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Raman-scattering study of high-pressure effects on the anisotropy of force constants of hexagonal boron nitride

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Frequency shifts of two species of Raman-active modes in layered hexagonal boron nitride have been measured in the pressure range from 1 bar to 110 kbar at room temperature. From the observed shifts it was found that, while the increase of an intralayer force constant of the crystal was only six percent, the interlayer shear force constant increased by four times as much at 110 kbar compared with the value at 1 bar. The pressure effects on the mode Grüneisen constants of the two distinct modes and on the shear elastic constant c_{44} of the crystal are discussed.

INTRODUCTION

Recently, Raman scattering of various crystals with layer structures has been studied extensively. A remarkable feature of the spectra is the existence of the considerably-low-frequency modes conventionally called rigid-layer modes in crystals whose c_0 dimensions extend to two or more layers.[1]

Raman scattering of layered hexagonal boron nitride (hexagonalBN) has been studied by several authors.[2-4] Two species of Raman-active modes belonging to the irreducible representation E_{2g} of the point group D_{6h} of the crystal have been observed; the high-frequency mode is an intralayer inplane vibration and the low-frequency mode is a shear-type rigid-layer vibration. On the other hand, instrumentations for spectroscopy including Raman scattering at very high pressures have recently been developed and successfully applied to the study of several materials.[5-8]

The present paper reports on the effects of high pressure on the Raman spectra of a single layer compound hexagonalBN and on the anisotropy of the force constants of the crystal. It also deals with a simple relation between the frequency of a shear-type rigid-layer mode and the elastic constant c_{44} of the layer compound, and with the pressure dependence of the c_{44} of hexagonalBN calculated with this relation.

EXPERIMENTAL

A powder of hexagonalBN annealed in a molybdenum induction furnance at 2100°C in a nitrogen atmosphere was used in the experiment. The powder sample belongs to the same lot as the powder used in the previous experiment on Raman scattering[4] for comparison with single crystals of hexagonalBN. The concentrations of the various defects in the powder are estimated to be considerably low from the results[9] of an analysis on powder samples annealed by the same method. The powder was put into a hole with a diameter of 0.2 mm pierced through the center of an Inconel gasket with a width of 0.2 mm whose open surfaces were both covered by $\frac{1}{8}$-carat diamonds with flat and smooth surfaces of 0.5 mm diameter.

The powder was pressurized in this diamond-anvil cell with a structure similar to that reported by Bassett *et al.*[10] A mixture of 4 parts methanol and 1 part ethanol was used as a pressure medium in the cell.[11] The pressure was measured by the shift of the R_1 fluorescence line of ruby[12,13] and was estimated to be quasihydrostatic to over 80 kbar, by the shape of the R_1 line.[12]

The Raman spectra of the crystal were measured at room temperature with a Spex Ramalog 4 spectrometer and a Spectra Physics model 165 argon-ion laser. The spectra obtained by excitation with the 488-nm line fell in ranges containing the two Raman lines on the Stokes side and the small-shift line on the anti-Stokes side.

RESULTS OF RAMAN SCATTERING

Figure 1 shows the pressure dependence of the frequencies of the Raman-active modes of the crystal. The frequencies of the two modes shifted to higher frequencies as pressure increased. The pressure dependence of the frequency shift of the intralayer mode was nearly linear, although a weak quadratic effect was observed. For the frequency shift of the shear-type rigid-layer (SRL) mode, the dependence showed a large quadratic effect, which may relate to the considerably large dependence on pressure of the c-axis parameter, as reported by Lynch and Drickamer.[14] The mean shifts of the SRL and intralayer modes in the pressure range from 1 bar to 110 kbar were 0.50 $cm^{-1} kbar^{-1}$ and 0.40 $cm^{-1} kbar^{-1}$, respectively.

