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A setup for the measurement of ultrasonic properties of single crystals at high pressure in the 10 GPa range is presented. In order to validate this new device, based on the ''Paris–Edinburgh'' press, the elastic properties of germanium have been measured and compared with the published data. The transit times of the ultrasonic waves are directly measured. The three elastic moduli and their pressure derivatives are obtained up to 6 GPa through three different methods of calculation, which are presented and compared. These results are in good agreement with previous results and hence validate the device. The Paris–Edinburgh press enables *in situ* measurement of ultrasonic and x-ray diffraction on the studied sample. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Measurement of the pressure dependence of the sound velocity is an important task in condensed matter physics, in chemistry as well as in geophysics. Actually, significant changes in crystal structure or electronic character of materials are often clearly revealed through changes in elastic properties; even subtle variations in magnetic, electronic, and structural states may be detected. At ambient conditions, the most accurate measurements of the elastic properties of materials are obtained by ultrasonic methods (provided sufficiently large samples are available). Under high pressure, the most used technique to investigate elastic properties is Brillouin scattering, but it is generally restricted to the study of transparent samples. Nevertheless, progress in the design of high pressure presses and high frequency ultrasonic transducers opened in the last decade the possibility to measure the elastic properties of materials, like minerals in the 10 GPa range.[1] In the most advanced setups, the pressure generation is made by multi-anvil large volume presses of the SAM85 type.[1] These presses enable simultaneously high pressure and high temperature measurements, but their large weight and dimensions make it quasi impossible to move.

The aim of this article is to present a technique, which allows high accuracy measurements on samples that may be opaque at high pressure. Initially, developed for high-pressure neutron scattering, the Paris–Edinburgh press (PE press) (Ref. 2) allows pressurizing large volume samples (few mm^3) up to 30 GPa.[3] Its reasonable dimensions (25 X25X25 cm^3 and 50 kg) make it a very amenable tool to study the high-pressure properties of samples with various probes, like x-ray diffraction or neutron scattering. We have made some adaptations to the PE press, which now fulfills the requirements for simultaneous ultrasonic and x-ray diffraction measurements. In order to validate this new setup, the elastic properties of a single crystal of germanium were measured under high pressure up to 6 GPa and compared with published data obtained by McSkimin *et al.*[4] using a low-pressure ultrasonic setup, which is a routine setup, and by Goncharova *et al.*[5] using another high-pressure ultrasonic setup.

In ultrasonics, the measured physical quantity is the transit time of an elastic wave through the sample. Three different methods of calculation were used to deduce the elastic constants, the bulk modulus and its pressure derivative, and the equation of state of germanium from the transit time.

II. EXPERIMENT

A. Samples

The studied samples were cylinders and the sound velocity was measured along the cylinder axis. The parallelism between the two faces was better than 1°. Two ~3-mm-long samples were studied, one with the ultrasonic wave propagation direction along the [100] and the other one along the [110] crystallographic direction. Two diameters of cylinders were used; the first one of 3 mm allows measuring ultrasonic transit time up to 4 GPa and the second one of 2.4 mm up to 6 GPa.

B. High-pressure setup

In the PE press, the samples are compressed between two opposite toroidal tungsten carbide anvils. The force is generated by a hydraulic press connected through a capillary to the piston.

In order to adapt this cell for ultrasonic measurements, the anvil profiles have been modified: the rear face of both anvils were flattened and polished. A 2 μm gold foil was introduced between the WC anvil and the sample in order to smooth the contact surface and to enhance the mechanical bonding at high pressure: the contact between the sample and

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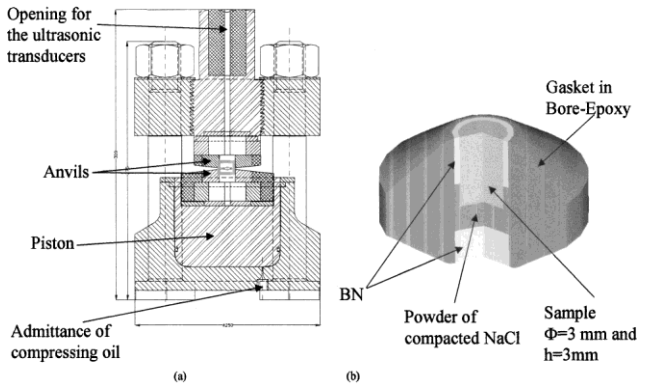

