Surface acoustic waves in the diamond anvil cell: An application of impulsive stimulated light scattering

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Impulsive stimulated light scattering (ISS) has been used to probe the pressure dependence of the surface acoustic waves supported at the interfaces formed by single crystals of Ge and Ta in contact with the pressure-transmitting media liquid methanol and solid Ar, respectively. In the former system, the relevant excitation is a Scholte wave; its velocity has been measured as function of direction in the crystal surface to a pressure of 2.2 GPa. In the latter system, the velocity of the Stoneley wave has been measured in the same way to a pressure of 7.7 GPa. In both cases, calculated velocities, obtained by evaluating the surface perpendicular elastodynamic Green's function, agree closely with measured velocities. When combined with additional information, such as the bulk modulus, these type of measurements provide a means to precisely determine the high pressure behavior of the individual elastic constants of opaque materials.

The technique of impulsive stimulated light scattering (ISS) begins with crossing in the sample 2 near infrared laser pulses at a known angle of convergence. This generates a transient thermal grating whose wavelength and orientation matches that of the optical interference pattern. The grating, in turn, impulsively stimulates acoustic waves, the frequencies of which are determined by monitoring the time-dependent diffraction of a pulsed probe. Finally, the velocity of the waves is given by the product of the frequency and the grating wavelength.

In nearly transparent materials the infrared pulses stimulate waves of a predominantly bulk character. In opaque materials, on the other hand, waves localized at, or close to the sample surface are stimulated. The scattering configuration relevant to the present high-pressure measurements is depicted in Fig. 1.

Heating effects in transparent samples have been negligible; in opaque samples, because the depth over which the infrared energy is deposited is small, they may be more significant. However, a simple calculation shows that for the energies used in these measurements, the temperature is raised by at most a few tens of degrees, and in a region small by comparison with the penetration depth of the surface waves.

ISS has been shown to be an effective tool for investigating the behavior of material elastic properties at elevated pressures within the diamond anvil cell (DAC). Under these conditions, it has, until now, been limited to the study of transparent materials, examples of which include oxygen, water, methanol, and various silicate minerals.[1] The use of ISS to study opaque materials in the DAC, is somewhat more complicated, since it necessarily implies probing a material interface formed by the sample in contact with the pressure medium. In general the acoustic behavior of this interface is dependent on the elastic properties of both components. To model the behavior we have employed the computational procedure developed by Every *et al.*,[2,3] which evaluates the surface perpendicular component of the relevant elastodynamic Green's function. The procedure is general and may be applied to any combination of crystal symmetry and orientation. It has been used to successfully interpret the results of surface Brillouin scattering studies (as well as those obtained using other techniques such as acoustic microscopy[2]), including one at high pressure,[4] but so far has not been used in the context of ISS.

We discuss the results acquired from the Ge/methanol system first. Ge was chosen as a test material for its well characterized physical properties and ready availability of samples of good surface quality. The single crystal sample was cut from (100) wafers (approximately 35 μm thick), using a stainless steel tube of internal diameter 250 μm together with diamond grit. It was mounted on one of the anvils of a miniature Merrill-Bassett cell. Spectra were acquired for various directions of propagation around the sample normal, first in air at 1 bar, Figs. 2(a), and then in methanol at the pressures given in Fig. 2(b)–2(d). Measurement precision was better than 0.2%.

The dominant frequency in the spectra was that of the "Scholte wave."[2] This is analogous to the Stoneley[5] wave which may exist at the interface of two solid materials of semi-infinite extent. It replaces the familiar Rayleigh and pseudosurface waves (RW and pSAW) that may be observed on unloaded surfaces [see Fig. 2(a)], but which are damped when the surface is loaded with a fluid. The character of the
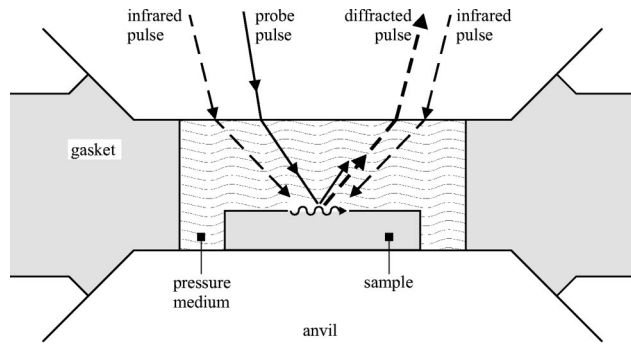
FIG. 1. Schematic of cell cavity showing sample orientation and scattering configuration. The solid and long dashed lines represent the paths taken by the probe pulse and infrared pulses, respectively; the short-dashed lines represent that of the first-order diffracted probe.

