Elastic properties of water under negative pressures

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Using Brillouin scattering we have investigated the elastic properties of water under negative pressures. The samples were H_2O liquid–vapor inclusions in α-quartz which could be heated to their homogenization temperatures (in the range 120–370 °C); on cooling, negative pressures as high as 1000 bars were reached before a vapor bubble nucleated. The velocity of sound results obtained from our Brillouin experiments indicate that nucleation occurs long before reaching the mechanical instability region where the bulk modulus is zero.

INTRODUCTION

Since the discovery that liquids can sustain an applied tension, the technique developed by Berthelot[1] to study this phenomenon has been considerably refined and improved.[2-4] These techniques allowed tensions of up to ≈ 10 MPa (100 bars) to be achieved, but these tensions are considerably lower than the estimated homogeneous nucleation pressures which can be as high as 150 MPa.[5,6] The reason for the relatively low tensions achieved in Berthelot tubes is presumably because of nucleation centers which exist in any macroscopic device. Recently[7,8] it has been shown that the liquid inclusions which can be found in most naturally occurring minerals provide excellent systems in which to investigate the phenomenon of liquids under tension. In these investigations on H_2O inclusions, tensions as high as 140 MPa, which are very close to the predicted homogeneous nucleation values,[5,6] were achieved.

The biggest drawbacks of studying these inclusions are (i) their size, which makes it necessary to use 'microscopic' techniques and (ii) their isolation, i.e., it is not possible to connect leads or insert probes within a given inclusion. The most common method of investigation is simple direct visual observation; this typically yields the homogenization and nucleation temperatures. When coupled with equations of state (and it must be stressed that in the negative pressure regime these are obtained from extrapolations from positive pressures) these results can be transformed into thermodynamic variables such as pressure and temperature. Other determinations such as the freezing temperature allow the concentrations of other components such as salts and noncondensable gases to be estimated. The only probe which has been used to directly measure a property of the included liquid is Raman scattering, however, since this probe measures a property which is internal to each molecule and which is only very weakly affected by interatomic distances, it yields limited information on the macroscopic properties of the liquid.

Here we report Brillouin scattering experiments on H_2O inclusions in quartz, from which we obtain the velocity of sound. As in Refs. 7 and 8 our investigation addresses the issue of metastability of water under negative pressures: our results, however, cover a broader range of densities and provide a quantitative measure of the stability. Along the liquid–vapor equilibrium line our results are in good agreement with published values. At negative pressures our results are consistent with extrapolations from existing positive pressure regime, and they show that when nucleation occurs even at -100 MPa the H_2O inclusions are still far from the expected mechanical instability caused by a zero bulk modulus.

EXPERIMENTAL DETAILS

One of the host samples in which inclusions were investigated was a natural crystal of quartz of unknown origin and composition: it contained many inclusions all of which homogenized at ~ 120 °C. On subsequent cooling vapor bubbles nucleated over a wide range of temperatures in the different inclusions; in one particular inclusion however we were able to reach 0 °C before nucleation occurred. Fluid inclusions in naturally occurring samples are less than ideal for these studies because all natural fluid inclusions contain varied, and usually unknown, amounts of dissolved components. In particular, small amounts of volatiles, such as CO_2, N_2, CH_4, etc., can have a significant effect on both the slope of the isochores and, more importantly with respect to this study, the vapor pressure in the inclusion at homogenization, for example, addition of 0.5 molal CO_2 to a pure water inclusion will raise the vapor pressure at 250 °C from 69 to 108 bars. As described in Ref. 9, this amount of CO_2 would not be easily detected in a natural inclusion.

For the above reasons most of the samples we investigated were fabricated as described in Refs. 10–13 and each one contained inclusions with a well defined homogenization temperature in the range 135–374 °C.[11] Although the samples are prepared using doubly distilled water and high purity quartz crystals it is still conceivable that impurities dissolved in the water, in particular silicic acid produced by the reaction of SiO_2 with H_2O, could influence the results of our measurements. Using the known solubility of