FIG. 1. (a) Paris–Edinburgh press. (b) Experimental volume: the studied sample and its surrounding.

the anvil has to be as good as possible to provide a good transmission of the ultrasonic wave in the sample. Therefore, a minimum pressure of 1 GPa is needed to obtain ultrasonic echoes. The upper anvil is used as a buffer rod. The press and the sample surroundings are shown in Figs. 1(a) and 1(b).

The sample is surrounded by a hexagonal boron nitride (BN) cylinder, which is used as a pressure-transmitting medium. Compressed NaCl powder used as a pressure gauge is located below and around the cylindrical sample. This setup is placed into a boron epoxy gasket (5:1 in mass) that has a low x-ray absorption.

C. X-ray diffraction

The pressure was determined by the following procedure: the sodium chloride lattice parameter is measured, and the corresponding pressure is obtained from the Murnaghan equation of state using B_0=24.01 GPa and B'=4.18.[6] Energy dispersive x-ray diffraction was carried out on the DW11 wiggler beamline of the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE), Orsay, France. The pressure is determined *in situ* with an accuracy of ±3%.

D. Ultrasonics

Longitudinal and transverse waves are generated by lithium niobate plates, which are fixed on the upper face of the anvil (Fig. 2). The Y +90° and Y +168° cuts generate, respectively; pure longitudinal and pure shear waves. In order to maintain a good directivity of the ultrasonic beam, the resonance frequency of the transducers was chosen around 20 MHz. A microwave frequency synthesizer is used as the signal source. A pulse generator modulates the continuous output of the signal generator. The pulse generator is capable of sending out a gating pulse with variable pulse widths. After propagating through the anvil, an initial pulse produced by the transducer is partially reflected at the anvil-sample interface, resulting in a first echo, while the other part is transmitted inside the sample. 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, giving rise to the sample echo following the anvil one. A digital oscilloscope records the ultrasonic wave echoes [Fig. 2(b)]. The time difference needed to superpose the two echoes corresponds to the two-way travel time of the pulse through the sample. This 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. The