According to a simple spring model[4] for the in-

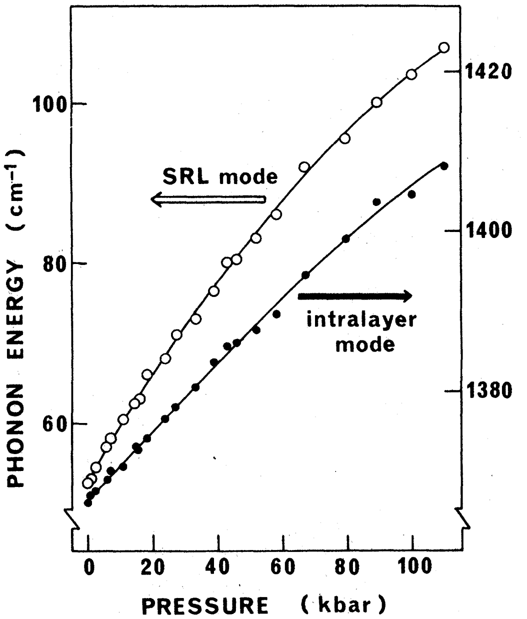

FIG. 1. Pressure dependence of wave numbers of the Raman-active phonons in hexagonal boron nitride at room temperature. Open and filled circles correspond to the shear-type rigid-layer mode and the intralayer mode, respectively.

teratomic binding of hexagonalBN, a constant α describing the degree of anisotropy in the binding force related with Raman-active modes of vibrations can readily be defined as

$$\alpha = (\omega_0/\omega_1)^2, \tag{1}$$

where ω_0 and ω_1 are the frequencies of the intralayer and SRL modes, respectively. Figure 2 shows the pressure dependence of the anisotropy constant, α. The constant α decreases considerably with pressure. Since the force contants are approximately proportional to the squares of the frequencies of the relevant vibrations, the interlayer shear force constant can be estimated to increase by four times as the pressure is raised from 1 bar to 110 kbar. On the other hand, the increment of the intralayer force constant in a similar pressure range is only 6%.

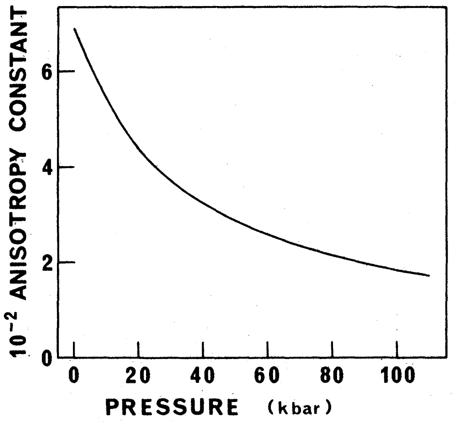

FIG. 2. Pressure dependence of the anisotropy constant, which is the ratio of the force constant related to the intralayer mode to that related to the shear-type rigid-layer mode.

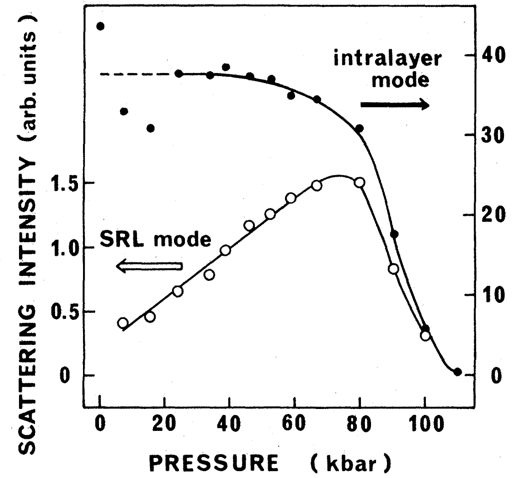

FIG. 3. Pressure dependence of the scattering intensities of the Raman lines observed on the Stokes side at room temperature. Open and filled circles correspond to the shear-type rigid-layer mode and the intralayer mode, respectively.

