HIGH PRESSURE AND HIGH TEMPERATURE SOUND VELOCITY MEASUREMENTS IN LABORATORY

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Abstract

The techniques usually used in the Physique des Milieux Condensés laboratory to measure the sound velocity of liquids and solids under extreme conditions are described. To illustrate the feasibility of such methods, recent results on the equation of state of water up to 9 GPa and 723 K and on the pressure variation of the $Fe_{0.64}Ni_{0.36}$ invar alloy incompressibility are given. A brief description of new developments and future directions of works conclude the article.

Introduction

From a very general point of view, the scientific production in the laboratory of Physique des Milieux Condensés is mainly devoted to physics and chemistry of matter under extreme conditions, which typically means a static compression between atmospheric pressure and about 1 million atmospheres, or 100 GPa (1 GPa = 10 kbar), and heating up to about 1000 K. It means that the studies are focused on the condensed matter for which the atomic or molecular structure is taken into account, thus excluding the plasmas.

Understanding the Earth interior is one of the greatest application of high pressure work in the GPa range. Up to now, the deeper core sampling has been extracted at a depth of only few kilometers, and more than 99% of the earth interior has to be study by indirect measurements as those performed in laboratory. For example, many studies of the composition of the Earth mantle involve the comparison of velocity-depth models derived from seismic data with sound velocities measured under extreme conditions in laboratory.

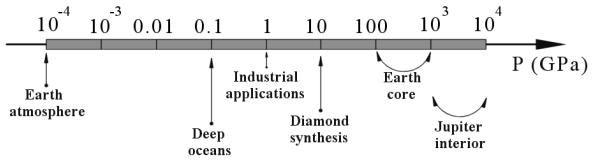

Figure 1: Typical pressure range that can be reached in laboratory with high pressure apparatus. Some examples from the Earth atmosphere to the interior of planets gives an idea of what means such thermodynamical conditions.

But beyond this application, the study of matter under pressure is a fascinating field and pressure appears to be one of the most powerful thermodynamical parameter to tune properties for understanding fundamental chemistry and physics. For example, it is well known that the effect of pressure at room temperature on the energetics of a crystal is much greater than the temperature change up to the melting point at room pressure. It means in particular that the pressure measurements of sound velocity or elastic moduli (which relate deformation to stress) of solids and liquids would enable to probe with a high sensitivity the most unknown part of the interatomic potential, say the repulsive one.

Moreover, the thermoelasticity study of stressed material not only provides a means for fundamental physics, chemistry and geophysics, but also gives crucial insight in the applied physics field trough, for example, the mechanical stability of solids, the indirect determination of the piezoelectric properties and the third-order elastic constants, or the understanding of properties of very important material from a technological point of view as semiconductors or metals.

Ultrasonic set-up for highly accurate sound velocity measurements under high pressure

Ultrasonic measurements under hydrostatic pressure up to 1 GPa

A classical piston-cylinder apparatus is used to generated an hydrostatic pressure up to 1 GPa in the chamber where the sample holder is completely immerse in the pressure transmitting medium (penthane, see figure 2).

The transducer is mounted on the crystal which dimensions are of about 10 mm. Figure 3 gives a schematic diagram of the sample with on its top flat face the lithium niobate transducer. Thickness and orientation of the transducer disk are chosen to generate pure longitudinal or pure transverse waves with a fundamental frequency on the order of 10 MHz. Electronic devices enable to cut such waves as short pulses (with a duration of about 100 ns), which propagate inside the sample and produce echoes after reflections on the par-

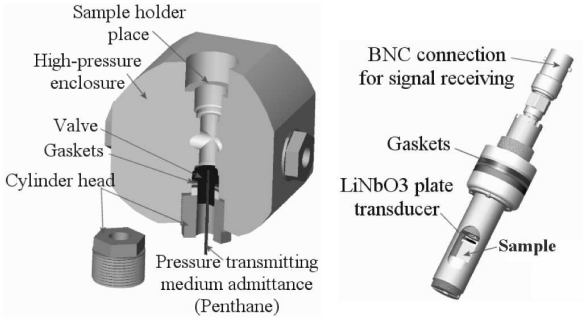

Figure 2: Ultrasonic scheme for achieving sound velocity measurements under hydrostatic pressures up to 1GPa.

allel faces of the sample. Finally, a digital oscilloscope records the ultrasonic wave echoes (figure 3). We use the classical pulse echo overlap method using a signal cross correlation section between two consecutive echoes to determine the time t (travel time) needed to detect the reflected pulse after one round trip through the sample. This travel time is thus simply related to the sound velocity v by 2d/t where d is the distance between the two parallel faces of the sample.

