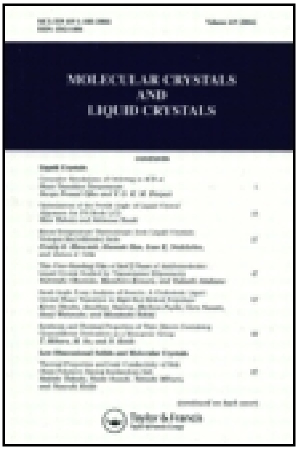

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High-Pressure Raman and Brillouin Scatterings in Hydrogen-Bonded Crystalline H_2S

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HIGH-PRESSURE RAMAN AND BRILLOUIN SCATTERINGS IN HYDROGEN-BONDED CRYSTALLINE H_2S

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Abstract In the pressure-induced orientationally disordered phase of H_2S ($P = 0.47 \sim 11$ GPa), the dynamics of hydrogen bonds is investigated by the pressure dependence of Raman frequencies. The following process repeats; molecular rotation → hydrogen-bonds formation → ν_1 oscillations → hydrogen-bonds breaking → molecular reorientation.

The best fitting of the angular dependence of Brillouin frquency shifts between experimental values and the calculation by the Every's expression for elastic waves of arbitrary direction, yields the evaluation for the orientation of a H_2S plastic-phase cubic crystal grown in the diamond anvil cell, and the determinations of the sound velocity, the refractive index, the density and elastic constants under pressures.

INTRODUCTION

Hydrogen sulfide (H_2S) is a typical molecular solid forming a quasi-two-dimensional hydrogen-bonded network.[1] Recently, we have measured the Raman spectra of solid H_2S up to 23 GPa at 300 K in a diamond anvil cell (DAC), and have found the pressure-induced phase transition at about 11 GPa from the orientationally disordered (plastic) phase I to a new solid phase IV.[2, 3]

In this paper, we investigate the dynamics of hydrogen bonds in the orientationally disordered phase and in the pressure-induced new phase above 11 GPa. Furthermore, we present the first study of the Brillouin scattering of solid H_2S under high pressures. From the angular dependence of Brillouin frequency shifts, we determine the crystallographic axes of a H_2S plastic-phase cubic crystal grown in the DAC, and estimate the sound velocity, the refractive index, the density and the elastic constants under high pressures.

EXPERIMENT

Commercial gaseous H_2S sample was usually condensed by spraying its vapor into the gasket hole of a high-pressure DAC cooled in liquid nitrogen.[2] When the hole is full of solidified H_2S, the upper diamond is translated to seal the sample. After adequate pressure is applied, the DAC is warmed to 300 K. The coexistance pressure of liquid and solid was about 0.47 GPa. A single crystal was grown by increasing the pressure on a seed crystal which looks like a sphere under the microscope. The pressure was measured by the ruby scale method.

For Raman measurements, the 514.5 nm line of an argon-ion laser was used at power levels from 50- to 200-mW input. Scattered light was collected in a back-scattering geometry. The Raman spectra were recorded with a Jasco double monochromator with the photon counting detection. The resolution was about 1 cm^{-1}.[4]

For Brillouin measurements, the 488.0 nm argon-ion laser line (λ_0) with single longitudinal mode was used at power levels from 100- to 300-mW input. The heart of the apparatus is a plane piezo-electrically scanned Fabry-Perot interferometer (Burleigh DAS-10) which was used in a 5-pass configuration. The 90° Brillouin scattering geometry was used principally to determine the acoustic velocity (V_{90}). The Brillouin frequency shift ($\Delta\nu_{90}$) is related to V_{90} by the expression

$$V_{90} = \Delta\nu_{90}\cdot\lambda_0/\sqrt{2}\ , \qquad (1)$$

which is independent of the refractive index of the medium.[5] The wave vector (q) of the acoustic phonon is parallel to interfaces of the first and second diamonds crossed by the laser beam. In order to estimate the adiabatic elastic constants C_{11}, C_{12} and C_{44} in the orientationally disordered phase I of crystalline H_2S grown in the DAC, Brillouin frequency shifts were measured for ~10° intervals of rotation angle ϕ with respect to the load axis of DAC, over total ranges of 180°. For this purpose, we developed a new type of DAC having symmetric conical openings with aperture angle of 98°.

