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Development of low-temperature and high-pressure Brillouin scattering spectroscopy and its application to the solid I form of hydrogen sulphide

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Abstract

A new experimental system has been developed for low-temperature and high-pressure Brillouin scattering measurements. The new system allows us to investigate the elastic properties of samples in a diamond anvil cell (DAC) down to liquid N_2 temperature ($\sim$80 K). In contrast to the case in our conventional technique, the optics in the system can be rotated for measuring the direction dependence of acoustic velocities of the samples in the DAC fixed in the cryostat. The new experimental technique was applied to the solid I form of hydrogen sulphide (H_2S). As a result, three ratios of elastic constants to density were successfully determined at $P = 3.70$ GPa, $T = 240$ K: $C_{11}/\rho = 16.4$, $C_{12}/\rho = 12.4$, $C_{44}/\rho = 7.57 \times 10^6$ m^2 s^{-2}. These values are almost the same as those obtained at room temperature.

1. Introduction

Brillouin scattering spectroscopy is a powerful tool for investigating elastic properties. Previously, we have developed an analytical method for the determination of elastic properties of molecular single crystals grown in a high-pressure diamond anvil cell (DAC) [1], and have determined the pressure dependence of the acoustic velocities, elastic constants, and refractive index for various molecular crystals.

Figure 1 shows a typical Brillouin scattering geometry used in our study. The wavevector ($\boldsymbol{q}$) of the observed acoustic phonon is parallel to the diamond interfaces (XY-plane). The velocity ($v_{2\theta_0}$) of the phonon is immediately obtained from the Brillouin frequency shifts ($\Delta\nu_{2\theta_0}$) without the refractive index of the sample using the following equation:

$$v_{2\theta_0} = \Delta\nu_{2\theta_0}\,\lambda/2\sin\theta_0, \tag{1}$$

where λ is the wavelength of incidence. Information on the elasticity for cubic crystals can be obtained from the following analysis. The dependence of the acoustic velocities ($v_{2\theta_0}$) on the propagation direction in the XY-plane is measured by rotating the DAC about the

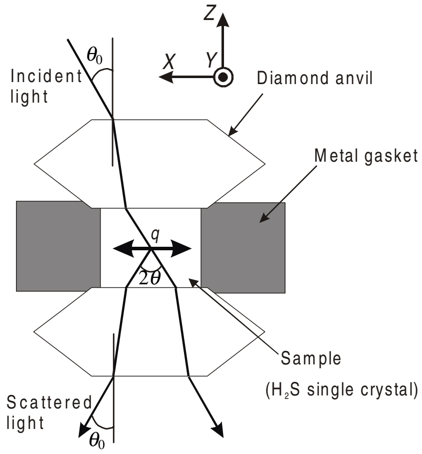

Figure 1. Brillouin scattering geometry with a DAC in a $2\theta_0$ scattering configuration. The actual scattering angle is 2θ. The set (X, Y, Z) are the coordinates of the laboratory reference frame. The vector $\boldsymbol{q}$ indicates the wavevector of the observed acoustic phonons in a sample.

Z-axis perpendicular to the diamond anvil faces. The directional dependence obtained for the velocities is reproduced theoretically by using the least-squares fitting technique, giving rise to three ratios of elastic constants to density (C_{11}/ρ, C_{12}/ρ, C_{44}/ρ) and the crystal orientation in the DAC as fitting parameters. Using the above technique, we have investigated the elasticity for pressure-induced molecular solids.

It is very important for understanding the potential function and the interaction between atoms or molecules to study elastic properties over a wide range of not only pressures but also temperatures. However, the above technique has been limited to experiments at room temperature because a DAC mounted on thermo-controllers such as cryostats cannot be rotated easily. Thus, we developed, in the present work, a new Brillouin optical system to extend our elastic study to low temperatures. This new Brillouin scattering system was applied to study the solid I form of hydrogen sulphide (H_2S) and the results are presented in this paper.

2. Development of the new Brillouin spectroscopy

Figure 2 shows the total system used for low-temperature and high-pressure Brillouin spectroscopy in the 60° scattering configuration. The DAC is mounted on a liquid N_2 cryostat, which is able to effect cooling to ~80 K, equipped with TCU-4 thermal controller (Iwatani Plantech Corp.). As the light source, the 514.5 nm line of an argon-ion laser was used, with single-mode operation. The radiation from the source was focused onto the sample by lens L1. The scattered light was put through a spatial filter (L3, P1, L4), and analysed by a tandem Fabry–Perot interferometer (JRS) with a photomultiplier and photon-counting system.

