Brillouin scattering at high pressure: an overview

Alain Polian*

Physique des Milieux Condensés, CNRS–UMR 7602, Université Pierre et Marie Curie, B77, 4 Place Jussieu, 75252 Paris Cedex 05, France

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Brillouin scattering allows the determination of acoustic velocities and adiabatic elastic moduli in matter. These data are crucial in many areas of science, such as fundamental physics, geosciences and technology, especially when measured as a function of the density (pressure). In this paper, we present a review of the work performed on Brillouin scattering under high pressure in diamond anvil cells, emphasizing the most recent results. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: Brillouin scattering—High pressure—High temperature—Elastic properties

INTRODUCTION

Sound waves propagate in matter, independently of its structure. Brillouin scattering consists in the inelastic scattering of light by the sound waves, or thermal excitation in a material, in particular acoustic phonons in a crystal. The energy of light is therefore modified, increased in the case of the annihilation of excitation, or decreased in the case of creation of excitation. The measurement of this energy difference gives information on the energy of the phonons and therefore on the interatomic potentials of the material.

The theory of Brillouin scattering has been extensively developed in the literature,1–4 so only the main ideas will be covered here. In the interaction process between a photon and thermal excitation, the energy and momentum are conserved:

\[
\hbar \omega = \pm \hbar (\omega_i - \omega_s) \tag{1}
\]

\[
\mathbf{q} = \pm (\mathbf{k}_i - \mathbf{k}_s) \tag{2}
\]

where \(\omega\) and \(k\) are the wavenumber and the wavevector of the photon, the subscripts \(i\) and \(s\) refer to the incident and scattered beams and \(\omega\) and \(q\) are the wavenumber and the wavevector of the phonon, respectively, the plus sign corresponds to the creation of a phonon (Stokes) and the minus sign to annihilation (anti-Stokes). It should be noted that the equations of conservation hold for both Brillouin scattering and Raman scattering because the physical processes are identical. From the experimental point of view, the differences are large, coming from the difference in the energies involved in the processes: the wavenumbers of the optical phonons giving rise to Raman scattering are of the order of 10–1000 cm\(^{-1}\) (1.2–120 meV), whereas the Brillouin wavenumbers are of the order of 0.1–6 cm\(^{-1}\). Because of this proximity with the elastically scattered Rayleigh line, apparatus of much higher resolution has to be used to discriminate the Brillouin scattered light compared with Raman scattering where a grating spectrometer is well suited. Such a high-resolution apparatus is the Fabry-Pérot (FP) interferometer. Recent advances in Fabry-Pérot spectroscopy have been reviewed5 and will be described here only briefly.

A Fabry-Pérot system consists basically of two partially transmitting plane mirrors, separated by a distance \(d\). A parallel beam of light is incident along the mirror axis. Owing to interferences between the two parallel mirrors, the light is transmitted only when

\[
nd = m \frac{\lambda}{2} \tag{3}
\]

where \(n\) is the refractive index of the medium between the two mirrors, \(\lambda\) is the wavelength of the light and \(m\) is an integer. Therefore, the wavelength of the transmitted light is selected by varying the optical path \(nd\) of the light, by changing either the distance between the mirrors or the refractive index of the inter-mirror medium.

Two parameters describe the quality of an FP system: the first is the contrast \((C)\), defined as the ratio of the maximum intensity transmission to the minimum intensity transmission, and this quantifies the ability of the set-up to measure signals that are small in comparison with the Rayleigh scattering. The second is the finesse \((F)\), defined as the ratio of the distance between two successive transmission peaks to the full width at half-maximum of a transmission peak, and provides the capability of measuring peaks close to the Rayleigh peak. The most important parameter is the contrast. For a good quality FP system, one typically obtains...
contrasts of the order of a few hundred, which is far from sufficient to measure Brillouin scattering in most materials. The solution to increase considerably the contrast is the multipass FP system, which was introduced by Sandercock and yields measured contrasts above $10^{10}$.

One measurement is not sufficient to determine the wavenumber of a phonon: this quantity is only determined modulo one ‘free spectral range’ (FSR), i.e. a wavenumber equal to the distance between two successive transmission peaks of the FP. The solution was again given by Sandercock, with the tandem FP interferometer, where two interferometers with different spacings are scanned synchronously.