RESULTS AND DISCUSSION

Raman Scattering: Dynamics of Hydrogen Bonds

The Raman spectra of intramolecular ν_1, ν_2 and ν_3 modes, and lattice vibrational modes were measured for the crystalline H_2S in the DAC up to 23 GPa at room temperature. In Figure 1 the frequencies of these modes are plotted as a function of pressure. These results indicate the existence of a pressure-induced phase transition at about 11 GPa ($=P_t$) from the orientationally disordered phase I to a new phase IV.[2, 3]

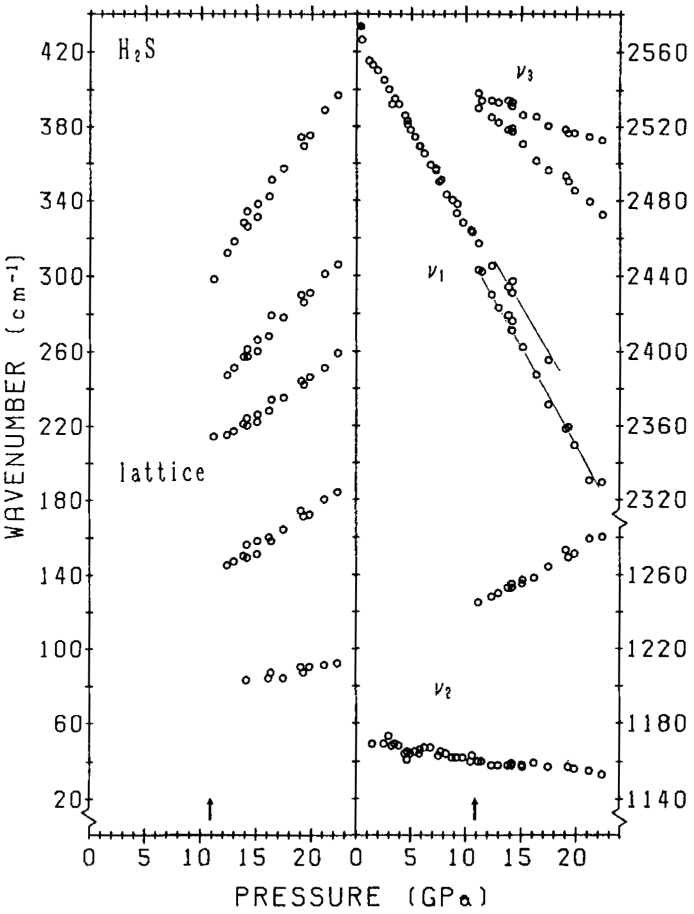

FIGURE 1 Pressure dependence of the intramolecular and the lattice vibrational frequencies (cm^{-1}) in solid H_2S at 300 K. The pressure-induced phase transition point is indicated by arrows.

In the plastic phase I, only ν_1 and ν_2 modes are observed. The slope of frequencies against pressure for the symmetric stretching mode ν_1 is $d\nu_1/dP = -10.1\ cm^{-1}/GPa$ up to P_t. This negative slope indicates the existence of hydrogen bonds in the orientationally disordered phase I. Hydrogen bonds may remain as the intramolecular ν_1 oscillating unit ($2500\ cm^{-1}=7.5\times10^{13}$ Hz) for several vibrational periods before being broken by the molecular reorientation. The process of molecular rotation → hydrogen-bonds formation → ν_1 oscillations → hydrogen-bonds breaking → molecular reorientation, repeats rapidly in the phase I. No observation of the intermolecular vibration implies that on a time scale comparable to the period of the lattice vibration ($200\ cm^{-1}$ $=6\times10^{12}$ Hz) we can not recognize the formation of hydrogen bonds.

Above P_t five lattice vibrational modes appear as shown in Figure 1. This result is interpreted as follows: hydrogen atoms are fixed at P_t, and the reorientational molecular motions stop and change to librational motions around the equilibrium orientation. Therefore, the new high-pressure phase above P_t, which persists to at least 23 GPa at 300 K, is ordered for the molecular orientation. These characteristics are also clearly confirmed on the pressure dependence of half band-width for the ν_1 intramolecular mode.[2,3]

Brillouin Scattering: Orientation of a Single Crystal Grown in DAC, and Elastic Constants

The crystallographic axes of a single crystal grown in DAC are usually determined by the X-ray diffraction method. We present here the first success of determining the crystal orientation by only the Brillouin scattering method, and evaluate acoustic velocities, the refractive index, the density, and elastic constants (C_{11}, C_{12}, C_{44}) under high pressures for cubic single crystals of unknown orientations.