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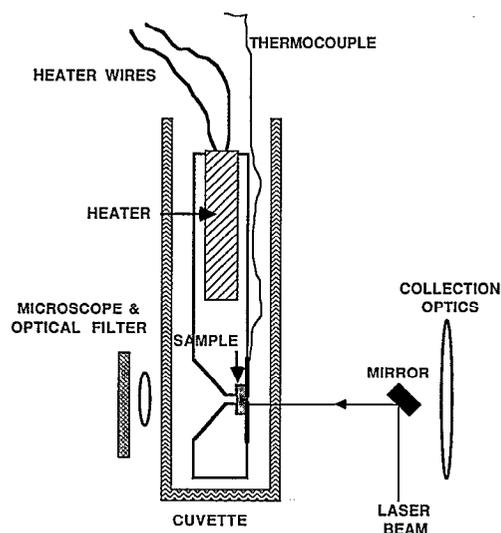
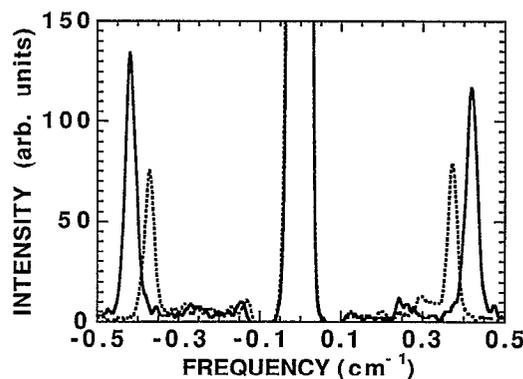FIG. 1. Schematic diagram of experimental setup.

FIG. 2. Brillouin spectra from a homogeneous water inclusion just before nucleation at 182 °C (dotted line), and just after nucleation at 180 °C (full line).

quartz, even at 250 °C we expect only a 10 ppm concentration of silicic acid. An even more pessimistic view using the solubility of fused quartz still only yields concentrations of 0.1% at 250 °C. These estimates are consistent with the known fact that 0.1% of NaCl in water changes the melting temperature by 0.06 °C and in our samples the melting temperature was found to be 0.0±0.05 °C. As described in Refs. 7 and 8 Raman scattering can be used to determine the purity of the water within the inclusions with a sensitivity of $\sim$0.1 mol %. Raman scattering results on our inclusions show no evidence of any impurities. Furthermore, since sound velocities are relatively insensitive to impurities (e.g., 1% of NaCl in H_2O changes the velocity by less than 1%) we can safely conclude that a maximum of 0.1% impurity concentration will not be detectable with our $\sim$1% accuracy.

The samples were mounted in an aluminium block shown schematically in Fig. 1; the block was heated by a resistance heater and the temperature measured by a thermocouple in contact with the metal close to the sample. The whole block was then placed in a cuvette to reduce thermal gradients. In spite of the above precautions, at the highest temperatures the sample was $\sim$10 °C cooler than the thermocouple as evidenced by the homogenization temperatures which had been independently and accurately measured. All temperatures mentioned in this article already contain this correction. Minor modifications of the sample holder also allowed us to cool the sample to $\sim$0 °C.

Many excellent reviews[14,15] can be found of the Brillouin scattering technique used to measure the sound velocity. Our spectra were excited with $\sim$150 mW of 514 nm radiation focused down to $\sim$5 micron diameter spot, light was collected by an f/1.1 lens, and a 3+2 tandem Fabry–Perot[14] was used to analyze the scattered light. The backscattering geometry was used and a microscope placed behind the sample allowed careful and reproducible choice of the inclusion to be studied. Two typical spectra are shown in Fig. 2: they were obtained from the same inclusion at the

same temperature of 181 ± 1 °C; the spectrum shown by the full line was from a liquid in equilibrium with its vapor, the dotted line is a spectrum from the homogeneous fluid obtained on cooling from the homogenization temperature. The difference in the position in the Brillouin peaks reflects the change in velocity between the normal and tensioned liquids.

Nucleation temperatures in a given inclusion were usually reproducible to within a few degrees but sometimes they nucleated at considerably higher temperatures on subsequent runs for no apparent reason. Experiments performed at lower laser powers showed no systematic changes in the nucleation temperature. Since the laser heating of the liquid can be estimated to be less than 1 °C this behavior is not unreasonable; the results do show however that any electric field induced effects are also negligible.

DATA ANALYSIS

The measured frequency shift Δv obtained from the spectra is related to the sound velocity (v) through

$$v = 7.7175 \Delta v / n, \tag{1}$$

where n is the refractive index and v is in km/s if Δv is in cm^{-1}. Along the liquid–vapor equilibrium line, the refractive index was taken from Ref. 16. We have assumed that n retains its value at the homogenization temperature on heating or cooling after homogenization, since the density remains essentially constant. This is reasonable because in the simple Claussius–Mossotti model it follows from the usual assumption that the molecular polarizability is independent of temperature and pressure.