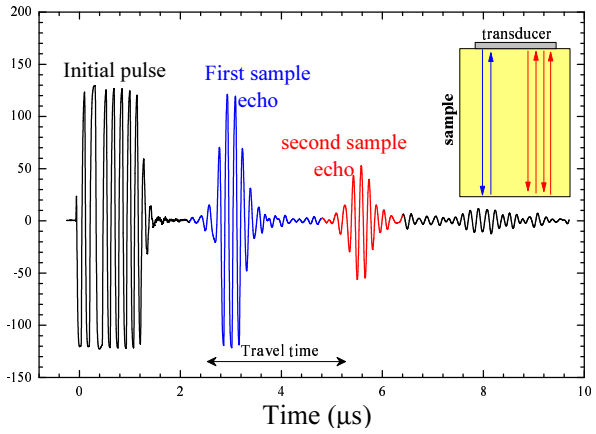

Figure 3: Typical spectrum of shear waves acoustic signal at 0.6 GPa. Four echoes can be seen and correspond (from the left to the right) to the initial pulse and one, two and three round trip of the pulse inside the sample respectively

Ultrasonic measurements under pseudo-hydrostatic pressure up to 10 GPa [1]

The challenge of such kind of measurements is to be able to compress a large-volume sample (needed for the ultrasonic measurements) above 2 GPa which is typically the upper limit of what can be generated with a piston-cylinder apparatus. We used an opposed-anvil systems allowing a compression of a mm-sized sample up to 10 GPa. The principle is shown in figure 4, where the sample can be seen to be surrounded by a boron nitride (BN) cylinder, which is used as a solid pressure-transmitting medium. Compressed NaCl powder used as a pressure gauge is located below and around the cylindrical sample. This set-up is put into a boron epoxy gasket which has a low X-ray absorption and a low shear modulus. The force on the anvils is generated by the Paris-Edinburgh press developed in the laboratory of Physique des Milieux Condensés, which belongs to the family of opposed-anvil systems. Its main characteristics are a high maximal force which can be generated on the anvils (about 2 MN) for a small weight and small dimensions (less than 30 cm). All details of this press can be found in the reference [2].

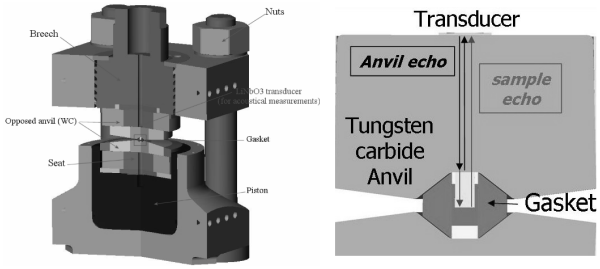

Figure 4: The High pressure apparatus (Paris-Edinburgh press) used for the ultrasonic measurements up to 10 GPa (left). A cross-section of the WC anvils and the boron-epoxy gasket assembly. The cylindrical mm-sized sample is surrounded by BN and NaCl used as solid pressure transmitting media.

The transducer, placed on the top of the upper anvil, is only submitted to the atmospheric pressure. After propagating through the anvil, an initial pulse produced by this transducer is partially reflected at the anvil-sample interface, while the other part of the acoustic energy is transmitted inside the sample (see the corresponding spectrum in figure 5). The large acoustic mismatch between the sample and the surrounding pressure transmitting medium (NaCl) leads to the total reflection of the signal at the far end of the sample. The time difference needed to superpose the buffer and the sample echoes corresponds to the travel time of the pulse through the sample (which means that the length of the sample has to be chosen in such a way that the anvil and the sample echoes do not overlap).

