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# Brillouin scattering from GaS under hydrostatic pressure up to 17.5 GPa

A. Polian and J. M. Besson

*Laboratoire de Physique des Solides, Associé au CNRS, Université Pierre et Marie Curie, T. 13, E. 2, 4, place Jussieu, 75230 Paris, Cedex 05, France*

M. Grimsditch<sup>a)</sup> and H. Vogt

*Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D 7000, Stuttgart 80, Germany*

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Brillouin scattering in GaS crystals has been measured under hydrostatic pressures up to 17.5 GPa. Frequency shifts of the Brillouin lines give the pressure dependence of the elastic constants  $C_{11}$  and  $C_{33}$ , and the index birefringence. Exponents derived from Murnaghan's equation of state are compared with a Lennard-Jones description of interatomic forces in GaS.

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Pressure is a fundamental thermodynamic variable and thus plays a dominant role in our understanding of matter. In diamond anvil cells, a variety of physical methods can now be used in the range of 100 GPa, that is, one order of magnitude higher than ten years ago. Under those conditions, variations in the bond strengths are comparable with the low-pressure interatomic forces themselves and pressures are of the same order as those encountered in the interior of the earth: this opens new possibilities in condensed matter physics, which are of interest to geophysics. The most serious drawbacks of the diamond anvil cell are the sample size (typically  $100 \times 100 \times 20 \mu^3$ ), and the difficulty of introducing electrical leads into the cell. Thus a few conventional measuring techniques cannot yet be utilized, and hence some physical properties remain unprobed at these high pressures. Elastic properties are a typical example: ultrasonic measurements have not yet been possible under these high-pressure conditions.

Brillouin scattering from NaCl up to 3.5 GPa has been reported<sup>1</sup> with a modified diamond cell, where the measurement of the refractive index versus pressure could be avoided. The experimental conditions in that case require a large optical aperture and thus limit the maximum pressure to a small fraction of the capabilities of the diamond anvil cell techniques ( $> 50$  GPa). In this letter we report results which were obtained in a normal-incidence, small aperture geometry, which can be used over the full range of pressure attainable by the diamond anvil cell technique. This method implies three distinct measurements in the same pressure run: (i) the compressibility of the sample by optical methods; (ii) the variation of the refractive index, from the observation of the interference pattern of a plane parallel sample; (iii) the shift of Brillouin lines in two different polarizations.

Gallium monosulfide was chosen for its high-scattering cross section<sup>2</sup> due to its layer structure. In the experiments we report here, pressure was limited to 17.5 GPa, since a transition to an opaque phase takes place. The method is

nevertheless applicable to optically transparent samples above this value<sup>3</sup> under homogeneous stress conditions.<sup>4</sup> The elastic constants  $C_{11}$  and  $C_{33}$  that we have measured are compared with existing equations of state. In the case of GaS, which is not cubic, we have assumed a dependence of the same form as that of Murnaghan's equation, but a function of the linear dimension of the sample. The fits we obtain and the magnitude of the pressure derivatives of the elastic constants are compared with the assumption of a simple Lennard-Jones potential to describe the interlayer forces.

The diamond anvil cell and the five-pass Fabry-Perot have been described in Refs. (4) and (5) respectively. The pressure was measured using the ruby luminescence scale. Stress inhomogeneity was smaller than 0.5 GPa up to 17.5 GPa; the pressure-transmitting medium was the classical 1:4 ethanol methanol mixture. The free spectral range of the Fabry-Perot was chosen to be an integral fraction of the frequency shift of the Brillouin lines of diamond in order to avoid overlap with the lines under study. The spectra were recorded using  $\sim 150$  mW of the 647.1-nm radiation from a  $\text{Kr}^+$  ion laser. As-grown hexagonal needles of GaS, obtained by vapor transport deposition,<sup>6</sup> were used. Those crystals have six natural faces parallel to the axis of the whisker ( $c$  axis) and can be readily cleaved perpendicular to the axis. Thus measurements can be readily performed with light incident parallel or perpendicular to the  $c$  axis.

Direct micrometric measurement<sup>7</sup> of the variation of the needle length ( $\bar{c}$  axis) and of the hexagonal faces ( $a$  axes) lead to the linear compressibilities. The observation of the interference extrema with light incident on plane parallel samples, cleaved normal to the  $c$  axis gives the variation of the optical path length, and, knowing  $\Delta c/\Delta p$ , the variation of the ordinary refractive index  $n_o$ . Brillouin measurements have to be made with light parallel and perpendicular to the  $c$  axis. It was found that, up to the highest pressures used here, the piezobirefringence of the diamonds induced negligible depolarization, which is not unexpected in this geometry, where the incidence of light is normal to the window faces and the unsupported area of the anvil kept at a minimum.