RESULTS

Figure 3 shows the velocity of sound obtained from our Brillouin spectra as described above. The crosses correspond to liquid–vapor equilibrium, the other symbols are for different inclusions after they have homogenized. Our velocity values in the liquid in equilibrium with its vapor are in excellent agreement with literature values[17] shown
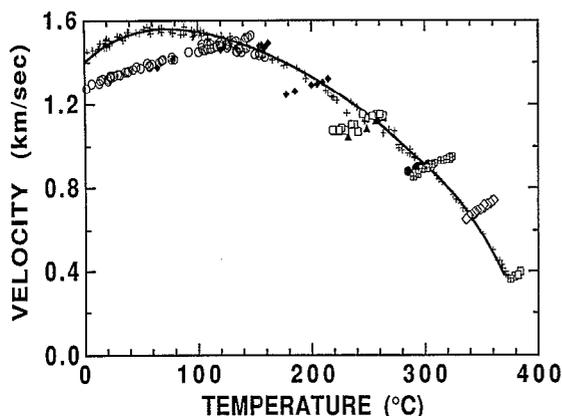
FIG. 3. Sound velocity vs temperature in water. The + signs are for liquid in equilibrium with its vapor, the other symbols are for inclusions which were homogenized. The full line represents the ultrasonic values from Ref. 17.

FIG. 5. Pressure changes on nucleation; full circles are our results and the full line is obtained as described in the text.

by the full line. This agreement between our velocities and those in the literature confirm our expectation that the effect of impurities is negligible.

After homogenization has occurred our velocity results correspond to experiments performed at constant volume. (Exceptions to this rule occur if the pressure becomes too great and the host crystal fractures (decrepitates),[18] and in one case to be discussed later, even negative pressures produced changes in volume.) From the results on the homogenized inclusions shown in Fig. 3 we obtain the derivative of the sound velocity at constant volume $(dv/dT|_V)$ which are shown in Fig. 4 (full circles) as a function of the homogenization temperature. Also shown in Fig. 4 are values calculated using

$$dv/dT|_V = dv/dT|_P + dv/dP|_T \times dP/d\rho|_T \qquad (2)$$

and the data from Refs. 19 and 20 (open circles). Both sets of data points have large errors: in our data they arise from a combination of the assumption of constant volume and also from the relatively small temperature range over

which the slope is measured. The errors in the open circles are large because they result from the difference of two terms of similar magnitude in Eq. (2) and also because $v(P)$ is nonlinear and hence introduces an uncertainty into $dv/dP|_T$. Within the experimental errors there is agreement between the two determinations. The remaining data point at 4 °C in Fig. 4 is obtained directly from experimental values of dv/dT at constant pressure since under these conditions the requirement of constant volume is also satisfied. The inclusion of this last point clearly indicates that $dv/dT|_V$ has a minimum somewhere in the range of 50–150 °C; this minimum, although surprising, is not inconsistent with other properties (e.g., density and sound velocity) which also show extrema in their temperature behavior.

In order to obtain the pressure at which the vapor bubble nucleation occurs we have used our measured differences in velocity just before and just after nucleation (Fig. 3) and the $dv/dP|_T$ data from Ref. 17. Although this involves an extrapolation of the literature values into the negative pressure regime, given the good agreement between our $dv/dT|_V$ measured at negative pressures and the values extrapolated from positive pressures (Fig. 4), the extrapolation of $dv/dP|_T$ seems justified. Figure 5 shows the measured pressure changes on nucleation obtained in this manner (full circles) plotted as a function of the nucleation temperature. The full line is the predicted pressure change obtained from the difference in the homogeneous nucleation pressure as given by Zheng et al.[8] (who follow Refs. 5 and 6) minus the pressure of the liquid–vapor equilibrium. As was concluded in Ref. 8 there is good agreement between the experimentally measured values and the calculated ones. Here one should bear in mind that the arguments given at the beginning of this section regarding the negligible effect of impurities on the sound velocities may not be valid for the phenomenon of homogeneous nucleation. However, given the reasonable agreement between theory and experiment, it is not unreasonable to infer that the influence of impurities is small.