Scholte wave is determined primarily either by the solid or the fluid depending on the ratio of the speed of sound in the fluid to that of the RW or pSAW of the unloaded solid. If the ratio is less than unity the Scholte wave is rather insensitive to the acoustic parameters of the solid and instead has a velocity very close to that of the speed of sound in the fluid [Fig. 2(b)]. As the latter increases (which typically occurs rapidly with increasing pressure) the acoustic parameters of the solid become dominant and the Scholte eventually takes on the character of the RW or pSAW of the unloaded solid, but with a velocity appropriate to the mass loading [Figs. 2(c) and 2(d)].

The curves in Fig. 2 represent the Scholte wave velocities obtained by evaluating the surface perpendicular Green's function of the Ge/methanol combination. The calculation was performed using the high-pressure literature values of the elastic constants and density of Ge (Ref. 6) and the density of methanol,[7,8] The speed of sound in methanol was treated as a free parameter. For the pressure range studied here, the acoustic relaxation times of methanol, according to Ref. 8 are very short; viscoelastic effects were consequently negligible.

The speeds of sound in methanol corresponding to the best fit curves in Fig. 2 are plotted in Fig. 3 along with those reported in Refs. 7 and 8.

We note, incidentally, that the procedure just described provides a way to use ISS to measure the speed of sound in liquids that absorb weakly, or not at all, in the infrared. To maximize the pressure over which this would be accurate, i.e., to minimize the dependence on the solid, it would be necessary to choose as fast a substrate as possible. One way of doing this would be to deposit a thin metal film directly onto one anvil.

At room temperature, substances remain simple fluids only to a maximum pressure of around 10 GPa (or less if viscoelastic effects are important). Making measurements at significantly higher pressures than this implies the use of a solid pressure transmitting medium. To demonstrate that this is feasible in the present context we have examined a system consisting of a Ta single crystal in contact with solid Ar.

The Ta sample of diameter 175 μm was cut from a (110) wafer of thickness 25 μm using the technique of electric
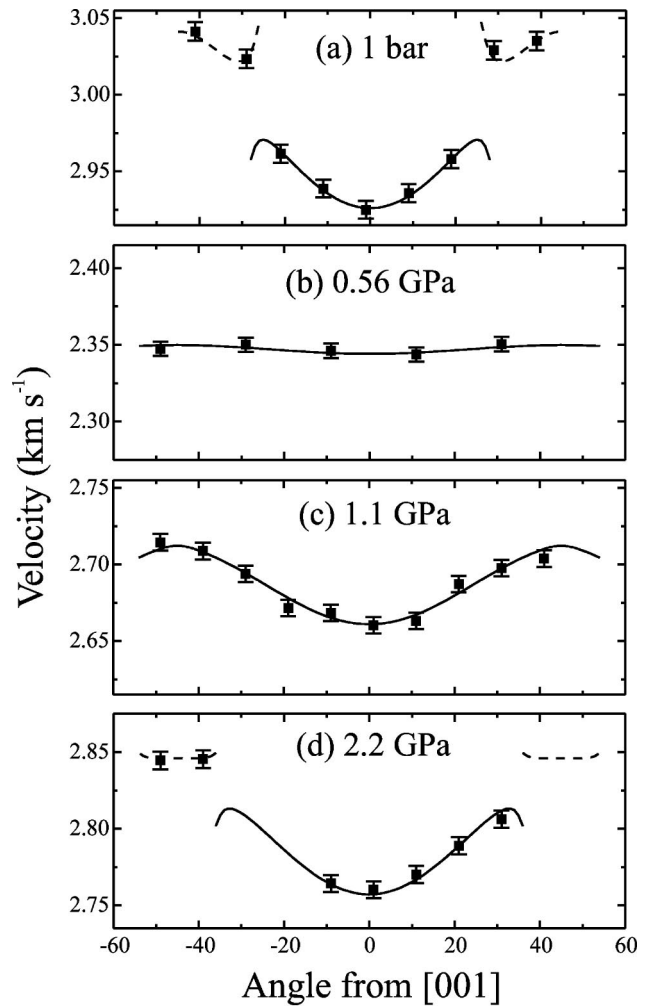

