Cubic boron nitride at high pressures: equation of state and Raman light scattering

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The technique of diamond anvils was used in a study of the Raman light scattering and x-ray determination of the density of cubic boron nitride under pressures up to 34 GPa. The Grüneisen constants for the $LO(\Gamma)$ and $TO(\Gamma)$ vibrational modes were 0.91 ± 0.01 and 1.20 ± 0.01, respectively, and were independent of the density. An analysis of the P–V data made it possible to determine for the first time the bulk modulus of boron nitride and its pressure derivative: $K_0 = 382 \pm 3$ GPa, $K_0' = 4.46 \pm 0.15$. The experimental results were in agreement with the postulate of a close relationship between the stability of tetrahedral covalent crystals at high pressures and the electron structure of the chemical elements forming these crystals.

INTRODUCTION

The problem of stability of covalent tetrahedral crystals with the diamond structure has recently been tackled in several theoretical and experimental investigations.[1-5] It is known that the diamond lattice with the central interparticle interactions is unstable under macroscopic shear and transverse acoustic vibrations. The stability of real tetrahedral crystals with the diamond structure is due to the action of strong noncentral forces of covalent origin, which are responsible for the rigidity of the tetrahedral configuration of the interatomic bonds. Naturally, in a specific case the values of the elastic constants and vibrational frequencies can be used as a measure of the strength of the noncentral interactions. From the purely utilitarian point of view it is worth noting that in crystals of this type the frequency of the optical $LTO(\Gamma)$ mode, which is easiest to study experimentally at ultrahigh pressures, also includes a considerable contribution from the noncentral interactions.[6]

It follows that compression of silicon, germanium, and their isoelectronic analogs, which finally results in a phase transition, is characterized by softening of transverse acoustic (TA) modes and a reduction in the Grüneisen parameter $\gamma = -d \ln \nu / d \ln V$ of the $LTO(\Gamma)$ mode.[7]

On the other hand, experimental results demonstrate that diamond does not exhibit any loss of stability at pressures right up to 1 Mbar, which is clear evidence of the special nature of the noncentral interactions in diamond. As stressed in Ref. 1, the reason for the unique stability of diamond is the special electron structure of the carbon atom (i.e., the absence of inner p electrons). Consequently, an equally stable substance should be the closest isoelectronic analog of diamond, which is boron nitride with the zinc blende (borazon) structure.[1)]

The present paper reports an investigation of the behavior of the $LTO(\Gamma)$ mode and of the equation of state of borazon at high pressures. The results are compared with the available similar data on diamond.[9]

EXPERIMENTS

Pressures were created in a diamond cell of special construction described in Ref. 9; the pressure-transmitting medium was compressed helium. We investigated a single-crystal plate of synthetic boron nitride of $60 \times 35 \times 15$ μm dimensions. The pressure was deduced from the shift of the R_1 luminescence line of ruby; the random error of the pressure values was 0.05 GPa.

The x-ray determination was carried out employing the usual DRON 2.0 two-circle diffractometer and Mo $K_{\alpha 1}$ radiation. The basal plane of the sample coincided with the (110) plane, but a steel spacer between the anvils allowed only one [440] reflection to be recorded. The interplanar distance was determined to within 10^{-4} Å.

The technique used in recording the Raman light scattering spectra between diamond anvils was described in Ref. 9. Strong background scattering by the anvils at frequencies close to the $LO(\Gamma)$ mode of borazon made it difficult to record the LO Raman scattering peak at low pressures and made measurements impossible at $P > 5$ GPa. The error in determining the spectral position of the TO peak was 0.5 cm^{-1}. The half-width of this peak was less than the instrumental half-width at pressures $P \leqslant 30$ GPa.

The Raman scattering spectra were recorded using the same sample and always under the same loads, which determined the interplanar distance. All the measurements were carried out at room temperature.

