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## PAPER

# *In situ* imaging of the dynamics of photo-induced structural phase transition at high pressures by picosecond acoustic interferometry

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Andreas Zerr<sup>3,4</sup> and Vitaliy E Gusev<sup>1,4</sup><sup>1</sup> LAUM, UMR-CNRS 6613, Université du Maine, Avenue O. Messiaen, F-72085 Le Mans, France<sup>2</sup> IMMM, UMR-CNRS 6283, Université du Maine, Avenue O. Messiaen, F-72085 Le Mans, France<sup>3</sup> LSPM, UPR-CNRS 3407, Université Paris Nord, F-93430 Villetaneuse, France<sup>4</sup> Authors to whom correspondence ought to be addressedE-mail: [majumalayil@gmail.com](mailto:majumalayil@gmail.com), [nikolay.chigarev@univ-lemans.fr](mailto:nikolay.chigarev@univ-lemans.fr), [samuel.raetz@univ-lemans.fr](mailto:samuel.raetz@univ-lemans.fr), [zerr@univ-paris13.fr](mailto:zerr@univ-paris13.fr) and [vitali.goussev@univ-lemans.fr](mailto:vitali.goussev@univ-lemans.fr)**Keywords:** picosecond ultrasonics, nanoscale imaging, laser ultrasonics, high pressure phase transitions, laser induced phase transitions, H<sub>2</sub>O ice phase transition, ICE VII to VI transitionSupplementary material for this article is available [online](#)

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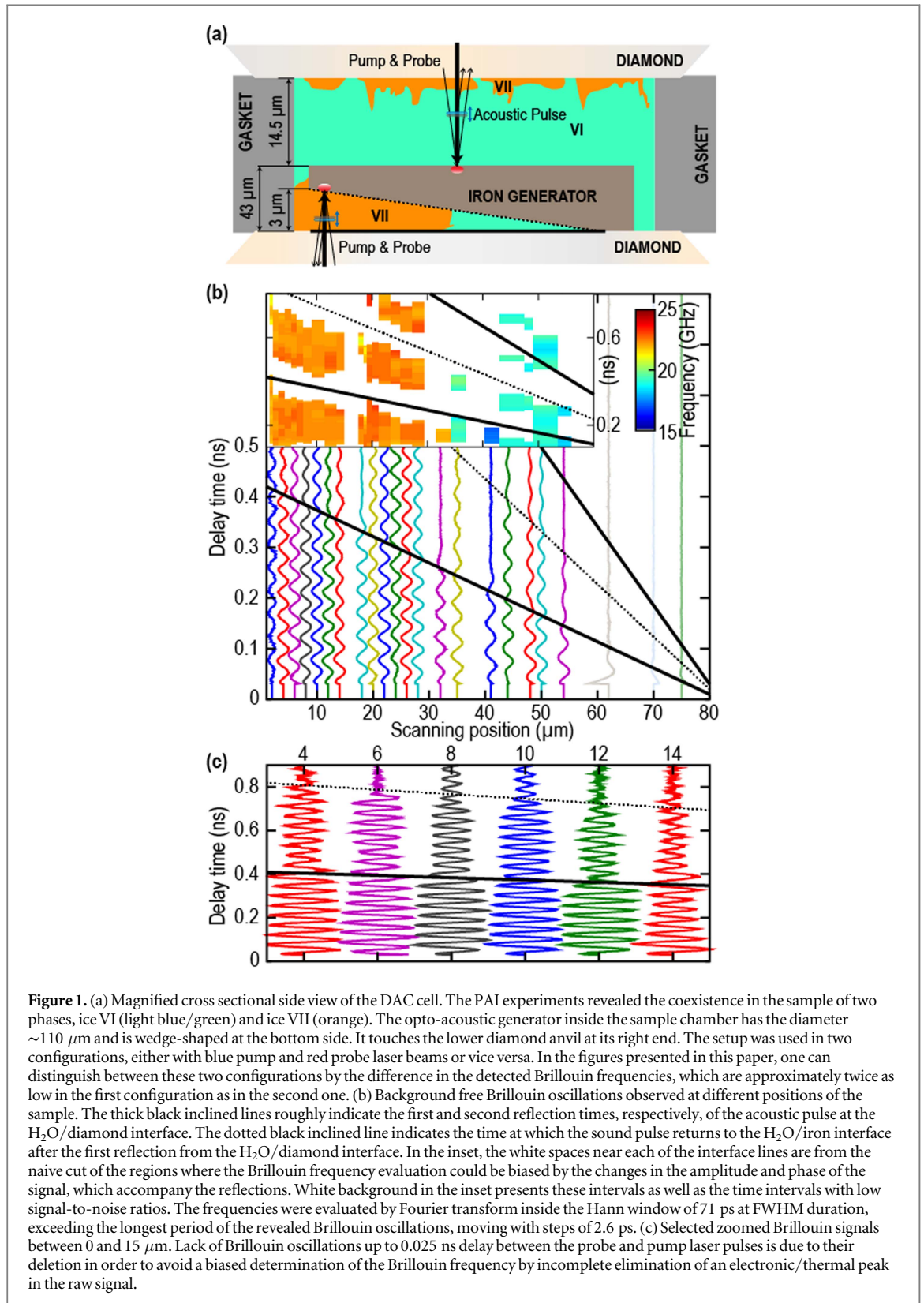
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**Abstract**

Picosecond acoustic interferometry is used to monitor in time the motion of the phase transition boundary between two water ice phases, VII and VI, coexisting at a pressure of 2.15 GPa when compressed in a diamond anvil cell at room temperature. By analyzing the time-domain Brillouin scattering signals accumulated for a single incidence direction of probe laser pulses, it is possible to access ratios of sound velocity values and of the refractive indices of the involved phases, and to distinguish between the structural phase transition and a recrystallization process. Two-dimensional spatial imaging of the phase transition dynamics indicates that it is initiated by the pump and probe laser pulses, preferentially at the diamond/ice interface. This method should find applications in three-dimensional monitoring with nanometer spatial resolution of the temporal dynamics of low-contrast material inhomogeneities caused by phase transitions or chemical reactions in optically transparent media.