**BRILLOUIN SCATTERING**

Brillouin scattering provides information about the acoustic branches at a given point of the dispersion curves of the material under study. The measured wavenumber shift of the radiation is equal to that of the phonon under consideration [Eqn (1)], and its wavevector is deduced from Eqn (2), so the sound velocity may be calculated by

$$ V = \Omega / q $$

This relation may also be written as

$$ \Delta \sigma (\text{cm}^{-1}) = \frac{2nV}{\lambda c} \sin \frac{\theta}{2} $$

where $\Delta \sigma$ is the measured wavenumber shift (in cm$^{-1}$), $n$ is the refractive index at $\lambda$, the wavelength of the exciting light, $c$ is the speed of light in vacuum and $\theta$ is the angle between $k_i$ and $k_d$. The sound velocity is related to the elastic constants by

$$ X = \rho V^2 $$

where $X$ is a combination of elastic constants depending on the direction of propagation of the phonon with respect to the crystallographic axis and $\rho$ is the density. For example, in a cubic crystal, a longitudinal phonon propagating along the [110] direction is related to $X = (C_{11} + C_{12} + 2C_{44})/2$ and the two non-degenerate transverse phonons are related to $X = (C_{11} - C_{12})/2$ and $X = C_{44}$. Therefore, by correctly choosing the geometry of the experiment, it is possible to determine the complete set of elastic constants.

Figure 1 shows scattering geometries commonly used in order to determine the elastic constants. In Fig. 1(a), the modulus of the phonon wavevector is equal to $nk/\sqrt{2}$, where $k \approx k_i \approx k_d$. In Fig. 1(b), $|q| = 2nk$. This is the geometry that produces the largest wavenumber shift. Figure 1(c) shows an interesting geometry for Brillouin scattering under pressure (provided that an ad hoc cell is available), because measurement of the refractive index is not required. Indeed, in the crystal the modulus of the wavevector of light is equal to $nk$. Owing to the incidence angle, $|q| = 2nksin(r)$, where

**Figure 1.** Most commonly used geometries in Brillouin scattering, (a) 90° scattering, $|q| = 2^{1/2}nk$; (b) backscattering geometry, $|q| = 2nk$; (c) platelet geometry, $|q| = 2nksin r i = 2ksin r$.

$r$ is the angle of the refracted photon inside the crystal with respect to the normal to the surface. Using the Descartes law of refraction, one obtains $|q| = 2ksin(i)$, where $i$ is the known angle of incidence.

The knowledge of the relative orientation of $k_i$ and $k_d$ with respect to the crystallographic axes allows the determination of that of $q$, and the selection rules allow one to deduce the related combination of elastic constants.

**BRILLOUIN SCATTERING IN A DIAMOND ANVIL CELL**

With a ‘classical’ diamond anvil cell (DAC), i.e. with only optical access along the axis of the diamond, it is basically only possible to use the backscattering geometry (only one experiment has been performed in the platelet geometry with this type of cell). Unfortunately in the backscattering geometry, the selection rules favor the longitudinal mode, so most of the experiments performed in this geometry only give information on these phonons. Another problem which occurs is due to the diamond anvils which have also acoustic phonons, and the difference in volume between the anvils and the sample make the intensity of the Brillouin of the former much more intense than that of the latter. The problem of the longitudinal modes of diamonds may be avoided by using a tandem FP set-up.

The ‘Swiss cheese’ DAC enables one to measure in the platelet geometry, and then gives information on the transverse modes. Nevertheless, the maximum pressure is achieved, on average, in a backscattering geometry.

Once the spectrum has been recorded, the sound velocity can be computed, which means that [Eqn (5)] the refractive index at the wavelength of the laser and at the desired density should be measured or computed. The measurement of the pressure dependence of the refractive index of compounds is not easy. Various techniques have been proposed and applied in a few cases for H$_2$ and D$_2$, GaS, xenon, argon and helium. In case where $n$ is not measured with pressure, a good approximation is given by the Clausius–Mosotti equation, provided that the equation of state is known.

