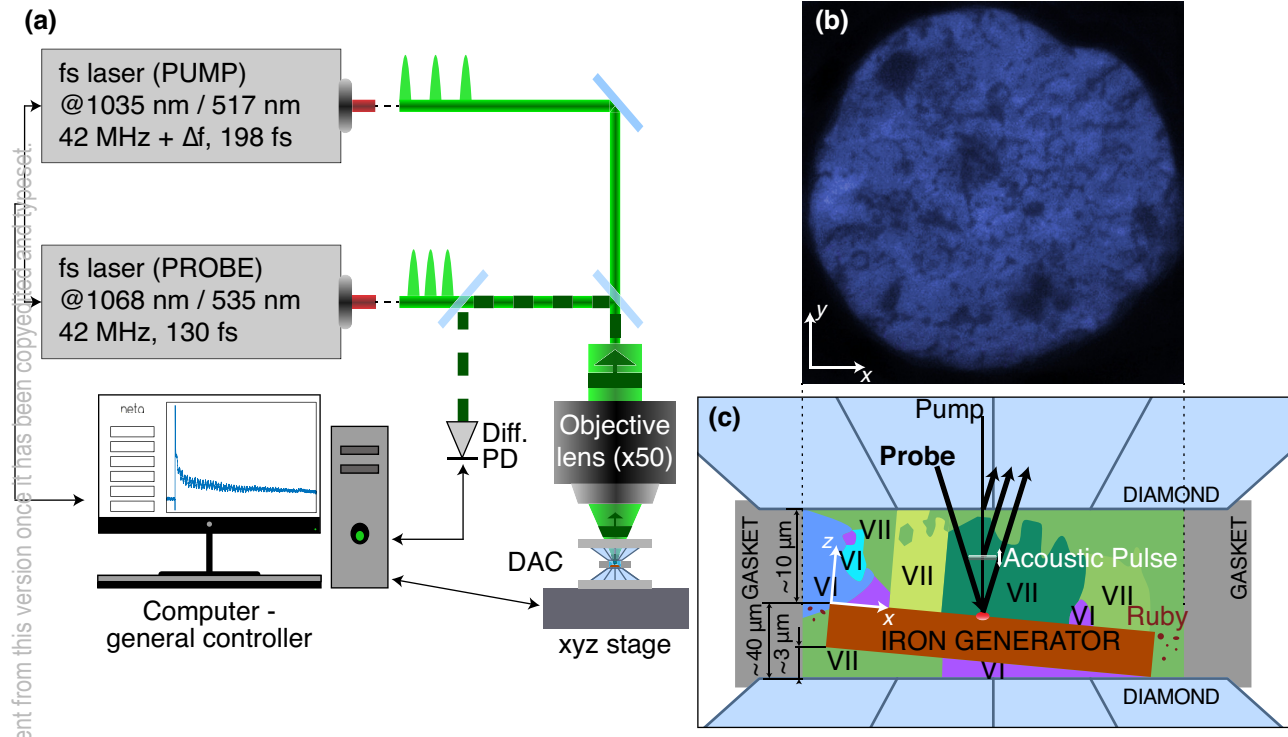
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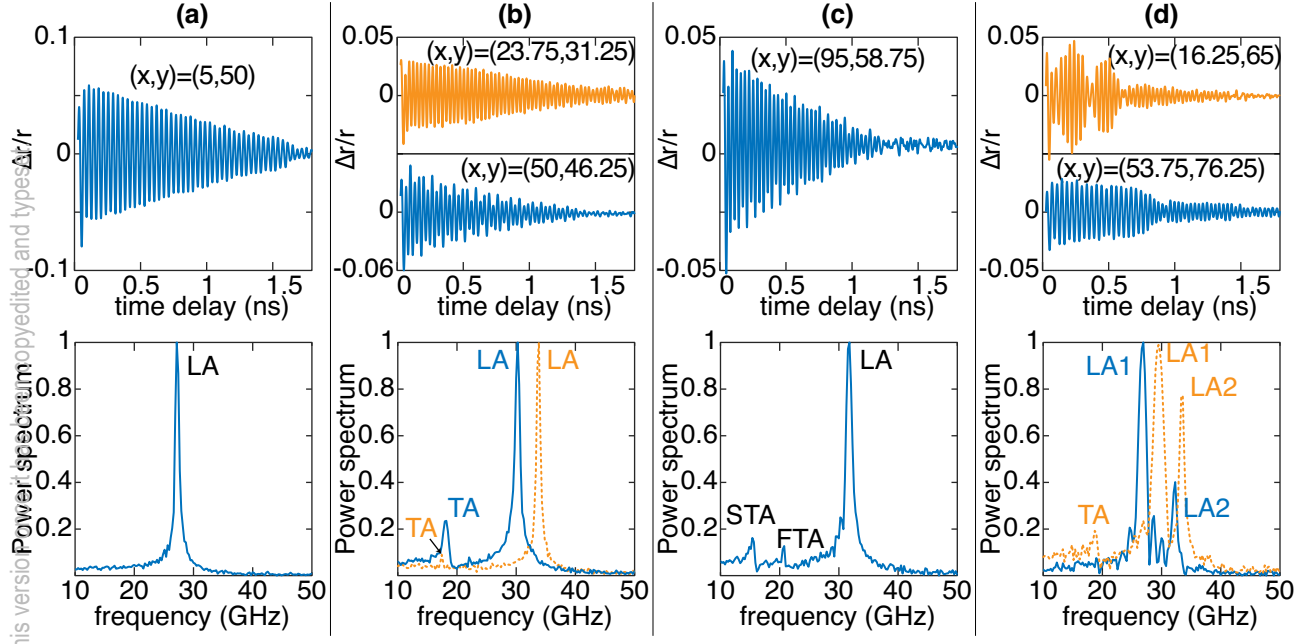