The visualization and characterization of inhomogeneities in optically transparent layers and thin microscopic samples, as well as of their evolution due to external actions, is a challenge when the optical and/or elastic properties of the inhomogeneities are of low contrast. An example could be a sample where a polymorphic phase transition takes place and both phases coexist at the chosen conditions. Here we applied, for the first time, picosecond acoustic interferometry (PAI) [1, 2] to examine a sample containing low contrast inhomogeneities appearing upon a high-pressure phase transition when both phases are still present but their amount and distribution are continuously changing due to the action of the pulsed laser radiation. PAI is an optical technique where the ultrashort pump laser pulses are used to launch coherent acoustic pulses, with durations of picoseconds and lengths in nanometers, in an optically transparent sample, while the time-delayed ultrashort probe pulses are used to detect the Brillouin scattering (BS) [3] from these moving spatially localized perturbations of optical properties of the sample material (figure 1(a)). As a function of the time delay between the probe and pump laser pulses, the contribution of the BS to the detected signal of optical transient reflectivity has the form of a sinusoid. In the case of probe light incidence along the propagation direction of the acoustic pulse, the frequency of this sinusoid is equal to the frequency shift measured in classic BS from incoherent thermal phonons in backscattering configuration [3], but the signal amplitude in this case is much larger than in classic BS. The Brillouin frequency value,  $f$ , is proportional to the product between the material sound velocity,  $v$ , and the material refractive index,  $n$ , divided by the wavelength,  $\lambda_{\text{probe}}$ , of the probe light:  $f = 2nv/\lambda_{\text{probe}}$  [1–3]. Perfect reflection of the acoustic pulses from the mechanically free or rigid surfaces is accompanied, in general, only by an abrupt phase shift of the sinusoid [4–6]. The time at which the acoustic pulse arrives at the interface can be identified through the observation of the phase and/or amplitude changes of the initial



**Figure 1.** (a) Magnified cross sectional side view of the DAC cell. The PAI experiments revealed the coexistence in the sample of two phases, ice VI (light blue/green) and ice VII (orange). The opto-acoustic generator inside the sample chamber has the diameter  $\sim 110 \mu\text{m}$  and is wedge-shaped at the bottom side. It touches the lower diamond anvil at its right end. The setup was used in two configurations, either with blue pump and red probe laser beams or vice versa. In the figures presented in this paper, one can distinguish between these two configurations by the difference in the detected Brillouin frequencies, which are approximately twice as low in the first configuration as in the second one. (b) Background free Brillouin oscillations observed at different positions of the sample. The thick black inclined lines roughly indicate the first and second reflection times, respectively, of the acoustic pulse at the  $\text{H}_2\text{O}/\text{diamond}$  interface. The dotted black inclined line indicates the time at which the sound pulse returns to the  $\text{H}_2\text{O}/\text{iron}$  interface after the first reflection from the  $\text{H}_2\text{O}/\text{diamond}$  interface. In the inset, the white spaces near each of the interface lines are from the naive cut of the regions where the Brillouin frequency evaluation could be biased by the changes in the amplitude and phase of the signal, which accompany the reflections. White background in the inset presents these intervals as well as the time intervals with low signal-to-noise ratios. The frequencies were evaluated by Fourier transform inside the Hann window of 71 ps at FWHM duration, exceeding the longest period of the revealed Brillouin oscillations, moving with steps of 2.6 ps. (c) Selected zoomed Brillouin signals between 0 and 15  $\mu\text{m}$ . Lack of Brillouin oscillations up to 0.025 ns delay between the probe and pump laser pulses is due to their deletion in order to avoid a biased determination of the Brillouin frequency by incomplete elimination of an electronic/thermal peak in the raw signal.

sinusoid and/or through the appearance of an additional sinusoidal contribution to the transient reflectivity at a different Brillouin frequency [7–15]. The PAI is useful for the acoustic pulse time-of-flight measurements [9, 14] and is commonly applied to derive velocities of the acoustic waves and thicknesses of thin films. The experiments conducted at several different angles of incidence of the probe light provide the opportunity to determine the refractive index of the material and the sound velocity separately [16, 17]. It is worth noting that in the earlier reported experiments in layered structures composed of homogenous materials, the PAI is usually applied to the analysis of a single transparent layer on a substrate and the arrival times of the acoustic pulses at the surfaces/interfaces are clearly