Figure 3 shows the pressure dependence of the integrated intensities of the Raman lines on the Stokes side. The intensity of the high-frequency line was nearly constant below about 80 kbar and decreased above it. The increase of the intensity of the low-frequency line in the low-pressure region may be due to the increase of the Raman-scattering factor corresponding to a modulation effect on the polarizability enhanced by the increase of interactions between atoms across the layer gap. For the integrated intensity of the intralayer mode, however, the modulation effect of the vibration on the polarizability may be small because of the weak pressure dependence of the a-axis parameter, as reported in Ref. 14. The cause of the apparent decrease of the intensities of the two lines above 80 kbar has not yet been clarified. Though the structure of hexagonalBN may partially have been changed, no new lines were observed in the Raman spectra.

MODE-GRÜNEISEN CONSTANTS

According to the spring model for the interatomic binding of hexagonalBN, ω_0 and ω_1 depend mainly on the force constants k_0 of the intralayer binding

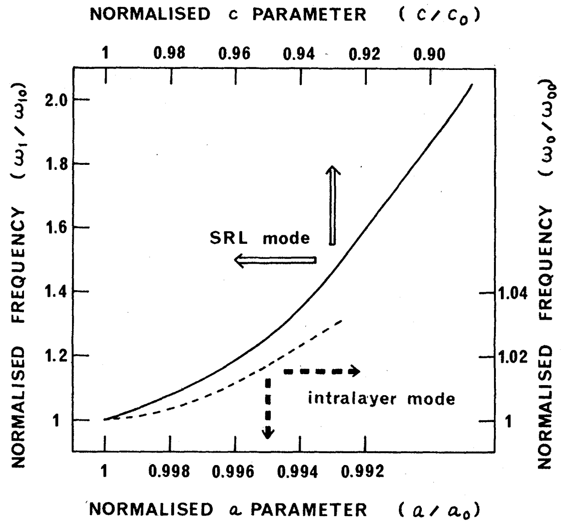

FIG. 4. Dependence of the frequencies of the Raman lines on lattice parameters. ω_1 and ω_0 denote the frequencies of the shear-type rigid-layer mode and the intralayer mode, respectively. The last subscript 0 of each symbol means that the symbol indicates the value under the pressure of 1 bar.

and k_1 of the interlayer binding of the crystal, respectively, and the dependence of ω_0 on k_1 and of ω_1 on k_0 can approximately be neglected. The constants k_0 and k_1 depend on the lattice parameters a_0 and c_0, respectively. Figure 4 shows the a_0 dependence of ω_0 and the c_0 dependence of ω_1; we used the data by Lynch and Drickamer[14] on the pressure dependence of the lattice parameters.

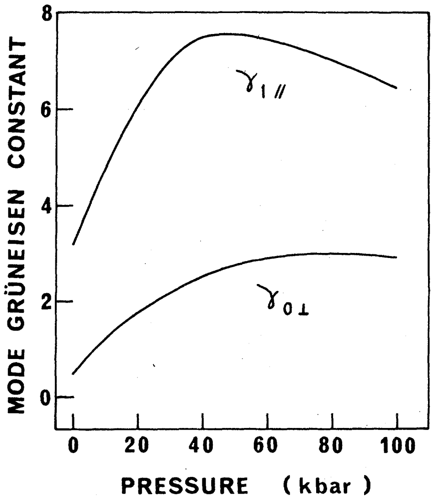

FIG. 5. Pressure dependence of the mode-Grüneisen constants. $\gamma_{0\perp}$ and $\gamma_{1\parallel}$ correspond to the a-axis component of the constant corresponding to the intralayer mode and the c-axis component of the constant corresponding to the shear-type rigid-layer mode, respectively.

Though the data calibrated by the ruby scale should be used here, we made no modification on their original data since the pressure difference[15-17] between the MgO scale in that paper and the ruby scale[12] is at most 2% below 110 kbar.