From the ultrasonic travel-time to the sound velocity and the incompressibility modulus

We have seen that the sound velocity is deduced from the travel time t through v=2d/t, where d is the length between the two parallel sample faces. In the same manner, the elastic constants and the incompressibility modulus B are function of the sample density and the square of the sound velocities. In other words, all

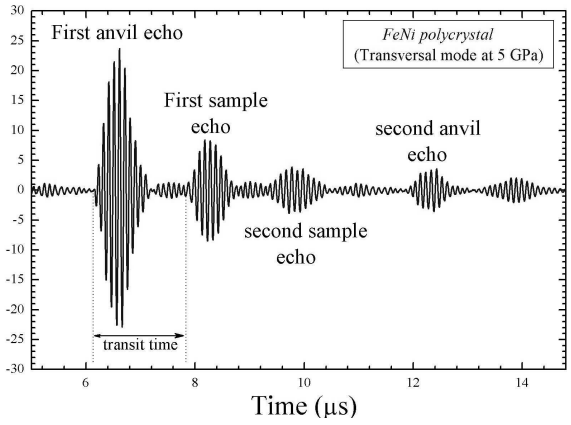

Figure 5: Typical spectrum recorded from a ultrasonic measurements (transversal wave) performed at 5 GPa on $Fe_{64}Ni_{36}$.

previous thermoelastic parameters can only be determined under pressure if the pressure variations of the length and of the density of the sample are known. In some case, the equation of state P=f(V) has been already measured and the determination of the length and density pressure dependence is thus straightforward. In the opposite case, we have to make the hypothesis of a linear pressure volume variation between two consecutive measurements at different pressure (equivalent to the Murnaghan hypothesis [3]). The thermodynamic definition of the incompressibility modulus $B = -V(\partial P/\partial V)_S$ is then given by $B = -V(\triangle P/\triangle V)_S$, and, with the knowledge of t(P) and the ambient conditions values of V and B, an iterative calculation enables to obtain step by step all thermoelastic quantities as function of pressure.

High Pressure and high temperature Brillouin scattering set-up [4]

In Brillouin scattering, light interacts inelastically with thermal acoustics phonons in a material. The energy of the scattered light is thus modified, increased in the case of an annihilation of a phonon, decreased in the case of a creation. The energy range encountered in Brillouin scattering from thermal excitations is on the order of the GHz. The corresponding wave number shift is given by:

$$\triangle\sigma = 2nv * sin(\theta/2)/(\lambda_0 c_0)$$

where v is the acoustic phonon velocity, n the refractive index and θ the angle between the incident and the scattered light (λ_0, c_0 being respectively the wavelength and the velocity of the light in vacuum). Due to the small frequency shift and the high contrast between the inelastically (Brillouin) and elastically scattered light (Rayleigh), a high dispersive power spectrometer is used, namely the sandercock spectrometer, made of two Fabry-Pérot interferometers in tandem. A typical spectrum recorded on water at high pressure and high temperature is shown in figure 6.

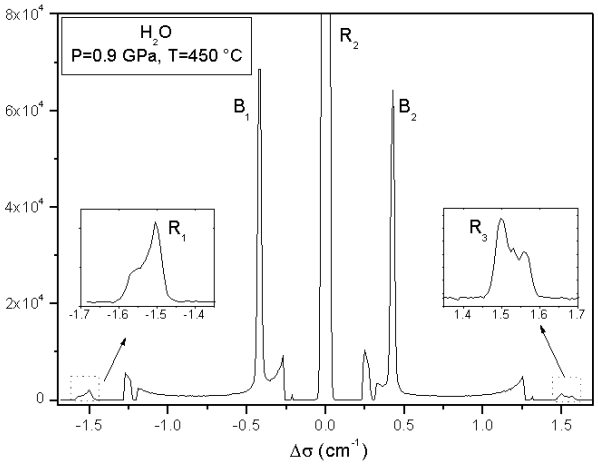

Figure 6: Backscattering Brillouin scattering spectrum of water at 0.9 GPa and 450 degrees C. The central unshifted Rayleigh peak is labelled R2. The Brillouin peaks are labelled B1 and B2. According that the refractive index is known, the sound velocity is then deduced using the following equation: $\triangle\sigma = 2nv/(\lambda_0 c_0)$.