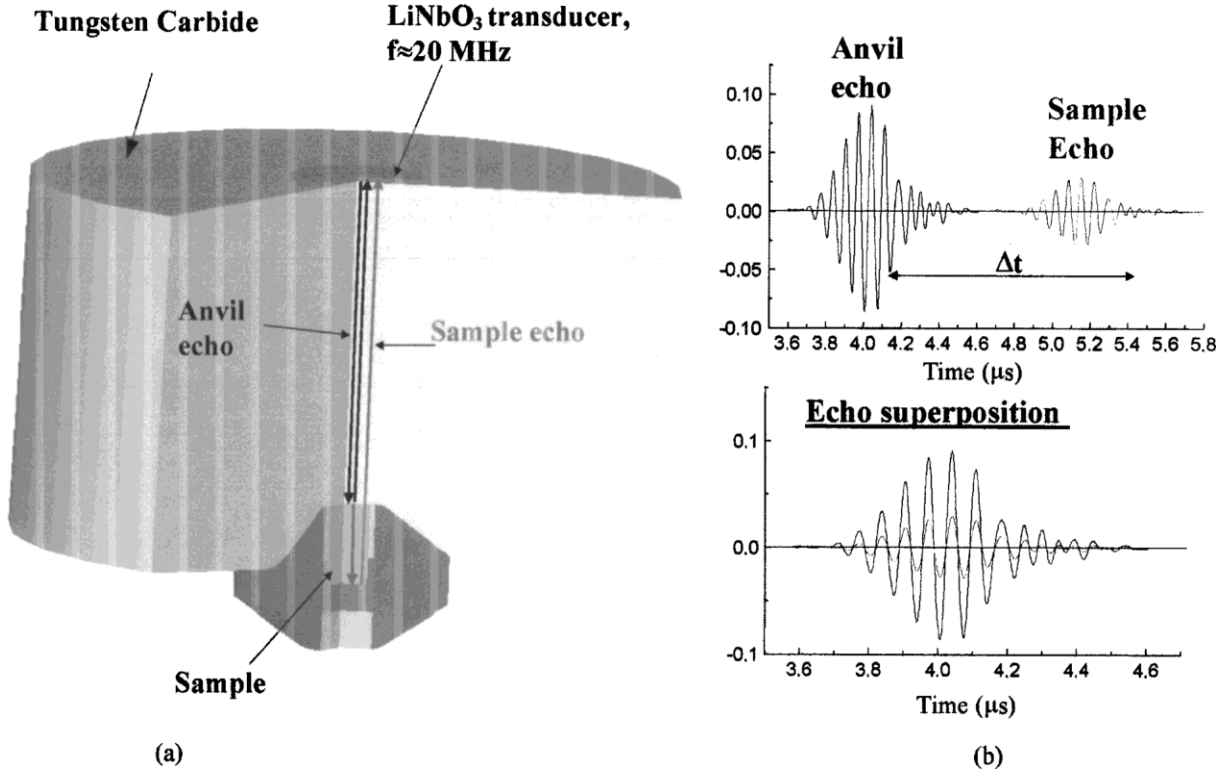

FIG. 2. (a) Ultrasonic paths through the anvil and the sample. (b) Example of recorded signals and superposition of echoes in order to measure the transit time.

effect of the bond phase shift in ultrasonics measurements under pressure has been shown[7] to change the intrinsic travel time t as $t = t_{mes} - \varphi/2\pi f$, where φ corresponds to the total bond phase shift between the buffer rod (anvil) and the sample, t_{mes} is the experimental travel time and f the ultrasonic frequency. It is difficult to quantify the bond phase shift contribution. However, in one experiment of the present work, the pressure dependence of the travel time has been determined with different frequencies between 20 and 60 MHz. The dispersion is less than 1%, indicating that the frequency used in the other experiments (20 MHz) was sufficiently high to vanish the bond phase shift perturbation ($\varphi/2\pi f$) due to the gold foil.

III. CALCULATION METHODS

From the measured transit times, the elastic constants of germanium under pressure are calculated by three different methods. Two basic assumptions are made for these acoustic measurements: (i) the ultrasound in the sample is considered as plane waves and (ii) the pressure is supposed to be hydrostatic. We did not take into consideration the difference between the isothermal and the adiabatic elastic constants, and in view of Wallace theory,[8] we calculated the effective elastic constants.

In the first method, the equation of state of the studied sample has to be known. In that case, the elastic constants are directly calculated.

The second method, developed by Brugger and Thurston[9,10] may be used if the pressure remains negligible in comparison with the elastic constants.

The third one, developed by Cook[11] may be used in all other cases.

A. Method 1: Equation of state method

In a single crystal, the sound velocity v is related to the elastic moduli C_{ij} by

$$\rho v^2 = \sum a_{ij} C_{ij} = C, \tag{1}$$

where ρ is the density, the a_{ij} are coefficients depending on the propagation and polarization directions of the ultrasonic waves, and C is the linear combination of elastic moduli for the given propagation direction. ρ, v, and C are pressure dependent. The relations between the sound velocities and the elastic moduli in a cubic system are summarized in Table I.

In the case of ultrasonic reflection measurements, the measured transit times are linked to the sound velocities by the following expression:

$$v(P) = \frac{2d(P)}{t(P)},$$

where $d(P)$ is the length of the sample under pressure and $t(P)$ is the two-way transit time.

In a cubic system, the elastic moduli can be expressed by the following equation:

TABLE I. Elastic moduli as a function of the crystallographic directions of propagation and of the acoustic wave polarizations in a cubic system.