In Fig. 1, we present the measured frequency shifts as a

<sup>a)</sup>Present address: Argonne National Laboratory 9700 South Case Avenue Argonne, Ill. 60439.

function of pressure.  $\nu_1$  and  $\nu_2$  correspond to a phonon propagating in GaS perpendicular to the  $c$  axis, for polarizations of the electric vector of incident light respectively perpendicular and parallel to the  $c$  axis. The ratio of  $\nu_1$  and  $\nu_2$  directly gives the birefringence of the sample as a function of  $P$ , and it should be noted that, as the phase transition is approached, the crystal becomes optically isotropic. The frequency  $\nu_3$  corresponds to a phonon propagating along the axis. It is related to  $\nu_1$  and the elastic constants as

$$(\nu_1/\nu_3) = C_{11}/C_{33},$$

independent of refractive index or density changes. From Fig. 1, it is then also clear that the sample is approaching an isotropic bonding scheme, (i.e.,  $C_{11} \rightarrow C_{33}$ ). Using the variation of the refractive index and of the density of GaS with pressure, we calculate the elastic moduli  $C_{11}$  and  $C_{33}$  of GaS, which are shown in Fig. 2. Our values of elastic properties under high pressure can be compared with existing equations of state. In this letter, we have fitted our results with the Murnaghan equation<sup>8</sup>:

$$P = (B_0/B'_0) \left[ (\rho/\rho_0)^{B'_0} - 1 \right], \quad (2)$$

where  $B_0$  is the bulk modulus at atmospheric pressure,  $B'_0$  its derivative with respect to pressure, and  $\rho$  the density. From Eq. (2), it follows that

$$B = B_0(\rho/\rho_0)^{B'_0}. \quad (3)$$

In the case of an elastically isotropic medium,  $B_0 = C_{11} - 4/3C_{44}$ . Assuming that  $C_{44}$  is either small, or had the same density dependence as  $C_{11}$ ,

$$C_{11}(\rho) = C_{11}(0)(\rho/\rho_0)^{B'_0}. \quad (4)$$

Equation 4 may be extended to the noncubic case by assuming that the dominant forces that determine  $C_{11}$  and  $C_{33}$  are along the  $a$  and  $c$  directions, respectively, which leads to

$$C_{11} = C_{11}(0) (a_0/a)^{B'_1} \quad (5)$$

$$C_{33} = C_{33}(0) (c_0/c)^{B'_2}. \quad (6)$$

Those equations define  $B'_1$  and  $B'_2$  in such a manner that for a cubic crystal they coincide with  $B'_0$  of Eq. (4).

In Fig. 3, we plotted the logarithm of the elastic moduli versus  $a_0/a$  for  $C_{11}$  and  $c_0/c$  for  $C_{33}$  in GaS. The fit of the experimental results with straight lines yields  $B'_1 = 2.2$ , and

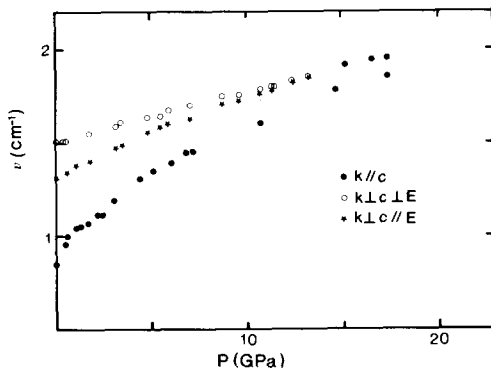


FIG. 1. Brillouin frequency shifts in GaS at room temperature vs pressure for three different geometries.

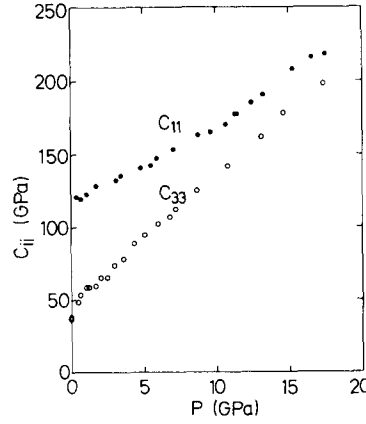


FIG. 2. Elastic moduli vs pressure (see text).

$B'_2 = 5.3$ .