Figure 3 shows the details of the new optical system, which corresponds to the area outlined with a broken line in figure 2. In contrast to the case in our conventional technique, the optical system can be rotated to measure the directional dependence of acoustic velocities. The arms of the sections A and B can be precisely adjusted to rotate in planes perpendicular to the Z-axis. Mirrors (M3, M4, M5, M6) and lenses (L1, L2) are fixed on each arm to retain the 60° scattering configuration. The point at which the beam is focused can be fixed within of the order of a hundred microns even if the optical system rotates. Thus, by rotating the optical sections of both A and B, the directional dependence of the Brillouin frequency shifts could be measured.

To measure the pressure, the fluorescence of ruby in the DAC can also be detected by inserting a mirror (M10) (figure 2). The fluorescence signal was collected onto an optical fibre, and guided to a monochromator (C5095) equipped with a MCD.

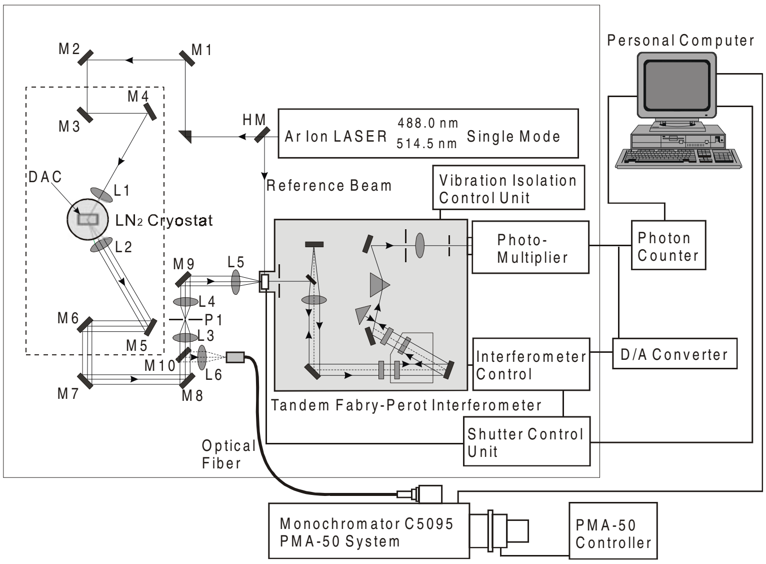

Figure 2. The system used for low-temperature and high-pressure Brillouin spectroscopy in the 60° scattering configuration: M: mirror; L: lens; P: pin-hole. The DAC is mounted on a liquid N_2 cryostat. The fluorescence of ruby can also be detected in this system.

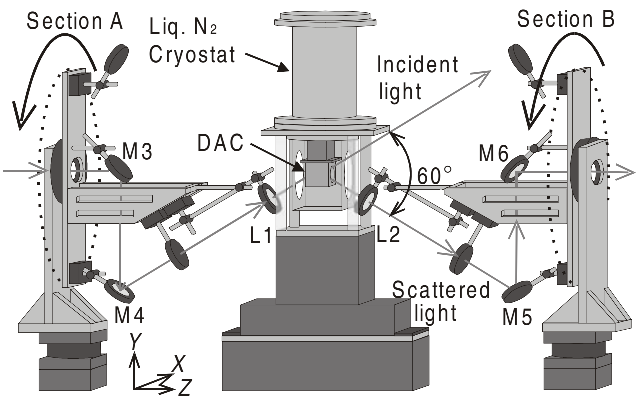

Figure 3. The new optical system for low-temperature and high-pressure Brillouin scattering measurements. It is possible to measure the directional dependence of the acoustic velocities of the samples in the DAC fixed in the liquid N_2 cryostat.

3. Application to solid H_2S

The solid I form of H_2S was chosen as a sample for the following reasons. (1) Solid H_2S is suitable for verifying the new optical system because the Brillouin scattering intensity is strong, and the spectra are rather easy to measure. (2) The solid I form of H_2S is an orientationally disordered phase in which molecules are rotating at each lattice point. According to the previous study [2], the molecular rotation strongly affects the elastic properties. Experiments at low temperatures in which the rotational motion is hindered will give us significant information on the influence of rotation on the elasticity.