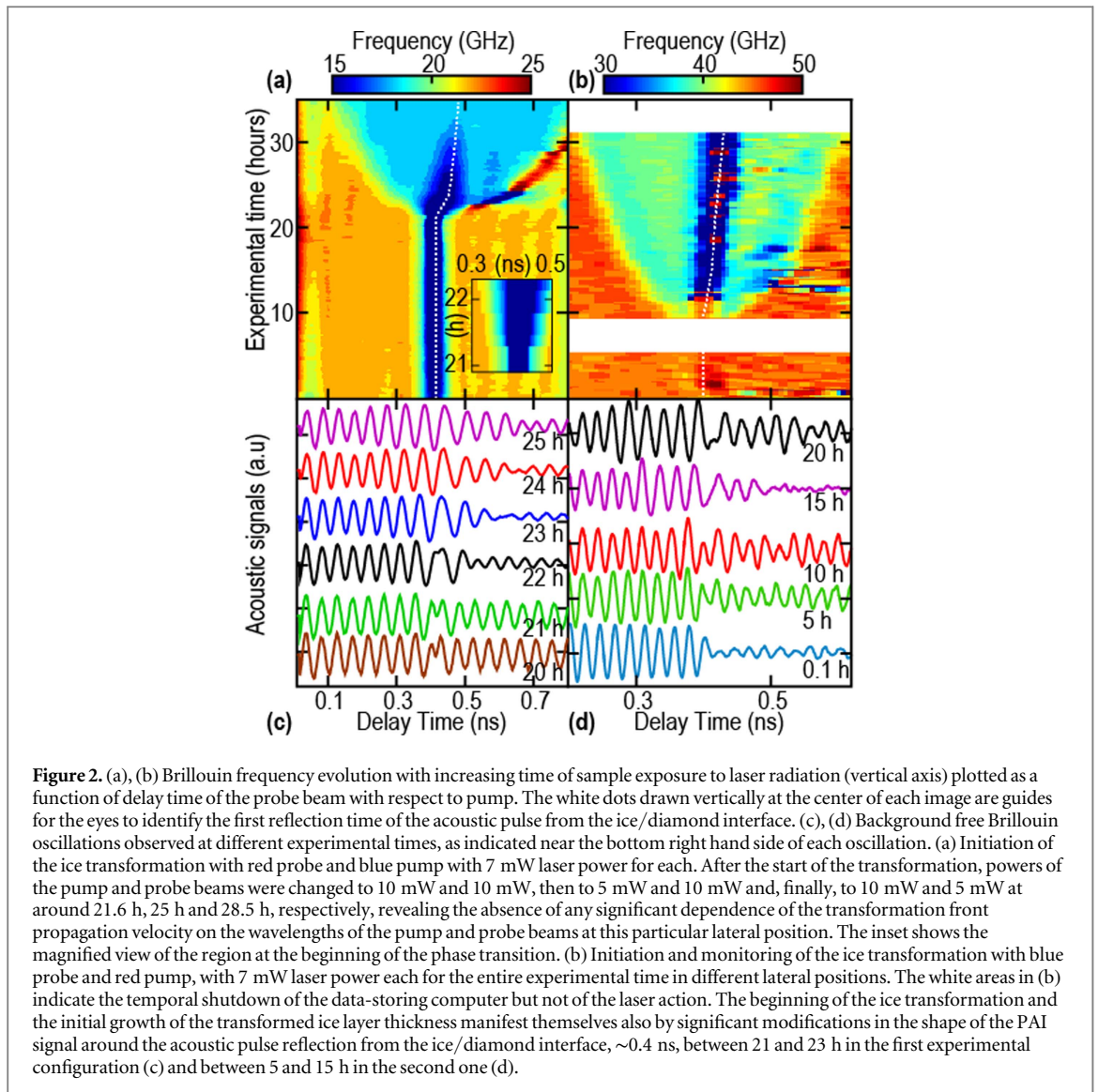
observed because of the abrupt and significant modification of one or several signal parameters (phase, amplitude, frequency) [9, 10, 12, 14, 15]. However, the measurements of the acoustic attenuation by the PAI through the evaluation of the amplitude decay of the detected sinusoid [15, 18, 19] clearly indicated that it is possible to detect continuous weak variations of the signal which can be of various physical origins. This was confirmed by the application of the PAI to the depth-profiling and later to two- and three-dimensional imaging of inhomogeneous porous materials [6, 17], ion-implanted semiconductors [20], polycrystalline textured aggregates [14, 21] and of biological/animal cells [22, 23]. Note that depth-profiling by PAI of nanoporous film [6] and of the ion-implanted subsurface region of a bulk semiconductor sample [20] were realized with 40 nm and 30 nm in-depth spatial resolution, respectively. Quite recently the use of the PAI for the evaluation of other physical processes influencing the propagation of coherent acoustic pulses, such as acoustic nonlinearity [24, 25] and acoustic focusing [26], has started. In the present work we apply PAI for the monitoring of the photo-induced motion of an abrupt phase transition interface between two thin layers composed of two high-pressure phases of water ice exhibiting very similar acoustical and optical properties. The low contrast interface, characterized by the relative variations of the Brillouin frequency,  $\Delta f/f \propto 0.01$ , sound velocity,  $\Delta v/v \propto 0.04$ , optical refractive index,  $\Delta n/n \propto 0.01$ , and acoustic impedance,  $\Delta Z/Z \propto 0.1$ , is the interface between the coexisting phases VII and VI of water ice at 2.15 GPa pressure in the region of the phase equilibrium, which has been reported to take place at 2.1–2.2 GPa at room temperature [27–31]. The PAI, applied only at normal incidence of the probe light on the sample surface, provides the opportunity to evaluate the velocity of the inter-phase boundary motion, the relative acoustic and optical parameters of the phases, to identify their nature and to speculate on the physical mechanisms initiating the phase transformation.