The experimental relationships between the measured quantities were practically linear and could be represented quite accurately by the following expressions

$$\rho/\rho_0 - 1 = (4{,}95 \pm 0{,}03)(\lambda/\lambda_0 - 1) - (5{,}7 \pm 2{,}3)(\lambda/\lambda_0 - 1)^2, \tag{1}$$

$$\nu_{TO}/\nu_{TO}{}^0 - 1 = (5{,}93 \pm 0{,}04)(\lambda/\lambda_0 - 1) - (8{,}4 \pm 2{,}7)(\lambda/\lambda_0 - 1)^2, \tag{2}$$

$$\nu_{LO}/\nu_{LO}{}^0 - 1 = (4{,}54 \pm 0.04)(\lambda/\lambda_0 - 1), \tag{2'}$$

where ρ, ν_{TO}, ν_{LO}, and λ are the current values of the density, Raman scattering frequencies, and wavelength of the R_1 luminescence line of ruby; ρ_0, ν_{TO}^0, ν_{LO}^0 and λ_0 are the same quantities at $P = 0$. It follows from our measurements that

$$\rho_0 = (1.693 \pm 0.003) \cdot 10^{22} \text{ atoms/cm}^3, \ \nu_{TO}{}^0 = 1055.8 \pm 0.5 \text{ cm}^{-1},$$

$$\nu_{LO}{}^0 = 1306.3 \pm 0.5 \text{ cm}^{-1}.$$

The coefficients in Eqs. (1) and (2) were calculated by the least-squares method and the numerical errors given above corresponded to the 65% confidence limit.

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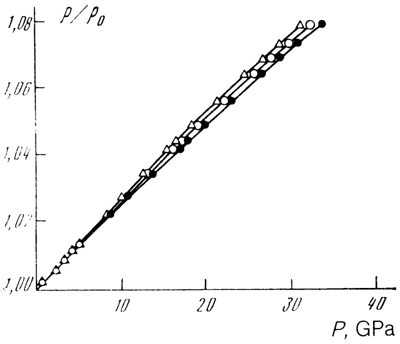

FIG. 1. Pressure dependence of the density of borazon. Initial density $\rho_0 = (1.693 \pm 0.0003) \times 10^{23}$ at/cm^3; △, ○, and ● represent the results of the present study and the pressures were calculated using different calibration dependences from Refs. 10, 12, and 9.

Equations (1) and (2) can be converted to the form $\rho(P)$ and $\nu(P)$ provided we know $P(\lambda)$ reliably. As shown in Ref. 9, the modern scale of high pressures[10] cannot be used to match the results of ultrasonic investigations of diamond under pressure[11] to the experimental equation of state of diamond deduced using diamond anvils.[9] A new "diamond" calibration dependence $P(\lambda)$ proposed in Ref. 9 does satisfy this requirement. For the sake of comparison, we analyzed our results using the scales in Refs. 9, 10, and 12.

DISCUSSION OF RESULTS

1. Equation of state of BN

Figure 1 shows the function $P(\rho)$ calculated from Eq. (1) using calibration functions from Refs. 9, 10, and 12. In view of the exceptionally low compressibility of boron nitride and the small relative value of the compression, the Hall nonlinear $P(\rho)$ curve can be described by the first two terms in the expansion of the pressure in powers of deviation of the density from its equilibrium value:

$$P=A(\rho/\rho_0-1)+{}^1/_2B(\rho/\rho_0-1)^2. \qquad (3)$$

The coefficients of this expansion can be defined in terms of the properties of matter at zero pressure: $A = K_0$, $B = K_0(K_0' - 1)$, where K_0 and K'_0 represent the bulk modulus and its first derivative with respect to pressure at $P = 0$. The numerical values of K_0 and K_0' obtained from Eq. (3) are listed in Table I together with the theoretical results from Ref. 13 and the corresponding data on the elastic properties of diamond.[9,11]

In the light of the available data on the elastic properties of covalent crystals,[7,9] the value $K_0' = 4.46$ for BN is to be preferred (see Table I). In turn this supports the diamond high-pressure scale proposed in Ref. 9.