For making an analytic treatment of the elastic-wave propagation for arbitary directions, it is necessary to use the usual Brillouin equation and Every's closed-form expressions[6] relating sound velocities (frequency shifts) to the elastic constants. We can easily modify the Every's velocity expression [Eq.(4) in Ref.6] to our experimental system by using the Euler angles (θ, ϕ, χ) which relate any direction in the laboratory reference frame to the crystal axis frame.[7, 8] Namely, this enables the transformation of the acoustic wavevector q from the laboratory frame, in which its direction is known, to the crystal Cartesian coordinates with respect to which the elastic constants are evaluated. The velocities or the frequency shifts of three acoustic modes (LA, TA_1 and TA_2) can therefore be expressed as a function of six parameters : $V_i^2 = f\ (C_{11}/\rho,\ C_{12}/\rho,\ C_{44}/\rho,\ \theta,\ \phi,\ \chi)$, where ρ is the density.

Brillouin measurements at 90° scattering geometry were made for ~10° intervals of rotation angle ϕ in the laboratory frame, namely, the rotation of DAC ($\because$ q) about the load axis (see the inset in *Figure* 2). *The observed frequency shifts* at 1.50 GPa in the plastic phase are plotted as a function of ϕ in Figure 2. A least-squares fitting method was applied to determine two Euler angles and three elastic constants. The calculated "best fit" frequency shifts which correspond to elastic constants are represented by dotted lines. Good agreements between the observed and the fitted values yield that $C_{11}/\rho = 98.0$, $C_{12}/\rho = 73.1$ and $C_{44}/\rho = 43.2$ kbar·cm^3/g.

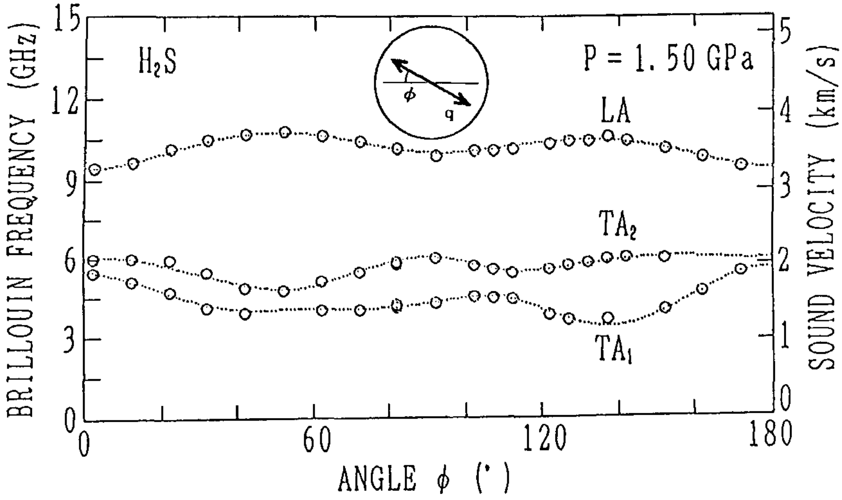

FIGURE 2 Brillouin frequency shifts (GHz) of LA, TA_1 and TA_2 modes as a function of orientation angle ϕ , and P=1.50 GPa in the orientationally disordered phase of H_2S. Open circles indicate experimental points and the dotted lines represent the "best fit" frequency shifts. The circled inset shows the rotation angle ϕ about the load axis of DAC.

Next, in order to estimate the ρ under high pressures, we also measure the Brillouin spectra at back-scattering geometry (180°). Then, the Brillouin frequency shift ($\Delta\nu_{180}$) is related to V_{180} by the expression

$$V_{180} = \Delta\nu_{180}\cdot\lambda_0/(2n), \qquad (2)$$

where n is the refractive index, and V_{180} is the velocity along the direction perpendicular to the diamond interfaces. By using the observed $\Delta\nu_{180}$ and the calculated V_{180} by the best fitting method, the n was estimated to be 1.66 from Eq. (2). Moreover, the Lorentz-Lorenz relation $(n^2-1)/(n^2+2) = 4\pi N\rho\alpha/3M$ yields ρ=1.32 g/cm^3, where N is the Avogadro's number, the polarizability α=3.78x10^{-24} cm^3, M the molecular weight. The value of ρ enables the conclusive determination of C_{11}= 132, C_{12}=98.3 and C_{44}=58.3 kbar at 1.50 GPa. More detailed study will be published elsewhere.

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