## Experimental

The experiments were conducted with water ice formed upon compression of liquid water in a diamond anvil cell (DAC), schematically presented in figure 1(a). To launch acoustic pulses into ice, an iron prism was used as an opto-acoustic thermo-elastic transducer. The existence of a thin layer of ice between the iron transducer and one of the anvils, with laterally varying thickness as depicted in figure 1(a), was revealed by the conducted PAI experiments.

The experiment is based on a conventional pump and probe setup with a Ti:sapphire laser, the details of which can be found elsewhere [14]. The setup was used in two configurations, either with a blue pump and red probe laser beams or vice versa. In the figures presented in this paper, one can distinguish between these two configurations by the difference in the detected Brillouin frequencies, which are approximately twice as low in the first configuration as in the second one. In both configurations the focusing of light beams on the iron surface was the same: the focused blue light was elliptical in shape with axes of 2.5  $\mu\text{m}$  (perpendicular to the scanning direction) and 1.1  $\mu\text{m}$ , while the focused red light was circular in shape with a 2.5  $\mu\text{m}$  radius, all at  $1/e^2$  in intensity. In figure 1(b) the Brillouin signals detected in the first configuration during the lateral scan along one of the anvil surfaces are presented. The detectable picosecond acoustic pulses were launched only from the iron/ice interface. This is confirmed by the absence of any detectable PAI signals in the case of the pump and probe lights incident in the gap between the generator and the gasket where only water ice is present. The first arrival of the acoustic pulse on the ice/diamond interface is accompanied by a change in the amplitude and the phase of the Brillouin signal, which is clearly visible for the lateral positions between 4  $\mu\text{m}$  and 14  $\mu\text{m}$  in the zoomed signals presented in figure 1(c). For the positions between 15  $\mu\text{m}$  and 50  $\mu\text{m}$ , a shortening of the acoustic propagation time across the ice layer can be noticed in figure 1(b), without zooming. In the inset of figure 1(b) we present the variations of the detected Brillouin frequency as a function of the delay time of the probe pulse relative to the pump pulse and of the lateral position. All frequencies obtained in these measurements are grouped around the two distinct values of 18 GHz (blue/green regions) and 23 GHz (orange regions), indicating the presence of regions exhibiting different acousto-optic behavior. The inset clearly reveals multiple reflections of the acoustic pulse at the interfaces of ice with diamond or iron. The inclination of the low frequency and high frequency regions is an indication of a decrease in the ice layer thickness, estimated to be  $\sim 3 \mu\text{m}$  at the left edge of the generator and zero at the position around 85  $\mu\text{m}$ . The dominance of two groups of different frequencies (colors) in the inset clearly demonstrates the presence of two different water ice ‘types’ in the sample. Earlier studies on single crystal ices by other BS techniques demonstrated that these could be either ice VI and ice VII, or just ice VI regions with two different orientations of crystallographic axes of grains or groups of grains relative to the direction of the acoustic pulse propagation [27–30]. Thus, the PAI revealed lateral spatial inhomogeneity of the bulk of compressed water ice. Another manifestation of the lateral spatial inhomogeneity of the sample in figure 1(b) is the clear changes in the magnitude of the acoustic pulse reflectivity at the ice/diamond interface, which varies from  $\sim 0.8$ , close to the theoretically expected value for an ideal interface (lateral position of 10  $\mu\text{m}$ ), to values close to zero (positions of 18  $\mu\text{m}$  and 41  $\mu\text{m}$ , for example). Thus, the PAI technique revealed a strong lateral acoustic inhomogeneity of the ice/diamond interface as well.

In the other series of our experiments, it was found that increasing the duration of the sample exposure to pump and probe laser beams causes the transformation of one type of the ice into another. In figure 2(a) we