We conclude this subsection by drawing attention to the practically identical volume dependences of the bulk modulus of diamond and cubic boron nitride (Fig. 2). Obviously, the difference between the total energies of diamond and borazon does not vary faster than the first power of the volume. The universality of the $K(V)$ curve was not trivial in this case because the bulk elasticity of cubic silicon carbide (β-SiC) does not obey the dependence shown in Fig. 2.

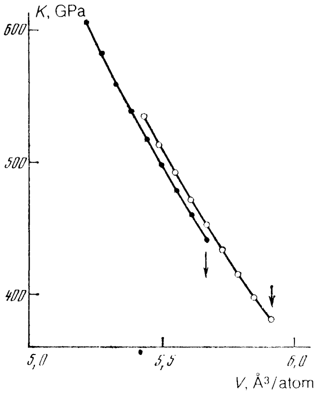

FIG. 2. Volume dependence of the bulk modulus of diamond (●) and borazon (○) calculated from the P–V data. The arrows identify the volumes corresponding to $P = 0$. The indeterminacy of the value of K at high pressures is due to indeterminacy of the high-pressure scale[9] but it does not affect the proximity of the curves.

2. Raman light scattering

As pointed out above, the Raman scattering spectra were recorded simultaneously with determination of the interplanar distance (using the same sample and always under the same loads). This made it possible to determine experimentally the dependence $\nu_i(\rho)$ shown in Fig. 3 and to calculate directly the Grüneisen parameter

$$\gamma_i=-d\ln \nu_i/d\ln V=d\ln \nu_i/d\ln \rho.$$

An analysis of the experimental results showed that for compression in the range $1 \leqslant \rho/\rho_0 \leqslant 1.08$ the value of γ_i was independent of the density and this was true both of LO and TO phonons. A calculation carried out in the same approximation yielded $\gamma_{LO} = 0.91 \pm 0.01$ and $\gamma_{TO} = 1.20 \pm 0.01$.

It should be pointed out that the results of a different experimental investigation[14] of the dependences $\nu_{LO}(P)$ and $\nu_{TO}(P)$ for borazon were in good agreement with our data. On the other hand, the numerical values of the Grüneisen parameters $\gamma_{LO} = 1.2 \pm 0.1$ and $\gamma_{TO} = 1.5 \pm 0.1$ obtained in Ref. 14 differed considerably from our value. Clearly, the discrepancy was due to the fact that in the experiments reported in Ref. 14 the volume of the substance during compression was not known, so that the Grüneisen parameters were determined from

TABLE I. Bulk moduli K_0, their pressure derivatives K_0', and Grüneisen parameters of $LTO(\Gamma)$ modes of diamond and borazon.

Substance	K_0', GPa	K_0'	γ
Diamond	442±3 [а]	4,0±0,7 a	0,965±0,005 b
Borazon	385±3 [в]	2,35±0,21 c	1,20±0,01 (*TO*) f
	379±3 [г]	3,50±0,20 d	0,91±0,01 (*LO*) f
	382±3 [д]	4,46±0,15 e	0,954 (*LTO*) f
	367 [ж]	–	–

Note. [a] Data from Ref. 11; [b] data from Ref. 9; [c] our results, pressure scale from Ref. 10; [d] our results, scale from Ref. 12; [e] our results, scale from Ref. 9; [f] our results; [g] data from Ref. 13.