Once the sound velocity has been determined, Eqn (6) gives the effective elastic modulus corresponding to the
direction of propagation of the measured phonon. In order to determine the linear combination of elastic constants involved, one has to know the crystallographic orientations of the crystal inside the DAC. This may be done when the sample is solid under ambient conditions. When the sample is loaded as a fluid in the DAC, there is no control on the crystal orientations, and the determination of individual elastic constants is not straightforward using the classical methods. The first attempt was made in backscattering geometry. In this geometry, only the longitudinal acoustic (LA) modes are detected. The pressure dependence of the velocity was measured for unknown directions, without identifying the crystal orientation. The envelope for all experimental points corresponds to maximum LA velocities, \( v^2 = \left[ (C_{11} + C_{12} + 4C_{44})/\rho \right] \) along the (111) direction and to minimum velocities along (100), \( v^2 = C_{11}/\rho \). For the determination of all the elastic moduli, the isothermal bulk modulus \( B = (C_{11} + 2C_{12})/3 \) is used. Two problems may arise by using this technique. First, it is assumed that the maximum and minimum values of the sound velocities are really reached, and second, the ratio of the specific heats, \( c_p/c_v \), is supposed to be constant and equal to 1.

The problem was solved for cubic crystals by Shimizu and Sasaki using the platelet geometry, a large aperture cell and a method first proposed by Every. Rotating a wavevector relative to the axes of the cubic crystal by

\[
\rho v_j^2 = g_j(C_{11}/\rho, C_{12}/\rho, C_{44}/\rho, \theta, \phi, \chi)
\]

where \( \rho \) is the density of the crystal. The wavevector direction may be expressed as a function of the Euler angles of the crystal, \( \theta, \phi, \chi \) and hence:

\[
v_j = g_j(C_{11}/\rho, C_{12}/\rho, C_{44}/\rho, \theta, \phi, \chi)
\]

The rotation angle \( \phi \) is varied, and \( v_j \) is then determined by a least-squares fit between the calculated \( g_j(\phi) \) and the experimental elastic moduli. Using this technique, the orientation of the crystal is also precisely obtained.

A similar, but somewhat simpler, procedure is now commonly used when working on compounds which are crystalline under ambient conditions, i.e. in platelet geometry, and rotating the cell around the load axis. The orientation of the sample is known from the beginning, and in that case the full set of elastic moduli may be obtained for samples of lower symmetry. Nevertheless, it should be noted that the highest pressures are obtained in the backscattering geometry.

Table 1 presents an extensive review of the results obtained at ambient temperature in a DAC. It is clearly

<table>
<thead>
<tr>
<th>Material</th>
<th>Scattering geometry</th>
<th>Max. pressure (GPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
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</tr>
<tr>
<td>H2, D2</td>
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<td>22</td>
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<td>10</td>
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<tr>
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<td>Platelet + rotation</td>
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<td>49</td>
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<td>NaCl, KCl</td>
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<td>51</td>
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<tr>
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<td>Platelet + rotation</td>
<td>24</td>
<td>52</td>
</tr>
<tr>
<td>N2O</td>
<td>Platelet + rotation</td>
<td>4.5</td>
<td>53</td>
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<td>(MgFe)SiO4</td>
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<tr>
<td>HCl</td>
<td>Platelet + rotation</td>
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<tr>
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Table 1. Summary of the compounds studied by Brillouin scattering in a DAC
seen that in recent years, most of the experiments have been performed in the platelet geometry, so that the complete set of elastic moduli is obtained up to the highest pressure.

Most of the results obtained to date at high pressure in a DAC were obtained at ambient temperature. Nevertheless, some preliminary results at high temperatures have been published on liquid H$_2$O$^2$ and low-temperature data were obtained on H$_2$S.$^6$ Figure 2 represents the Brillouin spectrum obtained at high pressure and high temperature in water. This study was undertaken up to 450 °C at 9 GPa (F. Datchi and A. Polian, to be published).

One application of the determination of the full elastic moduli set is the establishment of a thermodynamic pressure scale. The measurement of both the volume and the elastic constants as a function of the same secondary pressure scale enables one to eliminate this scale and to establish a primary pressure scale. This has been done using x-ray diffraction and Brillouin scattering on MgO up to 55 GPa by Zha et al.$^{35}$ (Fig. 3). The primary pressure scale determined in such a way, expressed in the ‘classical’ form

$$P(\text{GPa}) = \left( \frac{A}{B} \right) \left[ \left( \frac{\lambda}{\lambda_0} \right)^B - 1 \right]$$

holds with $A = 1904$ GPa and $B = 7.715$, in good agreement with the previous determination with $A = 1904$ GPa and $B = 7.665$.

**CONCLUSION**

We have briefly reviewed the results obtained to date with Brillouin scattering under high pressure in a diamond anvil cell. It should be noted that even with the limitation that it is necessary to work with transparent samples, it is a powerful technique, one of the few that can determine the properties of amorphous compounds or fluids.

**REFERENCES**