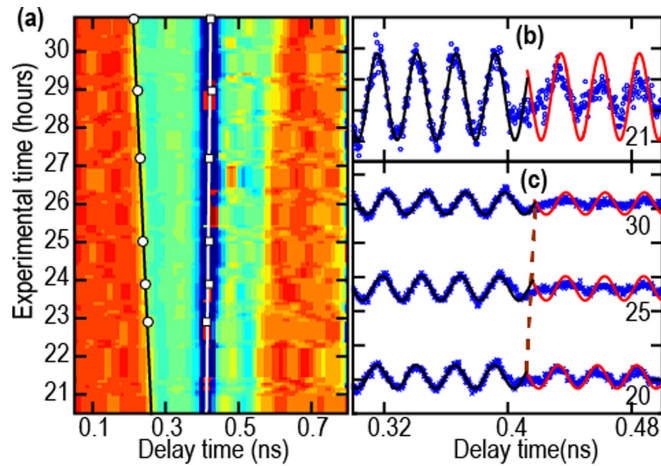


**Figure 2.** (a), (b) Brillouin frequency evolution with increasing time of sample exposure to laser radiation (vertical axis) plotted as a function of delay time of the probe beam with respect to pump. The white dots drawn vertically at the center of each image are guides for the eyes to identify the first reflection time of the acoustic pulse from the ice/diamond interface. (c), (d) Background free Brillouin oscillations observed at different experimental times, as indicated near the bottom right hand side of each oscillation. (a) Initiation of the ice transformation with red probe and blue pump with 7 mW laser power for each. After the start of the transformation, powers of the pump and probe beams were changed to 10 mW and 10 mW, then to 5 mW and 10 mW and, finally, to 10 mW and 5 mW at around 21.6 h, 25 h and 28.5 h, respectively, revealing the absence of any significant dependence of the transformation front propagation velocity on the wavelengths of the pump and probe beams at this particular lateral position. The inset shows the magnified view of the region at the beginning of the phase transition. (b) Initiation and monitoring of the ice transformation with blue probe and red pump, with 7 mW laser power each for the entire experimental time in different lateral positions. The white areas in (b) indicate the temporal shutdown of the data-storing computer but not of the laser action. The beginning of the ice transformation and the initial growth of the transformed ice layer thickness manifest themselves also by significant modifications in the shape of the PAI signal around the acoustic pulse reflection from the ice/diamond interface,  $\sim 0.4$  ns, between 21 and 23 h in the first experimental configuration (c) and between 5 and 15 h in the second one (d).

present results of the Brillouin frequency evolution as a function of the delay between the pump and probe laser pulses (horizontal axis) and the exposure duration (vertical axis), where we have used the equal beam powers of 7 mW. The signals were accumulated for 46 h ( $\sim 5$  signals per minute) and analyzed at every 10 min (by averaging 100 accumulations) with an overlap of 50 accumulations to the adjacent time steps. The laser action initiates after  $\sim 21.3$  h a transformation of one ice type (with higher Brillouin frequencies) into another (with lower Brillouin frequencies) starting from the ice/diamond interface.

In figure 2(b), we present the results of the experiment, where the pump and probe beams were interchanged while their powers were kept constant and equal to those in the previous experiment, namely 7 mW. The transformation front velocity decreases by more than half, from  $67 \text{ nm h}^{-1}$  ( $19 \text{ pm s}^{-1}$ ) at around 0.31 ns (vertical axis  $\sim 13$  h) to  $29 \text{ nm h}^{-1}$  ( $8 \text{ pm s}^{-1}$ ) at around 0.21 ns (vertical axis  $\sim 29$  h). Thus, both experiments reveal the deceleration of the front as it goes away from the anvil, indicating that the ice transformation process is due to the direct light interaction with the diamond and not with the water ice. For exactly the same pump and probe powers the transformation of ice starts in the second experimental configuration more than 10 h earlier, manifesting strong lateral inhomogeneity of the diamond/ice interface, this time not for sound reflection but for a possible heat and/or charge carriers transfer across it. The beginning of the ice transformation and the initial growth of the transformed ice layer thickness manifest themselves also by significant modifications in the shape of the PAI signal around the acoustic pulse reflection from the ice/diamond interface,  $\sim 0.4$  ns, between 21 and 23 h in the first experimental configuration (figure 2(c)) and between 5 and 15 h in the second one (figure 2(d)).

In an attempt to understand the physical nature of the observed laser-induced transformation, we analyzed more precisely the signals presented in figure 2(b) in the limited time interval of the experiment where the front propagation velocity is nearly constant, as indicated by the straight black line in figure 3(a).



**Figure 3.** Illustration of the method applied for the PAI signals processing in order to precisely evaluate the relative physical parameters of the two types of ice separated by moving transformation boundary. (a) Linear fits to the evolution with the experiment duration of the time instants of coherent acoustic pulse arrivals at the interface between the two ices (black line) and at the interface of ice and diamond (white line). (b) Determination of the pulse arrival time at the ice/diamond interface from the intersection of the Brillouin oscillations, corresponding to the incident acoustic pulse, and a scaled one, corresponding to the reflected acoustic pulse. (c) Zoomed fits revealing increase, linear in exposure duration, of the pulse propagation time across the ice layer, caused by the photo-induced phase transition.