This technique is particulary well adapted to study the pressure evolution of adiabatic elastic moduli by combining Brillouin spectroscopy with a diamond anvil cell (DAC) [5]. The principle of high pressure generation with DAC is shown in figure 7 and can be briefly described as the following : a metal gasket is placed between the small flat faces of two diamond anvils. The sample (with a typically volume of 100*100*20 μm^3) is placed in a hole (about 200 μm in diameter) drilled in the gasket together with a pressure transmitting fluid (helium, nitrogen,...) and a ruby chips (10 μm in diameter) which allows the in-situ pressure measurement by the luminescence method. The high pseudo-hydrostatic pressure is generated on the sample through the displacement of the piston due to the membranes deformation (itself produced by a low-pressure of helium gas).

Sound velocity of water up to 723 K and 9 GPa by Brillouin scattering experiment in DAC

Liquid water has a very interesting evolution under pressure, going from a highly-structured molecular liquid with strong hydrogen bonds, to a ionic conductor and eventually to a metal. The knowledge of its thermodynamic properties at extreme conditions is of great importance for a number of scientific problems in material sciences, Earth and planetary physics, and even biology. However, there exists rather few data on the sound velocity of water under extreme conditions. We

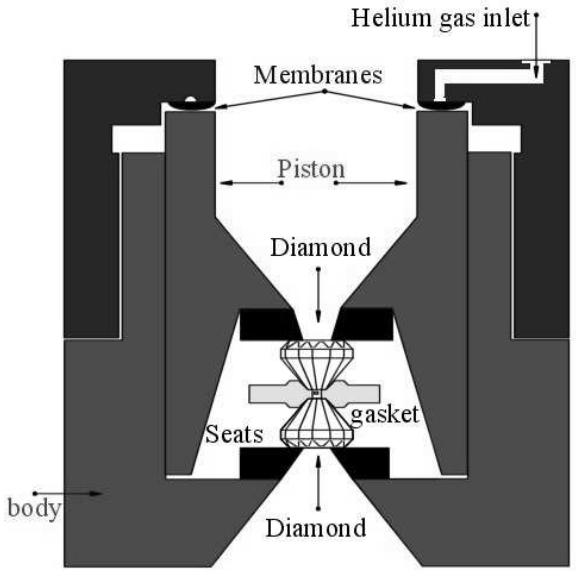

Figure 7: Diamond anvil cell principle. A metal gasket confines the sample within the ruby ball and the pressure transmitting medium, and is also used as anvils support. Diamond is chosen for its huge hardness and its transparency in a wide range of energy.

present here a study of the speed of sound and equation of state of liquid water up to 723 K and 9 GPa. This was achieved by Brillouin scattering experiments in a diamond anvil cell up to 9 GPa and 723 K, which is a good example of what can only be achieved with this technique, since, up to now, ultrasonic experiment in this (P,T) range can not be performed on liquids. The measured velocities are used to obtain an experimental equation of state (EoS). This EoS is compared to the 58-parameter EoS derived by Saul and Wagner [6] on the basis of an extensive data set. Moreover, this study is a good opportunity to check the continuity of the elastic properties, and more specifically to probe a possible liquid-liquid phase transition.

Because water at high pressure is chemically very aggressive, These experiments used a specific experimental techniques. The diamond anvil cell was made of high-temperature steel which was heated by a resistive external heater. The temperature was controlled by a thermocouple glued onto the side of one anvil. The Brillouin scattering measurements were made in a backscattering geometry ($\theta = \pi$), using the 514.5 nm line of an argon laser. Water was confined in a rhenium/gold composite gasket since rhenium is well-adapted to high pressure and high temperature studies. Gold was used to prevent chemical reactions between the water sample and the rhenium gasket on one hand, and the pressure gauge ($SrB_4O_7 : Sm_{2+}$), on the other hand, the latter being dissolved at temperatures above 500 K. A ruby ball serves as an additional in-situ temperature gauge (see figure 8).