On the basis of this result, the mode-Grüneisen constants[18] of the two modes can be estimated as

$$\gamma_{0\perp} = -\frac{1}{2}\left(\frac{\partial(\ln\omega_0)}{\partial(\ln a)}\right)_c \approx -\frac{1}{2}\frac{\Delta\ln\omega_0}{\Delta\ln a}, \qquad (2)$$

$$\gamma_{1\parallel} = -\left(\frac{\partial(\ln\omega_1)}{\partial(\ln c)}\right)_a \approx -\frac{\Delta\ln\omega_1}{\Delta\ln c}, \qquad (3)$$

where $\gamma_{0\perp}$ is the a-axis component of the constant corresponding to the intralayer mode and $\gamma_{1\parallel}$ the c-axis component of the constant corresponding to the SRL mode. Figure 5 shows the pressure dependence of $\gamma_{0\perp}$ and $\gamma_{1\parallel}$. The values of $\gamma_{0\perp}$ and $\gamma_{1\parallel}$ increased with pressure up to 110 and 50 kbar, respectively, which shows that the intralayer and interlayer bond strengths do not uniformly harden, but the degree of increment of hardness increases, with pressure. Though such a feature may have a relation to the unique layer structure of the crystal, its origin remains to be clarified.

SHEAR ELASTIC CONSTANT

The frequency of the SRL mode in a uniaxial crystal with a layer structure has a close relation to the shear component of its elastic constant tensor c_{44}. In a simplified spring model, force constants relating to intralayer and interlayer bindings can be assumed to be mutually independent. According to this model, c_{44} is expressed as

$$c_{44} \approx \tfrac{1}{4}\rho d^2\omega^2, \qquad (4)$$

where ρ is the density of the crystal, d the interlayer spacing between the centers of adjacent layers, and ω the angular frequency of the SRL mode. Table I shows the frequencies of SRL modes and the c_{44} calculated with Eq. (4) for some crystals with layer structures by using Raman data.[4,19-23] Though direct measurements of c_{44} are difficult, approximate values for them can be obtained by this equation.

The pressure dependence of c_{44} in hexagonalBN can approximately be expressed as

$$c_{44} = 6.2 + 0.16p, \qquad (5)$$

where c_{44} and p are expressed in units of $10^9\ \mathrm{N\,m^{-2}}$ and kbar, respectively, and the pressure dependences of the lattice parameters reported in Ref. 14 are used. The c_{44} fractional increase with pressure, $(\Delta c_{44}/\Delta p)/(c_{44})_{p=0}$, is about 0.03 $\mathrm{kbar^{-1}}$ and considerably large compared with those of many nonlayered crystals. This feature may be due to

TABLE I. Frequencies of shear-type rigid-layer modes ω and shear elastic constants c_{44} of several uniaxial crystals with layer structures at room temperature. ρ and d are, respectively, the density and the interlayer spacing between centers of adjacent layers of the crystal.

Crystal	ω (cm^{-1})	c_{44} Present calculation (10^9 N m^{-2})	c_{44} Other data (10^9 N m^{-2})	ρ (g cm^{-3})	d (10^{-8} cm)
Hexagonal BN	52.5 [a]	6.2	···	2.27	3.33
Graphite	50 [b]	5.6	4.5 [c]	2.25	3.35
PbI_2 [d]	14.3 [e]	5.5	5.4 [e]	6.2	6.98
MoS_2	30 [f]	15	···	4.80	6.15
ϵ-GaSe	19.5 [g]	10.7	···	5.03	7.97

[a] Reference 4.
[b] Reference 19.
[c] Reference 20.
[d] D_{3d}^3 form.
[e] Reference 21.
[f] Reference 22.
[g] Reference 23.

the remarkably weak interlayer binding force of hexagonalBN.

SUMMARY

Remarkable pressure effects on the anisotropy of the binding force of layered hexagonal boron nitride were observed by the measurement of Raman scattering at high pressure. Further, a simple relation between the frequencies of shear-type rigid-layer modes and the elastic constants c_{44} of uniaxial crystals with layer structures was derived and shown to be useful for the estimation of c_{44} and particularly for studying its pressure dependence.

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