The single crystal of H_2S was prepared in the DAC as follows. We condensed commercial gaseous H_2S by spraying its vapour into the gasket hole of the DAC cooled in liquid nitrogen.

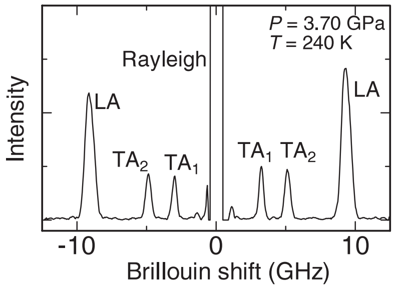

Figure 4. The Brillouin spectrum of the solid phase I form of H_2S measured by the newly developed Brillouin experimental system at $P = 3.70$ GPa, $T = 240$ K. LA, TA_2, and TA_1 label Brillouin signals from longitudinal, fast transverse, and slow transverse modes, respectively.

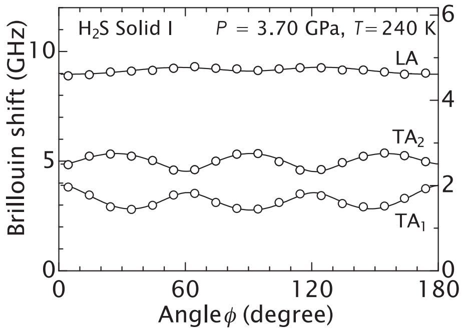

Figure 5. Brillouin shifts (acoustic velocities) of LA, TA_2, and TA_1 modes for the solid I form of H_2S as a function of angle ϕ. Open circles and solid curves indicate the experimental points and the theoretical best-fitted curves, respectively.

When the hole was full of solidified H_2S, the upper diamond was translated to seal the sample chamber. After adequate pressure had been applied, the DAC was warmed to 300 K. A single crystal was grown by increasing the pressure on a seed crystal, which coexists with the liquid at 0.47 GPa. The DAC was mounted on liquid N_2 and cooled down to a certain temperature.

Figure 4 shows a typical Brillouin spectrum of the solid phase I form of H_2S obtained at high pressure ($P = 3.70$ GPa) and low temperature ($T = 240$ K) using the new optical system. We were able to obtain the Brillouin signals denoted as LA, TA_2, and TA_1 corresponding to longitudinal, fast transverse, and slow transverse modes, respectively.

By rotating the optical system shown in figure 3, the directional dependence of the acoustic velocities was measured, as shown with open circles in figure 5. The right-hand axis shows the corresponding sound velocities. The velocities of three acoustic modes can be theoretically expressed as a function of six parameters [3]:

$$v_m = f_m(C_{11}/\rho, C_{12}/\rho, C_{44}/\rho, \theta, \phi, \chi),$$

where C_{ij} are the elastic constants, ρ is the density of the sample, the subscript m stands for the LA, TA_1, and TA_2 modes, and (θ, ϕ, χ) are the Euler angles relating the laboratory frame (the DAC) to the crystal reference frame. Using this expression, a computerized least-squares fitting procedure was applied to determining C_{ij}/ρ and the Euler angles. Solid curves in figure 5 represent the best-fitted theoretical curves. It is found that the experimental data are reproduced well with the theory, and there is no scattering of the data around the theoretical curves. Thus, we have verified that the data measured by the new experimental system are reliable. The fitting parameters obtained were as follows: $C_{11}/\rho = 16.4$, $C_{12}/\rho = 12.4$, $C_{44}/\rho = 7.57 \times 10^6$ m^2 s^{-2} at $P = 3.7$ GPa and $T = 240$ K. These values were almost the same as those obtained at room temperature ($C_{11}/\rho = 16.6$, $C_{12}/\rho = 12.3$, $C_{44}/\rho = 7.06 \times 10^6$ m^2 s^{-2}, $P = 3.69$ GPa, $T = 298$ K [1]). Experiments in which the temperature is changed systematically, in order to clarify the influence of rotational motion on the elasticity, are in progress in our laboratory.

4. Summary

A new optical system was developed for low-temperature and high-pressure Brillouin scattering measurements, and applied to the solid I form of H_2S to validate the new system. The quality of the data obtained at $P = 3.70$ GPa and $T = 240$ K was found to be as high as in our previous work.

A He cryostat for lower-temperature experiments and a gas-driven membrane DAC for the control of pressure at low temperature can be introduced in the present system, which allows one to study elastic properties over a very wide P–T region.

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