Propagation direction	Acoustic wave polarizations	Sound velocities	Elastic moduli
[100]	Longitudinal	v_1	C_{11}
[100]	Shear	v_t	C_{44}
[110]	Longitudinal	v_1	$\frac{C_{11}+C_{12}+2C_{44}}{2}$
[110]	Shear	v_{t1}	C_{44}
[110]	Shear	v_{t2}	$\frac{C_{11}-C_{12}}{2}$

$$C = 4\rho_0 d_0^2 \left(\frac{V_0}{V(P)}\right)^{1/3} \frac{1}{t^2(P)}, \tag{2}$$

where ρ_0, d_0, and V_0 are, respectively, the density, the length, and the volume of the sample at ambient conditions; $V(P)$ is the volume at the pressure P. Thus, if the density and the length of the sample at ambient conditions are known and the equation of state was previously measured or reproduced by a phenomenological model (for example, the Murnaghan equation of state), the elastic moduli are directly deduced from the measured ultrasonic transit time.

B. Method 2: Brugger and Thurston method

The Thurston and Brugger method[9] allows calculating the pressure derivative of the elastic moduli from the pressure derivative of the ultrasonic transit times. The details of the calculation are not described here but can be found in Ref. 8. This method is valid if the pressure is small in comparison with the elastic moduli. In view of the experimental measurements, it is convenient to eliminate the $d(P)$ dependence of the sound velocity by studying instead of the velocity the ''natural speed'' $W(P)$ defined by

$$W(P) = \frac{2d_0}{t(P)},$$

where d_0 is the length of the sample at ambient condition. In this case, the elastic moduli can be written as (the subscript 0 indicates the ambient pressure values):

$$C = \rho v^2 = (\rho_0 W^2) + P\left[\left(\frac{\partial(\rho_0 W^2)}{\partial P}\right)_0 + \frac{(\rho_0 W^2)_0}{3B_0}\right], \tag{3}$$

where B_0 is the bulk modulus at ambient conditions. Finally, the derivative of the elastic moduli is written as a function of the transit time pressure derivative as

$$\left(\frac{\partial C}{\partial P}\right)_0 = -2\frac{\rho_0 W_0^2 d_0}{t_0}\left(\frac{dt}{dP}\right)_0 + \left(\frac{\rho_0 W_0^2}{3B_0}\right). \tag{4}$$

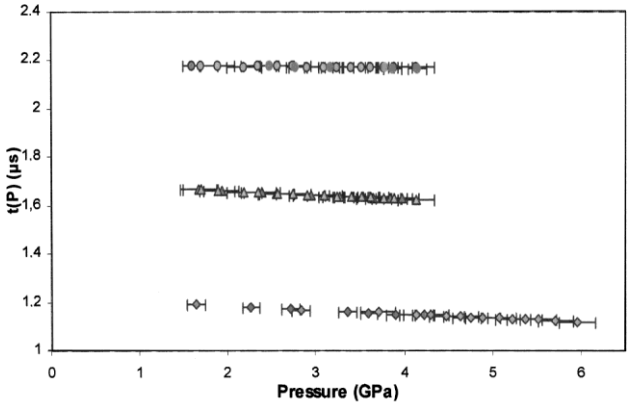

FIG. 3. Ultrasonic transit times under pressure. The diamonds show the longitudinal transit times in the [100] direction (C_{11}), the triangles show the shear transit times in the [100] direction (C_{44}) and the circles show the shear transit times in the [110] direction [$(C_{11}-C_{12})/2$].

C. Method 3: Cook method

The Cook method of calculation[11] enables to deduce the elastic constants of a cubic crystal under hydrostatic pressure from the experimental measurements of ultrasonic transit times.

In the case of a cubic crystal under hydrostatic pressure, a parameter $s(P)$ can be defined as

$$d(P)=\frac{d_0}{s(P)}.$$

The density of the sample can be expressed as a function of $s(P)$:

$$\rho(P)=\rho_0 s^3(P), \tag{5}$$

as well as the linear combination of elastic moduli:

$$\rho v_k^2(P)=\frac{4d^2\rho_0 s(P)}{t_k^2(P)}, \tag{6}$$

where t_k is the transit time corresponding to the sound velocity v_k in the studied crystallographic direction.