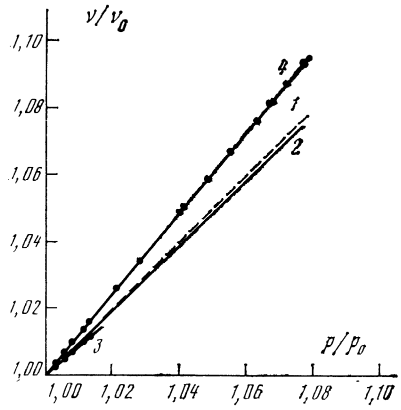

FIG. 3. Dependence of the frequency of long-wavelength optical vibrations of diamond and borazon on the density: 1) ν_{LTO} for diamond; 2), 3), and 4) $\bar{\nu}_{LTO}$, ν_{LO}, and ν_{TO}, respectively for borazon (see text).

$$\gamma_i = -\frac{d\ln\nu_i}{d\ln V} = \frac{K_0}{\nu_i}\frac{d\nu_i}{dP}.$$

Naturally, in such calculations the results depended on the high-pressure scale. Moreover, the authors of Ref. 14 used a highly overestimated empirical value of $K_0 = 465$ GPa. According to our calculations, the bulk modulus of borazon was $K_0 = 382 \pm 3$ GPa at $P = 0$ (see above).

In a direct comparison of the volume dependence of the optical vibration frequencies of diamond and borazon it is useful to introduce the average Grüneisen parameter of borazon representing the behavior of the "average" frequency of the *LTO* mode free of the Coulomb contribution. This can be done using the expression[15]

$$\bar{\nu}_{LTO}^2 = (\nu_{LO}^2\varepsilon_\infty + 2\nu_{TO}^2)/(\varepsilon_\infty + 2), \tag{4}$$

where ε_∞ is the hf permittivity of the material. In the case of borazon we have $\varepsilon_\infty^0 = 4.502\,(14)$ and $\bar{\nu}_{LTO}^0 = 1235\ \text{cm}^{-1}$ at $P = 0$.

By analogy with Si and C (Ref. 14), we shall assume that borazon is characterized by $\partial\ln\varepsilon_\infty/\partial\ln a = 1.8$ (a is the lattice parameter) Consequently, the experimental dependences $\nu_{LO}(V)$ and $\nu_{TO}(V)$ yield the average unsplit frequency obeying the Grüneisen law

$$\bar{\nu}_{LTO}(V) = \bar{\nu}_{LTO}^0 (V/V_0)^{-\gamma_{LTO}}, \tag{5}$$

where $\gamma_{LTO} = 0.954$, which is practically identical with the Grüneisen parameter of diamond (Fig. 3 and Table I).

CONCLUSIONS

We investigated the influence of compression on the lattice dynamics and elastic properties of borazon at pressures up to 34 GPa. The equation of state derived for borazon was used to calculate the bulk modulus $K_0 = 382 \pm 3$ GPa and its first derivative with respect to the pressure $K_0' = 4.46 \pm 0.15$ at $P = 0$, which were the two parameters that determined uniquely the equation of state in the investigated range of pressures. The value of K_0 was found to be quite close to the theoretical value obtained earlier.[13] The volume dependences of the frequencies of the $LO(\Gamma)$ and $TO(\Gamma)$ modes were determined directly and it was found that they obeyed the Grüneisen law $\nu/\nu_0 = (V/V_0)^{-\gamma}$. The values of the Grüneisen parameters γ_{LO} and γ_{TO} differed considerably from the results of an earlier investigation.[14]

Comparison of the dependences $K(V)$, $\nu_{LO}(V)$, and $\nu_{TO}(V)$ for borazon and diamond[9] revealed a certain degree of similarity between these two substances, as illustrated in Figs. 2 and 3. The Grüneisen parameters of the *LO* and *TO* modes of borazon and their "average" value did not decrease with pressure, so that the stability range of cubic borazon should be, like that of diamond, much wider than assumed earlier. Consequently, the hypothesis relating the unique stability of diamond to the absence of inner p electrons was confirmed once again. Naturally, a complete proof of the stability of these substances can be given only when information becomes available on the behavior of transverse acoustic phonons under pressure.

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[1)] It is interesting to note that investigations of an isoelectronic analog of diamond in the form of BeO revealed[8] that the low frequency $E_2(\Gamma)$ mode has a positive pressure coefficient, whereas this coefficient is negative for other compounds belonging to the II-VI family of compounds.

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