The results presented up to this point either agree with existing data, with extrapolations of existing data, or with
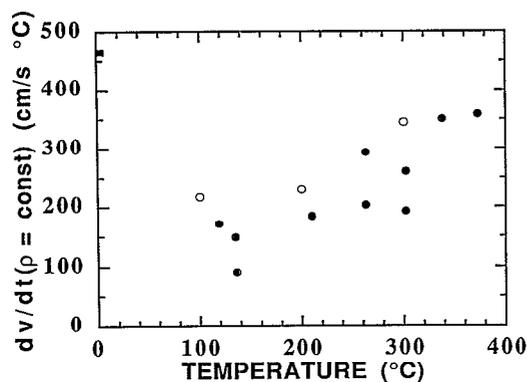

FIG. 4. Derivative of the sound velocity with respect to temperature at constant volume as a function of temperature. The full circles are our results, the open circles are obtained from Refs. 17, 19 and 20, and the full square is dv/dT at constant pressure at 4 °C.
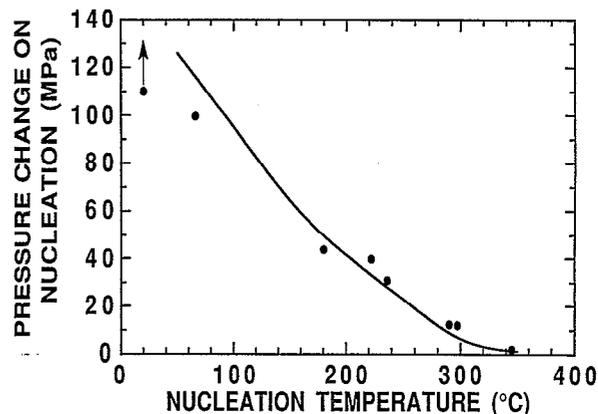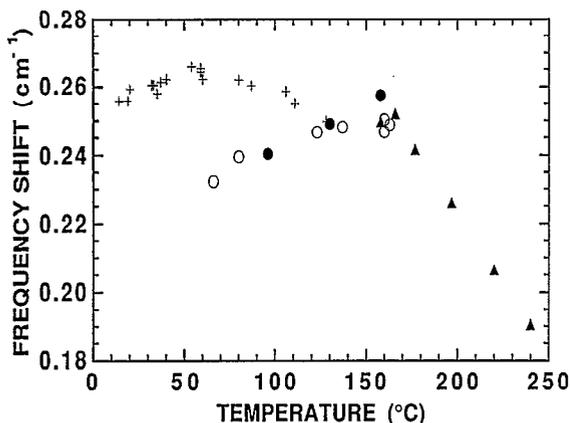
FIG. 6. Measured frequency shifts from an inclusion at various stages of decrepitation. Plusses are liquid–vapor equilibrium, full circles are prior to any sample damage, open circles are presumably after some microcrack formation, and triangles are during complete sample disintegration.
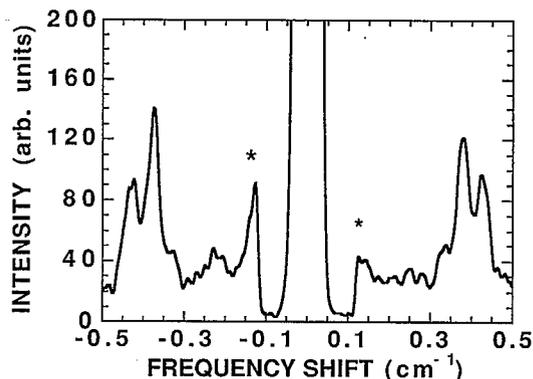
FIG. 7. Brillouin spectrum from an ~1 μm thick water inclusion showing the quantization of the wave vector due to the finite thickness; the thickness of the inclusion was estimated from the splitting of the peaks. The asterisks denote a peak of instrumental origin.

conclusions based on extrapolated equations of state. The results to be presented below are cases which show unusual behavior and which can be interpreted as changes in the volume of the individual inclusions. They are of interest not for any physical insight which they provide on the water, but because they reflect physical changes in the host crystal which, if the Brillouin results were not available, could lead to misinterpretation of data obtained from simple visual observation.

The first phenomenon to be discussed is reequilibration of fluid inclusions, a phenomenon well known to fluid inclusionists.[18,21] Reequilibration is a nonelastic increase in the volume of the inclusion that occurs when the internal pressure inside the inclusion exceeds the yield strength of the host crystal. Fluid inclusion reequilibration may be manifest by *stretching*, in which the inclusion volume increases by plastic deformation without loss of any fluid, by *partial leakage*, in which only a small portion of the fluid is lost from the inclusion along a microfracture, or by *decrepitation*, which is the explosive loss of all of the fluid from the inclusion.[21] Experimental studies show that most fluid inclusions in quartz reequilibrate by decrepitation, whereas most inclusions in softer minerals such as calcite, fluorite and barite reequilibrate by stretching.[21]