This particular interval of time has an additional advantage, namely that the transition front is located nearly in the middle of the ice layer, thus providing the opportunity to process Brillouin signals of comparable length for both types of ice. This permitted us to find out accurately the differences between the parameters of the two regions. In the first step, the Brillouin frequencies,  $f_{1i}$  and  $f_{2i}$ , are determined by processing selected parts of the Brillouin oscillation, with high signal-to-noise ratio and not biased by the interfaces, detected at a particular  $i$ th hour of the experiment before and after the transition front, respectively. The subscripts 1 and 2 are used to label the initial and the final phases of ice, respectively. The background free Brillouin oscillations, separately extracted for each of the parts, are fitted in the time domain by the least square minimization method to a sinusoidal function, keeping frequency, amplitude and phase as free fitting variables. This signal processing gave values of  $f_{1i}$  and  $f_{2i}$  with a typical uncertainty of 0.08 GHz. The best fitted signals are then extended to the complete observation time interval corresponding to acoustic pulse propagation across the two types of ice. While looking at these fits, overlapping in time, the region of transition front, as revealed by the moving windowed Fourier analysis (indicated by a black line in figure 3(a)), manifests itself as the time interval being best fitted in phase and amplitude by the two sinusoids simultaneously. This transition region from one oscillation frequency to another lasts one oscillation period  $T$ . The results of this visual inspection are confirmed by the evaluation of the residues of the fits, which were minimized exactly in the same region of temporal length  $T$ . So the position of phase transformation boundary was chosen to be in the middle of this time interval and with  $\pm(T/2)$  uncertainty. A white line in figure 3(a) shows the time instants when the acoustic pulse reaches the ice/diamond interface. The evaluation of these instants was similar to the one from the method described above: the  $f_{2i}$  frequencies, determined previously, are used to fit the amplitudes and phase shifts of the sinusoids corresponding both to the incident and the reflected acoustic pulses. Then, the amplitude of the second sinusoid is made equal to that of the first one and the reflection moment is determined as the time where an abrupt mirror-symmetric change from the first sinusoid to the second one is observed (see figures 3(b) and (c)). The precision of the two delay times determination  $t_{\text{front},i} \equiv t_{1,i}$  (figure 3(a), white circles) and  $t_{\text{reflection},i} \equiv t_{2,i}$  (figure 3(a), white squares) is  $\pm 10$  ps and  $\pm 0.4$  ps, respectively. The uncertainties come from the half period of the Brillouin oscillation and the half temporal distance between two consecutive points in any chosen signal. These introduced characteristic times,  $t_{1,i}$  and  $t_{2,i}$ , are related to the sound velocities,  $v_1$  and  $v_2$ , in the two types of ice and to the total thickness of the ice layer,  $H$ , as  $v_1 t_{1,i} + v_2 (t_{2,i} - t_{1,i}) = H$ . Because even iron is nearly an order of magnitude more rigid than water ice at 2.15 GPa, the dependence of the total thickness of the ice layer on the degree of ice transformation is negligible, which allows us to cancel out the right hand side part of the above mentioned relation by differentiating it over the exposure time,  $t$ . This opens the way for us to determine the ratio of the sound velocities from the ratio of the inclinations of the black and white straight lines in figure 3(a),  $v_1/v_2 = 1 - \langle dt_{2,i}/dt \rangle / \langle dt_{1,i}/dt \rangle$ . Note that  $\langle dt_{1,2,i}/dt \rangle$  were obtained by the best linear fit of all earlier evaluated times,  $t_{1,2,i}$ , respectively, using least squares minimization. As a result, the ratio of the velocities was determined very precisely,  $v_1/v_2 = 1.1050 \pm 0.0002$ . The value found for  $v_1/v_2$  cannot discriminate between a phase transformation of the ice VII into ice VI and a possible recrystallization of any of these water ice

phases. This is primarily due to the ranges of the sound velocity variations related to the elastic anisotropy in ice VI ( $5100 \text{ m s}^{-1}$ – $5500 \text{ m s}^{-1}$ ) and in ice VII ( $4900 \text{ m s}^{-1}$ – $5900 \text{ m s}^{-1}$ ) and, secondly, because of an overlap of these ranges [27–30]. To determine the nature of the transformation definitely, we additionally analyzed the Brillouin frequencies of both ice types found through the averaging of the accumulated values, as described earlier, at different durations of the experiment,  $f_{1,2} = \langle f_{1,2i} \rangle$ . This permitted a precise determination of the frequency ratio,  $f_1/f_2 = 1.164 \pm 0.006$ . As the ratio of the Brillouin frequencies is related to the ratios of sound velocities and refractive indexes, we were finally able to determine the latter,  $n_1/n_2 = (f_1/f_2)/(v_1/v_2) = 1.053 \pm 0.005$ . This result definitely excludes a recrystallization process, because cubic ice VII is optically isotropic and the optical anisotropy of the tetragonal ice VI is insufficiently strong [30, 32] to be responsible for such a change in the refractive index. The experimental results in reference [30] implied that the two indices of refraction,  $n_i$  and  $n_o$ , of ice VI are very similar, resulting in an almost spherical indicatrix, thus confirming the earlier observation [32] that the difference between  $n_i$  and  $n_o$  is less than 1%. Accordingly, we conclude that the evaluated laser-induced process is the structural phase transformation of ice VII into ice VI, which is known to be accompanied by a reduction in the optical refractive index [27, 29]. We also arrived at the same conclusion through another processing of the Brillouin signals (see supplementary material available at [stacks.iop.org/NJP/19/053026/mmedia](http://stacks.iop.org/NJP/19/053026/mmedia)).

The presence of both phases of ice in our sample, i.e. ice VII and ice VI, was also confirmed by the Raman scattering measurements (see supplementary material). The Raman measurements indicated the presence of both these water ice phases on the periphery between the generator and the gasket, where a PAI signal cannot be generated, and the presence of ice VII in the left hand thicker part of the gap between the iron and the lower anvil (figure 1(a)). However, our Raman measurements were too uncertain/noisy in the right hand narrower part of this gap, approaching a thickness of less than  $1 \mu\text{m}$ , and thus precluded a definite identification of ice VI there. This identification, as well as revealing the presence of relatively small quantities of ice VII near the surface of the upper anvil, as it is qualitatively indicated in figure 1(a), was accomplished by the PAI.