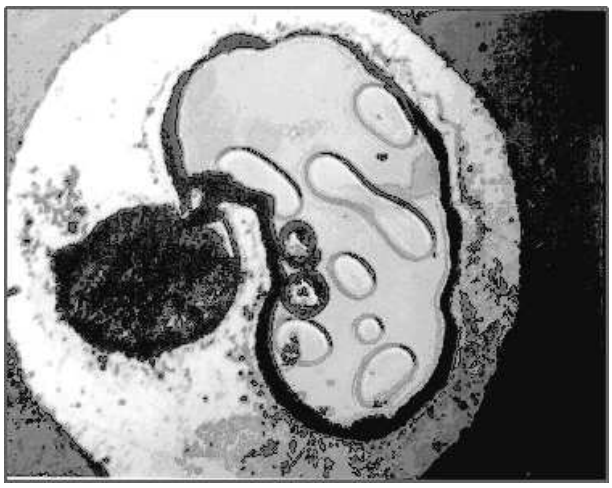

Figure 8: Picture of the rhenium gasket which confines H_2O samples at the liquid-ice VII transition (T=600 K and P=6.2 GPa).

Brillouin spectra have been collected along several isotherms between 300 K and 723 K. The measurements extend to the solidification pressure, which occurred usually a few kilobars above the melting point, unless for the 723 K isotherm where one of the anvils failed before completion. The following experimental data have been obtained in the backscattering geometry which means that we have to extract the refractive index variation to get the velocities. The experimental measurements of n recently published by Dewaele et al [7] have been used. The corresponding pressure variation of the sound velocity v in water along each isotherms is then used to calculate the variation of the density ρ by integrating the following thermodynamic equations:

$$(\partial\rho/\partial P)_T = 1/v^2 + T\alpha^2/C_P$$

$$(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)$$

where V is the volume, α the thermal expansion and C_P the specific heat at constant pressure. The first conclusion of this work, which is still on progress, is the good agreement of the Brillouin equation of state with the Saul and Wagner one, except at high temperature for the highest densities (see figure 9). Moreover, a clear continuity of the sound velocity provides the evidence of a local structure stability of water in this range of pressure and temperature.

Sound velocity of the invar alloy $Fe_{64}Ni_{36}$ up 7 GPa by ultrasonic measurements

About one century ago, it has bee found that for a particular chemical composition, Fe-Ni alloys do have

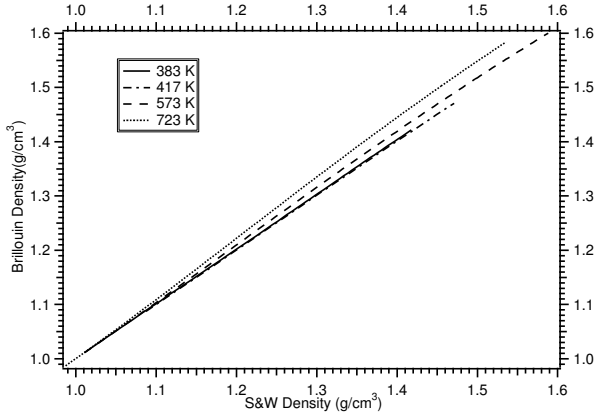

Figure 9: Comparison of the Saul and Wagner (S & W) equation of state with the present work (computation of Brillouin scattering sound velocity measurements).

almost no thermal expansion below the magnetic ordering temperature (so called invar compounds). More recently, high pressure studies of invar demonstrated that such alloys have also a small or even negative pressure dependence of the compressibility [8]. Both anomalies have the same origin, a magnetic contribution, which compensates the ever present volume expansion coming from the anharmonicity of the lattice vibrations by changing temperature, or which increases the classical volume collapse by applying pressure. On the other hand, while the macroscopic magnetovolume feature can be quantitatively understood, the microscopic mechanism leading to the magnetic contribution is still debated.