In a cubic system, the bulk modulus B_0 can be expressed as a function of C_{11} and C_{12} :

$$B_0=-V\left(\frac{dP}{dV}\right)_0=\frac{C_{11}+2C_{12}}{3}. \tag{7}$$

The combination of Eqs. (5) and (7) gives

$$ds=\frac{s}{C_{11}+2C_{12}}dP. \tag{8}$$

The ratio $1/(C_{11}+2C_{12})$ can be expressed as a function of $s(P)$ using Eq. (6) for several different elastic moduli. Finally, we obtain

$$ds=\frac{1}{4d_0^2\rho_0}f(\ldots,t_{k-1},t_k,t_{k+1},\ldots)dP, \tag{9}$$

where f is a function, which depends on the different transit times corresponding to the different elastic moduli used for the calculation. Integrating Eq. (9), the parameter $s(P)$ can be calculated for each pressure and the elastic moduli from $s(P)$ values using Eq. (6). The equation of state can be calculated directly from the following equation:

$$\frac{V(P)}{V_0}=\frac{1}{s^3(P)}. \tag{10}$$

TABLE II. Values of the pressure derivatives of the elastic constants of germanium in the 1– 6 GPa pressure range. For methods 1 and 3, the pressure derivatives are calculated by linear regression of the elastic constant values.

	$(\partial C_{ij}/\partial P)$				
C_{ij}	Method 1: Equation of state	Method 2: Thurston and Brugger[a]	Method 3: Cook[b]	McSkimin *et al.*[c]	Goncharova *et al.*[d]
C_{11}	4.99	4.90±0.2	4.82	5.25	4.89
C_{44}	1.74	1.75±0.1	1.73	1.55	1.12
C_{12}	4.39	4.32±0.4	4.16	4.45	4.39

[a]Reference 9.
[b]Reference 11.
[c]Reference 4.
[d]Reference 5.

IV. RESULTS AND DISCUSSION

The ultrasonic transit times of longitudinal waves along the [100] direction and the transit time of shear waves along the [100] and [110] directions were measured up to 4 or 6 GPa, respectively, depending on the diameter of the sample. The samples have different lengths, all around 3 mm. Thus, in order to compare the experiments, the ultrasonic transit times have been normalized for the same length (3 mm). The ultrasonic transit times are shown in Fig. 3. The reproducibility of the experiments is good. In view of the linear behavior of the transit times, their mean slopes are determined by linear regression.

The elastic moduli were determined by each of the three methods of calculation with an accuracy of ±1 GPa.

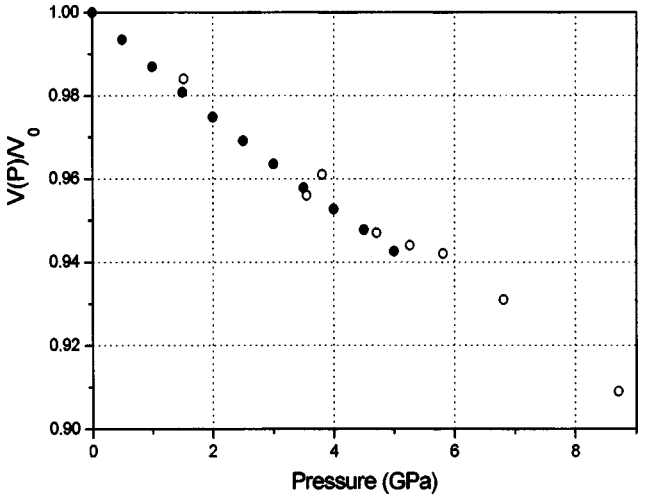

FIG. 4. Equation of state of germanium. The full symbols show our ultrasonic results (Cook method), and the empty ones the results of Menoni *et al.* (Ref. 11) obtained by x-ray diffraction.

First, the elastic moduli have been calculated using the Murnaghan equation of state

$$V = V_0 \left(1 + \frac{B' P}{B_0} \right)^{-1/B'}$$

and the values of the bulk modulus and its pressure derivative obtained by McSkimin *et al.*[4] (ρ_0=5.32 g/cm^3, B_0 =75 GPa and B'=4.71).