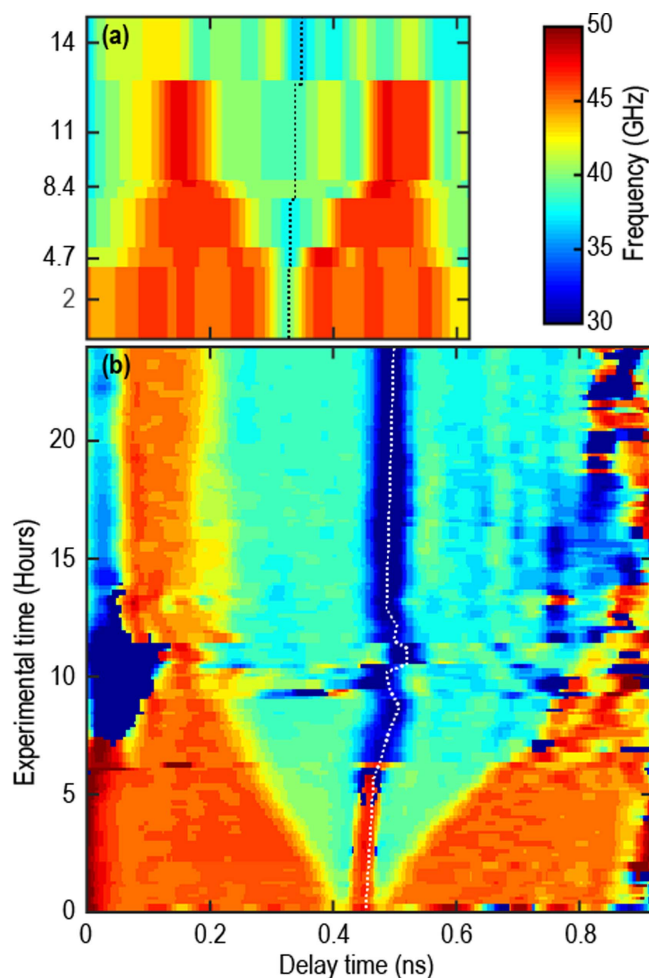
## Discussion

In multiple PAI experiments conducted on different positions of the acousto-optic generator we observed that the pulsed laser radiation initiated the transformation of ice VII into ice VI, but not vice versa, revealing that these ice phases co-exist in the pressure domain of the thermodynamic stability of ice VI. In fact, this was impossible to confirm through pressure measurements, because the pressure was determined, with the best possible precision that could be reached by the Ruby fluorescence scale, to be  $P = 2.15 \pm 0.05 \text{ GPa}$ , which is within the variation of the reported phase transition pressures at room temperature [27–31]. Also, variations in the pressure distribution in the sample were found to be negligible (see supplementary material). In favor of our conclusion, i.e., ice VII is metastable under our experimental conditions, are also our observations that we were never able to detect retransformation of ice VI, obtained through the laser-induced transformation of ice VII, into the initial ice VII phase state, even after several days of waiting and probing the ices using the PAI. An example of such PAI measurements, which were additionally accompanied by lateral scanning of the co-focused pump and probe beams in one of the directions along the generator surface to obtain two-dimensional images [14, 21] (see the supplementary material), also confirms that the structural transformation of ice is confined laterally only in the region of the laser light focusing.

The most puzzling result of our analysis of the laser-induced phase transitions seems to be the fact that, in a dominant number of experiments conducted at different lateral positions of the layer initially occupied only by ice VII (figure 1(a)), the ice transformation was observed to start and extend only from the ice/diamond interface (see, for example, figures 2 and 3). The results of a single experiment, where the phase transformation started at both interfaces, are presented in figure 4(a). In another single experiment, several hours of the laser beam action formed near the iron surface a region characterized by a Brillouin frequency lower than those expected in ice VI (figure 4(b)). This region presumably contained water, which could occur at such pressure for a local temperature above  $\sim 340 \text{ K}$  [31]. Currently, we can just propose the hypothesis that these exceptional observations are related to the possible oxidation of the iron opto-acoustic generator, caused in some lateral positions by multiple hours of exposure to laser radiation. This hypothesis correlates with our observations of a greatly increased level of photoluminescence in some lateral positions of the sample (see supplementary material).

Thus the puzzle is related to the observation that, in most of the experiments, there were no detectable ice phase transformations significantly spreading only from the iron/ice interface, which was estimated to be much more strongly heated by the laser beam action in comparison with the diamond/ice interface. However, the estimated stationary and transient temperature rises, even at the ice/iron interface, do not exceed  $3^\circ\text{C}$  and are smaller than the measured temperature variations in the experimental room, where the temperature was not





**Figure 4.** Brillouin oscillation frequencies plotted as a function of the experiment duration and the delay time of the probe beam with respect to the pump. Dotted curves, starting at the middle position of the horizontal axes ( $\sim 0.33$  ns in plot (a) and  $\sim 0.45$  ns in plot (b)) are just guides to the eyes indicating the time of the acoustic pulse reflection from diamond. A moving (with a 2.6 ps step) Hann window of 50 ps at FWHM was used for the Fourier analysis. (a) In contrast to all other results, the Brillouin signals were averaged over varying intervals of the experimental time, ranging from 20 min to 2 h (as one can see by the differences in vertical lengths of homogeneous regions) to compensate the changes in signal-to-noise ratio caused by the use of different laser powers (6 mW to 60 mW total power, irregularly) at different time intervals. (b) Brillouin oscillations used for the instantaneous frequencies extraction were collected with 14 mW constant laser powers and at a rate of five accumulations per minute, continuously over 25 h. The signals were averaged each 10 min with 100 accumulations in each average, while giving an overlap of 50 accumulations to the adjacent time steps. The blue frequency region between the vertical time intervals of  $\sim 7$  and  $\sim 12$  h, and up to  $\sim 0.2$  ns on the delay time axis, are suspected to be due to a possible presence of liquid water as it follows from a comparison of their estimated acoustic velocity values with those reported in the literature. This lowering of the sound velocity pushed the acoustic pulse arrival time at the diamond/ice interface to increase and induced its abrupt shifts by moving the echo position in the image.

controlled. These observations and estimates indicate that the phase transformation in most of the cases is not driven by laser-induced heating of the thermal phonons and the energy transportation by them. Note that the energy of a thermal phonon at room temperature is only 0.026 eV.