Among all theoretical models suggested to explain the invar effect, the two most popular ones, namely the 2 γ-state model [9] and the non-collinear model [10], are in contradiction for what concern the pressure variation of the invar bulk incompressibility modulus. The noncollinear model predicts the magnetic contribution to affect the thermodynamic properties through a continuous variation of the amplitude and the directions of the spins, giving rise to a continuous variation of the compressibility. On the other hand, the 2 γ-state model predicts a first-order transformation under pressure from a high-spin state to a low-spin configuration with a discontinuity of the incompressibility.

We study the pressure dependence of the sound velocity of a polycrystalline $Fe_{64}Ni_{36}$ invar compound using ultrasonic experiment under high pressure, which is the only method enabling to determine accurately and independently the pressure variation of the incompressibility modulus. The elastic isotropy of our sample limits the number of experiments to, at least, two corresponding to a longitudinal (L) and a transversal (T) polarization of the sound wave. The travel time change induced by the application of hydrostatic pressure to $Fe_{64}Ni_{36}$ up to 1 GPa and pseudo-hydrostatic pressure up to 7 GPa is given in figure 10.

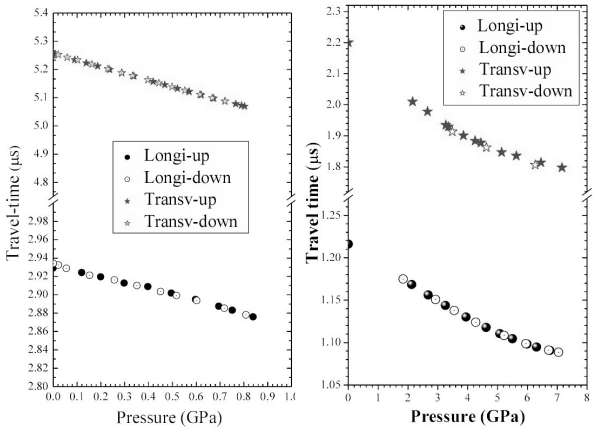

Figure 10: Pressure dependence of the ultrasonic travel time in $Fe_{64}Ni_{36}$. Between 0 and 2 GPa, the sample-anvil contact in the high pressure set-up (using the Paris-Edinburgh press) is not good enough to obtained reliable travel time measurements. Experiments using the piston-cylinder apparatus are in that sense complementary to high pressure measurements.

The incompressibility is then given by $B = \rho(v_L^2 - 4/3v_T^2)$ where ρ is the density of the polycristalline sample. Finally, using the ambient pressure value of ρ=8.066 g/cm^3 and B_0=117 GPa measured on the polycrystal, and the travel time data at each pressure, an iterative calculation (describe above) leads to the pressure variation of the incompressibility modulus (figure 11) in excellent agreement with the 2 γ-state model.

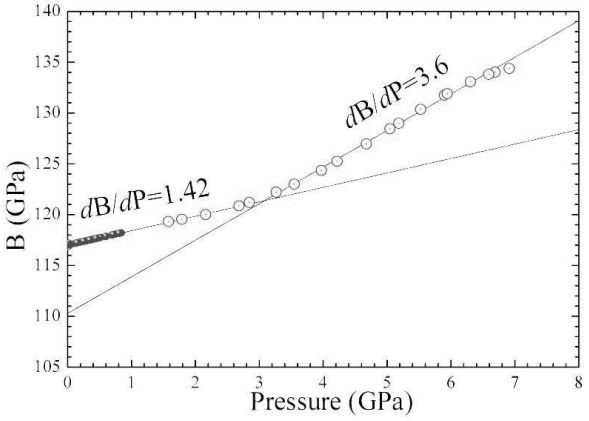

Figure 11: Pressure dependence of the incompressibility modulus of polycristalline $Fe_{64}Ni_{36}$.

New developments and future directions

High pressure and high temperature ultrasonic measurements

A recent development enable the ultrasonic sound velocity measurements at high pressure (0-6 GPa) and high temperature (0-800K). The principle, shown in figure 12 is based on the room temperature-high pressure set-up, where a graphite furnace has been introduced in the environment of the sample. The temperature is measured in-situ using a thermocouple and a cylinder of SiO_2 is placed between the upper anvil and the sample in order to thermally isolate the anvil (on which top face is glued the transducer) and to decrease the temperature gradient on the sample concomitant to the furnace geometry.