FIG. 2. Dependence on direction of propagation of the velocities of the surface waves of (100) Ge (a) in air at atmospheric pressure, and, (b)–(d), in methanol at the indicated applied pressures. At ambient pressure the measured velocities are those of the Rayleigh wave and pseudosurface acoustic wave. The solid and dashed lines represent the results of the one-component Green's function calculation of the velocities of the RW and pSAW, respectively. In contact with methanol, the measured mode is a Scholte wave; the lines represent the results of the two-component calculation. As evidenced by the growing anisotropy, the dependence on the acoustic parameters of the solid increases with increasing pressure. At 2.2 GPa the pseudosurface and Rayleigh-type waves are sufficiently separated in velocity to be resolvable as distinct branches.

discharge machining. Fine scratches on the sample surface, incurred during polishing, increased the degree of diffuse scattering of light, and hence gave rise to additional noise in the measured time series compared with those obtained from the Ge sample. The measurement precision was correspondingly reduced to about 0.8%. The anvil cell was cryogenically loaded with liquid Ar. At room temperature and the experimental pressures Ar is a (fcc) cubic solid and hence the measured excitation was a leaky Stoneley wave. (True Stoneley waves, i.e., those whose amplitudes decay exponentially with distance from the interface, exist only when restrictive conditions on the two sets of acoustic parameters are met.[5])
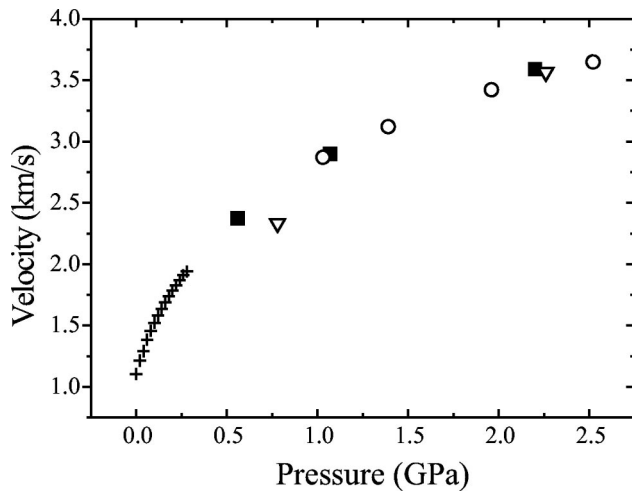
FIG. 3. The speed of sound in methanol (solid squares) corresponding to the best fits of Fig. 2. The crosses and triangles are the velocities reported in Refs. 7 and 8, respectively. The circles are additional velocities acquired using ISS in the manner described in Ref. 8.

Figure 4 shows the observed and calculated dispersion curves. As expected for this plane of propagation and anisotropy ratio $[2c_{44}/(c_{11}-c_{12})>1$ for Ta] there is no pSAW branch.

For the purpose of calculation, estimates of the elastic constants and densities of Ta were obtained by extrapolating the low pressure (0.5 GPa) ultrasonics data acquired by Katahara and Manghnani.[9] The corresponding values for Ar were interpolated from Brillouin measurements reported by Grimsditch and Polian.[10] Since we had no knowledge of the orientation of the Ar with respect to that of the Ta crystal we performed the calculation assuming each of three orientations for the Ar: (100), (110), and (111). In each case velocities were calculated with the Ar crystal rotated through a range of angles about the surface normal. This procedure yielded a maximum variation of about 10 m/s which was less than the estimated measurement precision. On the whole the discrepancy between the measured velocities and those calculated on the basis of the parameters obtained in Ref. 9 was within the measurement precision.