The energy transporting carriers, which can be much more energetic than thermal phonons and thus could potentially drive the observed phase transition, are nonequilibrium electrons generated by the absorption of pump and probe laser pulses in diamond and iron. For a qualitative explanation of our experimental observations, it is important to note that the electrons, photo-generated in the conduction band of diamond, are expected to be much more efficient in penetrating into ice than the nonequilibrium electrons photo-excited from the Fermi level of iron. This is because the electrons in the conduction band (CB) of diamond are closer to the CB of ice than the electrons photo-excited in iron from its Fermi level by the blue laser quanta,  $\cong 3.1$  eV, in our experiments. Note that the CB of ice is at  $\sim -0.1$  eV relative to the vacuum level [33]. The position of the diamond CB relative to vacuum level depends on the surface electron affinity of diamond and could vary depending on surface termination from  $\sim +1$  eV for hydrogenated to  $\sim -1$  eV for oxygenated surfaces [34, 35], while the work function of iron is  $\approx 4.7$ – $4.8$  eV. Moreover, our photoluminescence examination of the diamond anvils (see supplementary information) revealed spectral lines at 1.58 eV and 1.54 eV inside the broad photoluminescence peak of 0.3 eV at FWHM and centered at the first of these lines. The emission in this spectral

region from the diamonds of IA type, used for the anvils in our experimental cell, is known to be due to the presence of bulk donor nitrogen defect levels and surface defect levels, reported at 1.5–2.0 eV below the CB of diamond [36–40]. Thus, the red, 1.55 eV, light quanta in our experiments can potentially excite electrons only close to the CB minimum of diamond. When they are photo-excited from the bulk defect levels of diamond their penetration into ice could require tunneling through the potential barrier of about  $\sim 1$  eV height, which could exist in the case of positive electron affinity of the diamond surface [34, 35]. In contrast to the red light quanta, the blue light quanta of 3.1 eV can generate, from the lowest bulk and surface defect energy levels, electrons with energies above this potential barrier. Thus, they could penetrate ice in a ballistic regime, carrying the excess energy  $> 1.5$  eV relative to the conduction band of ice. Consequently, we hypothesize that in our experiments the photo-induced initiation of ice transformation dominantly takes place at the ice/diamond interface due to the exceptional electronic structure of diamond, of which the CB is relatively close to that of ice and, as a result, its donor defect levels are closer to the CB of ice than the Fermi level of iron. The diamond electronic structure is known to facilitate the photo-emission of electrons into other media also [34, 37]. The photo-emission of electrons from diamond is especially effective in the case of hydrogenated surfaces of diamond exhibiting negative electron affinity [34, 37].

It is worth noting that both phase transitions and chemical reactions, driven by the charge carriers emitted from diamond, have been reported earlier [34, 41]. In [41] it was demonstrated that even photo-electrons with energies below the CB of ice can penetrate it, by tunneling to the defect states in its forbidden energy gap, and can induce the transformation of the metastable amorphous phase into a stable crystalline phase. Other experiments [34] revealed that, illuminated with optical quanta exceeding the diamond energy gap, 5.5 eV, hydrogen-terminated diamond yields easy electron emission into water, thus inducing the reduction of  $N_2$  to  $NH_3$  at ambient temperature and pressure. The same chemical/photocatalytic process was observed, although with much lower efficiency, even at an oxygen-terminated diamond surface exhibiting positive electron affinity. These observations support our hypothesis that the transformation of ice VII into ice VI near the ice/diamond interface could be induced by the photo-emission of electrons from diamond. However, the totality of our experimental observations, which has been only partially discussed above, indicates strong quantitative dependence of the observed phenomena on the lateral position of the experiments through the lateral variation of the diamond/ice interface ‘resistance’ to the transport of phonons and charge carriers. This has prevented us from making any quantitative estimate in order to relate the experimentally measured phase transformation velocities to the concentrations of photo-generated charge carriers in diamond. Future experiments that could potentially provide quantitative data for such estimates should be conducted with preliminarily characterized, or, perhaps, even specially prepared by hydrogenation, surfaces of diamond anvils.

## Conclusions

In conclusion, we have reported experimental observations confirming the ability of the PAI technique to follow in time (with nanometers in-depth resolution and with micrometers lateral resolution) the material transformation characterized by low optical and acoustical contrasts between its two phases. Such application of PAI for the temporal monitoring of a phase transition has been reported only once [15]. Namely, a displacement rate of the interface between ice Ic and water vapor at a temperature of 110 K and ambient pressure was characterized in a single lateral position of the growing homogeneous ice layer. A strong acoustical contrast between the two phases of water in the experiments reported in [15] provided the opportunity to detect acoustic echoes reflected at their interface, which was impossible in the experiments reported here. The optical contrast between the two water phases in [15] was also significantly higher than in our experiments. Still, we have been able to determine the interface position and its displacement rate as a function of time, the ratios of the refractive indexes and the sound velocities of the ice phases. We also revealed the physical nature of the observed ice transformation by applying the PAI at a single direction of probe incidence. In addition, we have demonstrated the ability of the PAI to image spatial inhomogeneity of the physical parameters of the interfaces. Our experiments indicate the applicability of PAI to the 3D imaging of transient phase transformations in optically transparent media, in general, and those that could be laser-induced at high pressures in diamond anvil cells, in particular.

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