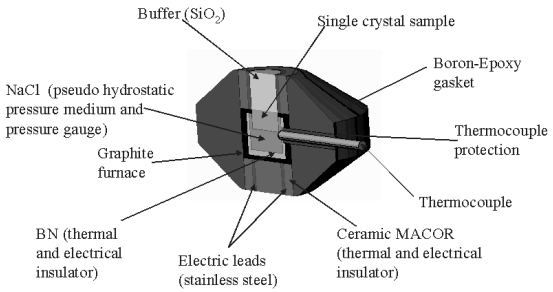

Figure 12: Cross-sectional view of the cell assembly for the high-pressure and high-temperature ultrasonic experiments in the Paris-Edinburgh press.

Using this set-up, the relative change in travel time of a single crystal of magnetite at 480K has been determined up to 6 GPa for three different direction of propagation and polarization (figure 13). Aside from confirming the feasibility of such measurements, these results are of interest from a geophysical point of view since it is confirm that the travel time of the magnetite is increasing under pressure, say the corresponding C_{44} elastic constant is softening which may have some implication on the mechanical stability of magnetite in the thermodynamical conditions of the Earth interior. Measurements of all independent elastic moduli of wüstite and magnetite under high pressure and high temperature are currently on progress using this technique.

High pressure ultrasonic measurements in laboratory

In the previous section entitled *"Ultrasonic measurements under pseudo-hydrostatic pressure up to 10 GPa*", the description of the cell assembly emphasized the presence of compressed NaCl powder used as a in-situ pressure gauge through its x-ray diffraction equation of state measurement. This last point is indubitably in contradiction with the title of this article. However, the use of same cell assembly with a buffer rod between the sample and the upper anvil (where the transducer is glued) will enable such measurements in laboratory (see figure 14). The principle, proposed by R. C. Liebermann [11], is to choose a buffer made on a compound for which the pressure dependence of the sound velocity is well known. The experimental determination of the pressure variation of its travel time will thus give an indirect in-situ high pressure marker.

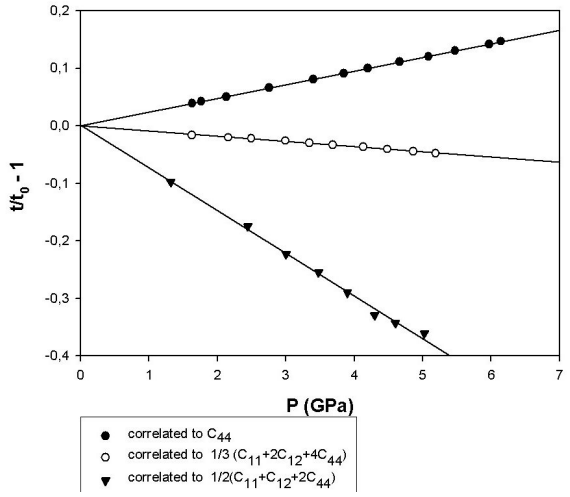

Figure 13: Relative pressure variation of the travel time of a magnetite single crystal under high temperature (400 K).

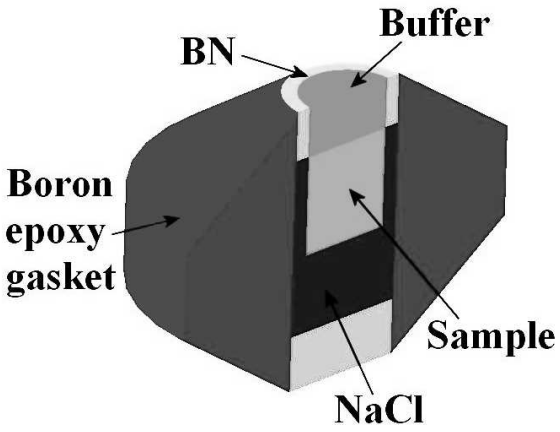

Figure 14: Cross-sectional view of the cell assembly for the high-pressure ultrasonic experiments in the Paris-Edinburgh press in laboratory.

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