Second, the elastic moduli were calculated by Thurston and Brugger's method. The results of McSkimin *et al.*[4] at ambient conditions (C_{11}=128 GPa, C_{44}=66 GPa, and C_{12} =48 GPa) were introduced in Eq. (4) in order to calculate the elastic moduli as a function of pressure.

Finally, the Cook method was applied. The linear interpolations of the transit times were introduced in the calculation in order to define the function f in Eq. (9).

The obtained pressure derivatives of the elastic constants of germanium in the 1– 6 GPa pressure range are given in Table II.

The three calculation methods show a good overall agreement. Our results concerning C_{11} and C_{12} are in good agreement with previous studies, whereas the pressure derivatives of C_{44} show discrepancies. The different pressure range could explain the difference with McSkimin's results, while it is difficult to account for the differences with Goncharova. The non-hydrostaticity of the measurements could explain the differences. The deviatoric conditions may be estimated from x-ray diffraction measurements of the lattice parameter of powdered NaCl, as deduced from the individual diffraction lines (Singh). Such a measurement has been performed in the Paris–Edinburgh press, and has been shown to be less than 5% below 10 GPa.

The equation of state was deduced from our ultrasonic results using the Cook method and Eq. (10). It is shown in Fig. 4 and compared with that of Menoni *et al.*[12] measured by x-ray diffraction on a powder sample using a diamond anvil cell to generate pressure. Fitting our results with a Murnaghan's equation of state, the bulk modulus and its pressure derivative were determined as B_0 =74±2 GPa and B_0'=4.4 ±0.5. The previous results obtained by Goncharova *et al.*, Menoni *et al.*, and McSkimin *et al.* are, respectively, 74.5, 74.9, and 75 GPa for B_0 and, respectively, 4.4, 3, and 4.71 for B'. Our results are in a good agreement with the previous determinations, except the B' determined by x-ray diffraction: there are three fitting parameters (at least) in the equations of state. When the stability range of a crystalline form is not sufficient (it is the case here) the parameters are determined with a poor precision, and most of the authors do fix arbitrarily the pressure derivative of the bulk modulus. It is one of the advantages of the *in situ* ultrasonic determination of the parameters to not depend of the stability range of the studied compounds.

We have hence demonstrated the validity of the ultrasonic measurements obtained with our experimental setup. Measurements up to 10 GPa are expected to be possible by reducing the size of the sample; this first study demonstrates this possibility. Moreover, the Paris–Edinburgh press enables to perform x-ray diffraction measurements under pressure. A technical development is under progress to allow x-ray diffraction measurements on the studied single crystal, and hence, to measure simultaneously the equation of state and the elastic moduli of the sample. Moreover, this setup allows to perform high-temperature measurements by inserting an oven in the experimental volume. The adaptation of this high-pressure and high-temperature setup to ultrasonic measurements is also in progress.

ACKNOWLEDGMENTS

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[1] A very good and recent review of the state of the art is given in R. C. Liebermann and B. Li, Rev. Mineral. **37**, 459 (1998).
[2] J. M. Besson, G. Hamel, and G. Weill, European Patent No. 0509928 (1991).
[3] J. M. Besson, R. J. Nelmes, G. Hamel, J. S. Loveday, G. Weill, and S. Hull, Physica B **180&181**, 907 (1992).
[4] H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **34**, 651 (1963).
[5] V. A. Goncharova, E. V. Chernyscheva, and F. F. Voronov, Sov. Phys. Solid State **25**, 2118 (1983).
[6] D. L. Decker, J. Appl. Phys. **36**, 157 (1965).
[7] I. Jackson, H. Niesler, and D. J. Weidner, J. Geophys. Res. **86**, 3736 (1981).
[8] D. C. Wallace, in *Solid State*, edited by F. Seitz and D. Turnbull (Academic, New York, 1970), Vol. 25, p. 301.
[9] R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).
[10] K. Brugger, Phys. Rev. **133**, A1611 (1964).
[11] R. K. Cook, J. Acoust. Soc. Am. **29**, 445 (1957).
[12] C. S. Menoni, J. Z. Hu, J. Z. Hu, and I. L. Spain, Phys. Rev. B **34**, 362 (1986).