The point at which a fluid inclusion decrepitates is easily identified on a plot of the frequency shift as a function of temperature. A typical plot of the measured frequency shift as a function of temperature for a multiply-scanned natural quartz sample is shown in Fig. 6. The plus symbols denote samples of liquid–vapor in equilibrium; the full circles correspond to a run in which the temperature of the sample had never exceeded 160 °C and hence the host crystal is still behaving elastically both in the positive and negative pressure regimes. The open symbols correspond to a run in which the samples had already suffered some microcracking around the inclusion; the lower values of the frequency shift measured at ~160 °C are an indication that these microcracks relieve some of the pressure inside the inclusion. The triangles are from a run in which the sample

suffered massive internal cracking and in which the host crystal can no longer maintain a substantial pressure inside the inclusion.

The second phenomenon to be discussed is the effect of negative pressures on the host crystal. The existence of this effect has been previously recognized and Zheng *et al.*[9] estimated its magnitude and found it to be small. It is not clear, however, if the magnitude of the effect will depend on the shape of the inclusion. What we wish to show here is that this effect can be very large in some inclusions. Figure 7 shows a Brillouin spectrum from a very thin platelet-like inclusion with an area of ~50×50 μm; the multiple peak structure of the Brillouin peak is due to the quantization of the wave vector determined by the thickness of the inclusion.[22] In such a platelet of thickness L the allowed phonon wave vectors are given by

$$q = p\pi/L \tag{3}$$

where p is an integer. From Eq. (3) we estimate the thickness of the inclusion to be ~1 micrometer. In spite of the slight ambiguity in determining the peak position in such spectra, in Fig. 8 we plot the measured frequency shift [related to the velocity by Eq. (1)] as a function of temperature. Before homogenization (open circles) the results agree with those in other inclusions. On cooling after homogenization (rhombs) the frequency shift shows a sharp upturn, instead of the expected monotonic decrease. For the sake of comparison the squares in Fig. 8 are for a normal inclusion in the same host crystal.

The results in Fig. 8 are consistent with the interpretation that the volume of the platelet inclusion has been substantially reduced due to the internal negative pressure. This conclusion is further substantiated by the fact that this particular inclusion could be cooled all the way to room temperature before it nucleated while all other inclusions studied in this sample nucleated above ~235 °C. Because on successive heating cycles the homogenization temperature in this anomalous inclusion did not change, it indicates that any deformation was purely elastic.
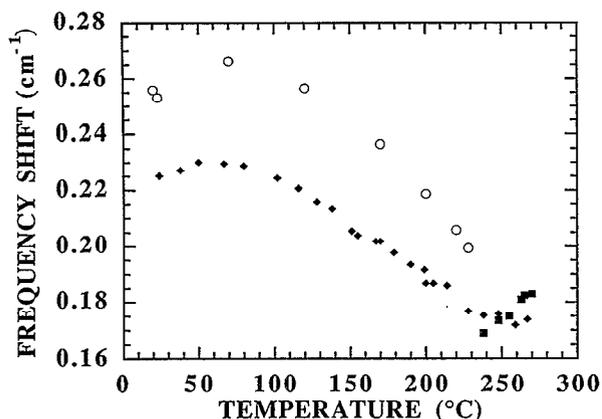
FIG. 8. Measured frequency shift in inclusions in a sample where they homogenized at 263 °C. Open circles are for liquid–vapor in equilibrium, the full squares represent a typical inclusion which always nucleated below ~235 °C, and the rhombs were obtained from the 1 μm thick inclusion described in the text.

Unless an alternative model can be found to explain the results in Fig. 8, their interpretation as a volume contraction due to the negative pressure in the inclusion underscores the possible pitfalls which could be encountered in extracting conclusions just from visual observations: e.g., since this inclusion often did not nucleate even at room temperature, if volume changes are neglected its pressure should be close to 500 MPa which would be well outside the predicted region of stability. Any quantitative conclusions of such visual observations must therefore also consider the specific shape of the inclusion under observation. For most inclusions which are roughly spherical the estimate in Ref. 9 appears to be appropriate and, to a good approximation, volume changes due to deformations of the host crystal can be neglected.

CONCLUSIONS

Using microscopic H_2O inclusions in α-quartz crystals we have measured the velocity of sound in liquid H_2O at large negative pressures reaching -100 MPa. Our results are consistent with extrapolations from the positive pressure domain.

We also show that the shape of the inclusion may be important in determining the deformation of the host crystal as the internal pressure is varied. For some shapes the induced volume changes are so large that they invalidate any conclusions which might be drawn from simple visual observations.

ACKNOWLEDGMENTS

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