- 954 I Properties of the high-pressure phases VI and VII of H<sub>2</sub>O ice near the pressure of 2.15 GPa and used to

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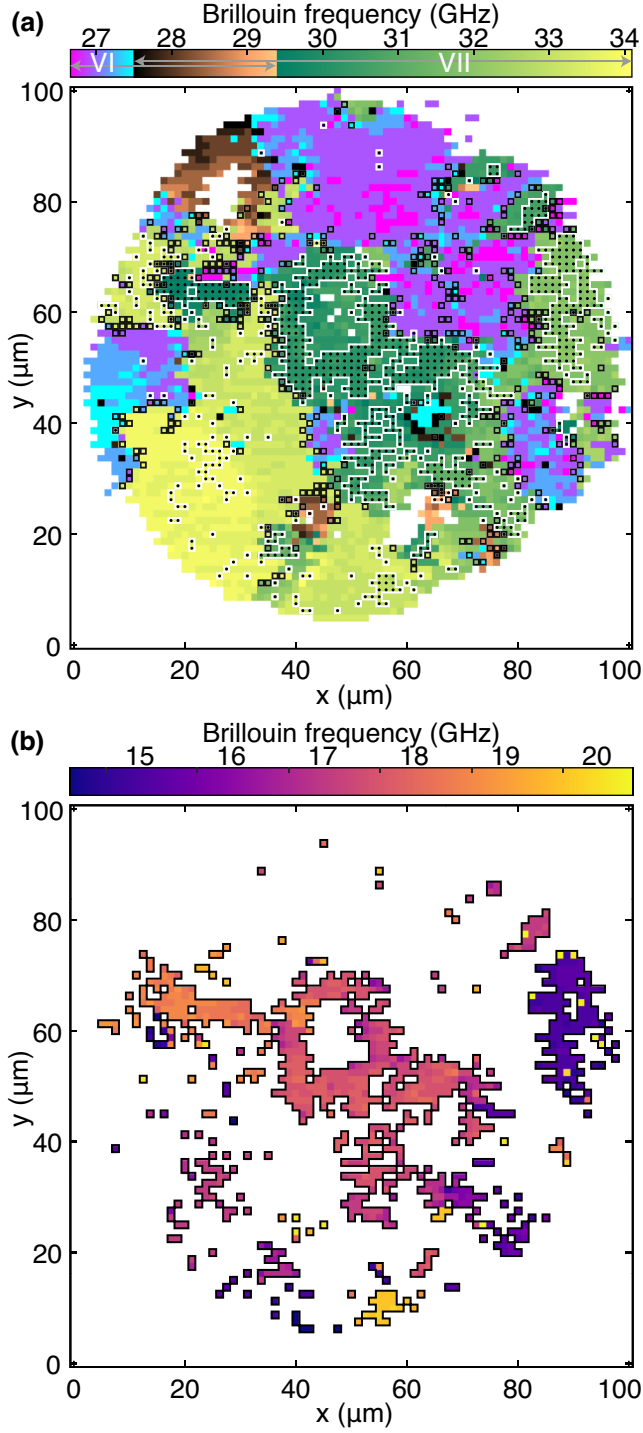


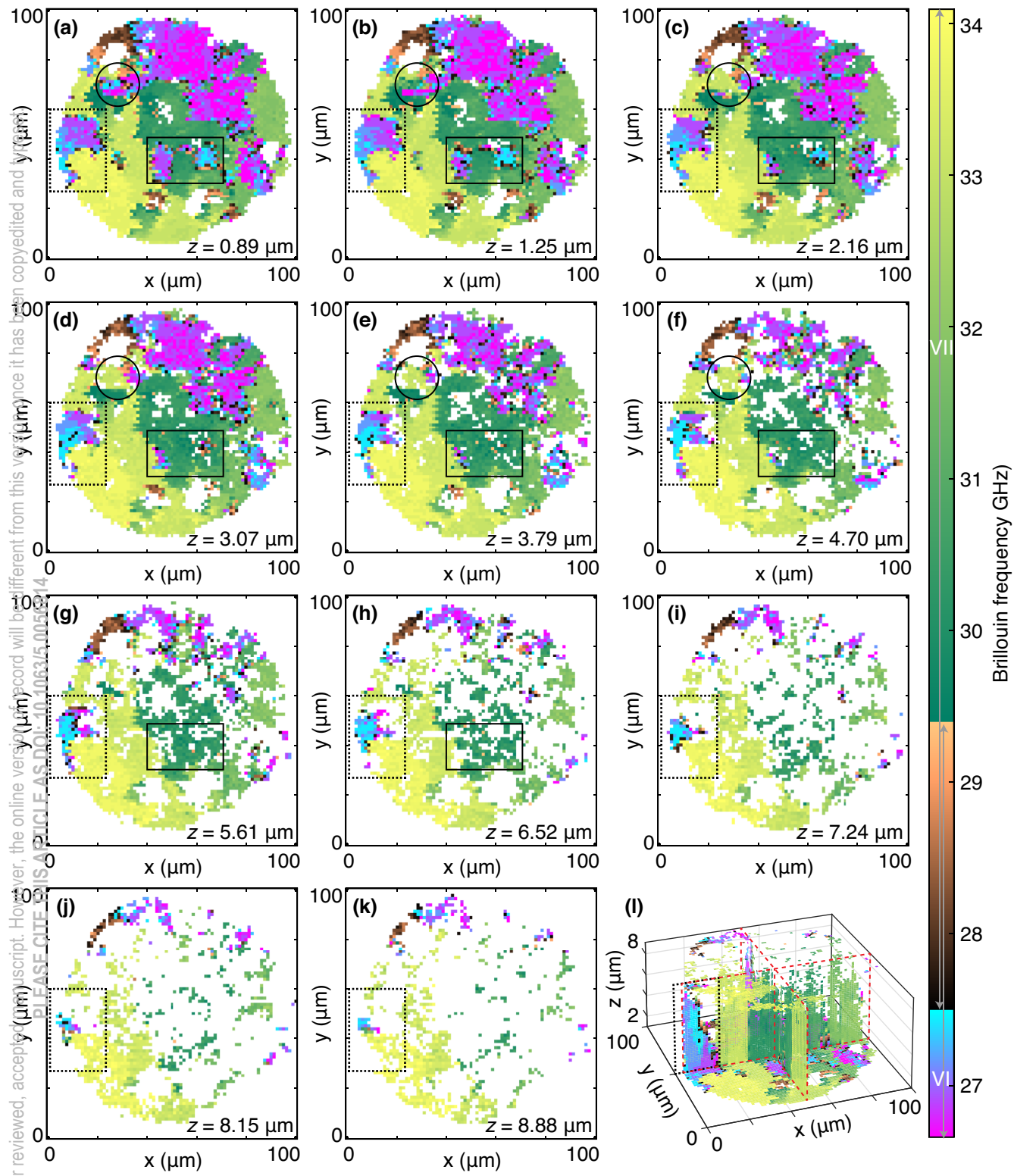


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