In conclusion, ISS has been shown to be capable of accurately measuring surface acoustic wave velocities at high pressure. The technique offers a higher measurement precision compared to that of surface Brillouin scattering, which at present is the only alternative method for making these type of measurements.[4] We note that the Green's function calculation discussed above is easily adapted to the inverse problem, i.e., extracting the elastic constants from the measured velocities. However, a problem encountered in surface wave studies, regardless of the computational procedure, is the difficulty in extracting all constants individually. The problem is, on the other hand, obviated if the pressure dependence of the bulk modulus, for example, is available.

Finally, we note that a problem that may be encountered at very high pressures using ISS is the difficulty of maintaining an adequate separation between the sample surface and the anvil. If this is a few microns, i.e., the penetration depth
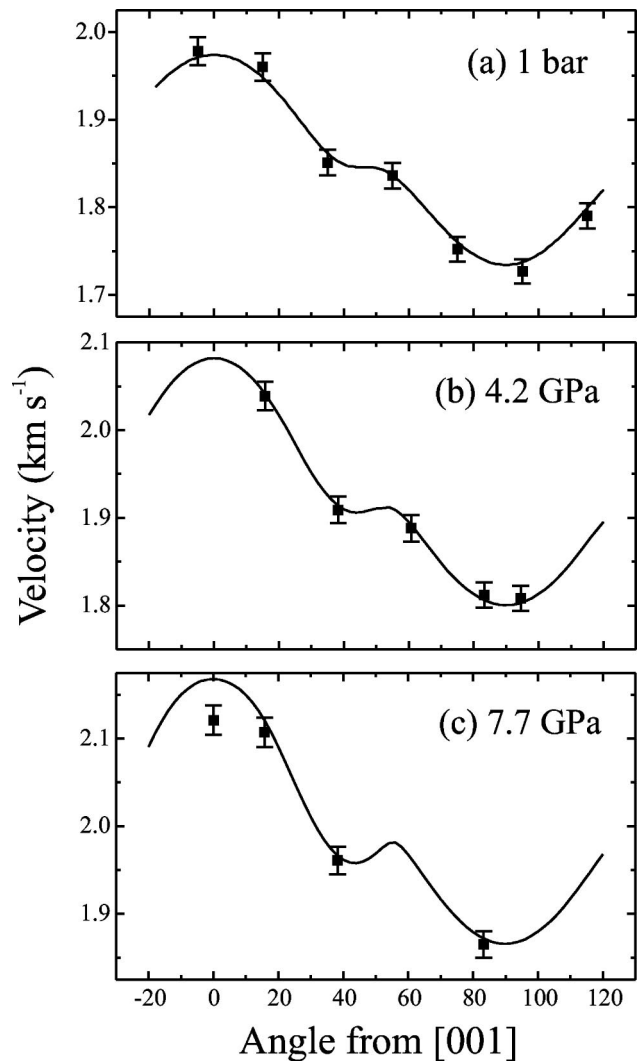

FIG. 4. Dependence on direction of propagation of the velocities of the surface waves of (110) Ta (a) in air at atmospheric pressure, and, (b)–(c), in solid Ar at the indicated applied pressures. At ambient pressure the measured velocity is that of the Rayleigh wave; at high pressures it is a leaky Stoneley wave. The high pressure calculations were made on the basis of the Ar acoustic parameters of Ref. 10 and those of Ta extrapolated from Ref. 9.

of the surface waves, or less, the system is in principle made up of three components consisting of three different materials. However, we have not found this to be problem to a pressure of so far 12 GPa (in measurements made on an FeNi alloy which will be reported elsewhere). In fact an adequate separation can probably be maintained to at least 50 GPa. Beyond this value it may be necessary to let the sample take the form of a thin film and allow it to be surrounded by the pressure medium. Although this would once again be a three component system (which may also be handled using the computational procedure described in Ref. 4) only two materials would be involved. In this case additional excitations would be present which would be akin to Lamb waves.

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