Those values may be compared with the isotropic case: in the course of these experiments, we also measured the Brillouin shift from the pressuretransmitting medium, a 1:4 mixture of ethanol and methanol, which is an overdriven fluid up to 10 G Pa. Brillouin shifts were measured under pressure. The density and refractive index variations were extrapolated from published data.<sup>9</sup> The empty stars in Fig. 3 represent the elastic modulus of the ethanol methanol mixture versus  $\rho_0/\rho$  [Eqs. (3) and (4)]. We find here that  $B'_0$  is close to 7. This value can be very simply explained using a Lennard-Jones-type interaction potential:

$$\Phi = (\alpha/r^{12}) - (\beta/r^6) \quad (7)$$

where  $r$  is the interatomic distance and  $\alpha$  and  $\beta$  are constants. Using the equilibrium distance and force constant at zero pressure as fitting constants, we obtain, accurate only to first order in  $\Delta r/r_0$ ,

$$C = C_0 (r_0/r)^{21}, \quad (8)$$

which is equivalent to  $B'_0 = 7$ . One would expect Eq. (8) to be a good approximation when Van der Waals forces are responsible for the attractive potential, e.g.,  $B' = 7.0$ . In fact, from the values we deduced for GaS, we see that  $B'_2$  is the order of magnitude of three-dimensional isotropic  $B'_0$  values. This is not the case for  $B'_1$ . This is to be related with the fact that, in hydrostatic compression, most of the deforma-

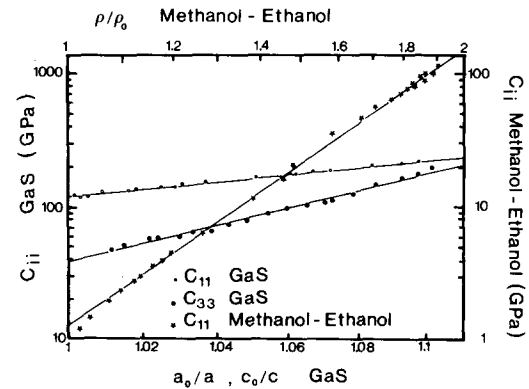


FIG. 3. Elastic moduli (log. scale) of GaS and the methanol-ethanol mixture vs the inverse of cell dimensions of GaS (lower scale) and vs reduced density for ethanol-methanol (upper scale). For the latter, we also included the data of Ref. (13) for  $\rho/\rho_0 < 1.2$ .

tion in GaS takes place within the interlayer space.<sup>10</sup>

In the previous paragraph, we have used Murnaghan's and related equations to fit our results. The reason for choosing this formula rather than other existing ones is that fits to  $C_{11}$  in ethanol methanol according to the equations of state<sup>11</sup> and Birch, Tait, or Linear-Secant Modulus are far from satisfactory.

In the geometry used here transverse modes were not observable. Nevertheless, those measurements are entirely feasible using different incidence conditions and more elaborate data acquisition methods. A more complete set of elastic constants could thus be obtained.

Thus direct measurement of the elastic constants, refractive index, and density are now possible in the 10–100-GPa range. This gives access to numerous fundamental properties such as sound velocities or equations of state, which are important in geophysics.

Moreover, Brillouin techniques are well suited to high-temperature measurements in the diamond anvil cell by power-laser local heating<sup>12</sup> within the device, since the emis-

sion from a given portion of the crystal can be optically isolated and studied independently.

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## Raman diffusion profilometry:OH in vitreous SiO<sub>2</sub>

F. L. Galeener and J. C. Mikkelsen, Jr.

Xerox Palo Alto Research Centers, Palo Alto, California 94304

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Techniques are described for using Raman spectroscopy to measure the concentration profiles of impurities that have been diffused into transparent host media. Profiles are presented for the diffusion of water into fused silica. Spatial resolutions of 50  $\mu\text{m}$  for concentrations of OH above 180 ppm (by weight) are demonstrated, and order of magnitude improvements over these values are confidently predicted.

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Water in the form of -OH units is an ubiquitous impurity in oxide materials, including vitreous ( $v$ -) SiO<sub>2</sub>. The presence of OH is undesirable in optical communication fibers, since it gives unwanted absorption in the infrared. In other applications, however, small (and even large) quantities of OH may be desirable, e.g., because they reduce the viscosity of  $v$ -SiO<sub>2</sub>. In many cases, the presence of OH is simply unavoidable; an example is the OH incorporated into films of  $v$ -SiO<sub>2</sub> which are fabricated by the steam oxidation of Si, a process of growing importance in Si based metal oxide semiconductor electronics. Of interest in these particular situations (and others) is the quantitative and qualitative nature of the hydration due to "diffusion" of water into otherwise pure SiO<sub>2</sub>.

In this letter, we describe a technique of Raman spectroscopy which proves useful for studying the spatial distribution of Raman-active impurities or defects in many transparent host materials and illustrate its use to measure the penetration of steam into fused silica. A more extensive presentation of results for this special case of diffusion of H<sub>2</sub>O into fused silica will appear elsewhere.<sup>1</sup>

The example to be described is based on the observation of Galeener and Geils<sup>2</sup> that very small concentrations of OH (> 1 ppm) are easily detected in the Raman spectrum of bulk fused silica. This is because the O-H stretch vibration at  $\sim 3700\text{ cm}^{-1}$  is strongly Raman active and is far removed from other features in the spectrum, as shown in Fig. 1. The origin of this line<sup>2-6</sup> and of other features in the spectrum<sup>7</sup> is