Equation of state and Raman scattering in cubic BN and SiC at high pressures

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The results of simultaneous measurements of first-order Raman spectra and the lattice parameter of cubic BN and SiC at pressures of up to 34 and 42.5 GPa are presented. The bulk moduli and their pressure derivatives at $P = 0$, and also the volume dependences of the Grüneisen parameters of the LTO(Γ) modes have been determined. The "average"[1)] Grüneisen parameter, $\bar{\gamma}_{\mathrm{LTO}}$, of boron nitride is found to remain essentially constant upon compression. In contrast, the Grüneisen parameter of silicon carbide, $\bar{\gamma}_{\mathrm{LTO}}$, decreases as a result of the application of pressure. A correlation is established between the electronic structure of the ion cores and the behavior of the optical modes under pressure in C, BN, SiC, and Si.

In the present letter we report the results of an experimental study of LTO (Γ) modes and the equation of state of cubic BN and SiC at pressures of up to 34 and 42.5 GPa.

The experiments were carried out in a specially designed diamond cell which could be used in single-crystal x-ray studies and in optical measurements in compressed helium. The test samples were single-crystal wafers of synthetic Bn and SiC measuring $\sim 60 \times 30 \times 15$ μm.

The pressure was determined from the shift of the R_1 luminescence line of a ruby detector, using the calibration plot[1] $P(\Delta\lambda)$. The ruby detector was placed next to the sample to be tested. The random error in measuring the pressure was ~ 0.05 GPa.

The specific volume of borazon was determined from the angular position of the [440] reflection and that of silicon carbide was determined from the positions of the [440] and [404] reflections which were measured by means of the standard, two-circle DRON 2.0 diffractometer, using MoK_{α_1} radiation. The interplanar spacing $d_{[440]}$ was determined within $\sim 4 \times 10^{-4}$ Å, consistent with the accuracy for the volume, $\sim 1.6 \times 10^{-2}$ Å^3/at, or $\sim 0.3\%$. The difference $d_{[440]} - d_{[404]}$ for SiC did not exceed the error in determining the interplanar spacing up to 42.5 GPa, suggesting that the hydrostatic pressure of the medium is sufficiently high.

The Raman spectra were excited by a light from an argon laser ($\lambda = 514.5$ nm) and were recorded using a double diffraction DFS-24 spectrometer in the photon-counting mode. The frequency of the Raman scattering was measured within ~ 0.5 cm^{-1}. A strong background scattering from diamond anvils in the frequency range close to the frequency of the LO oscillation of borazon limited the region in which this mode could be studied to a pressure of ~ 0.5 GPa.

The x-ray and optical measurements were carried out each time on the same

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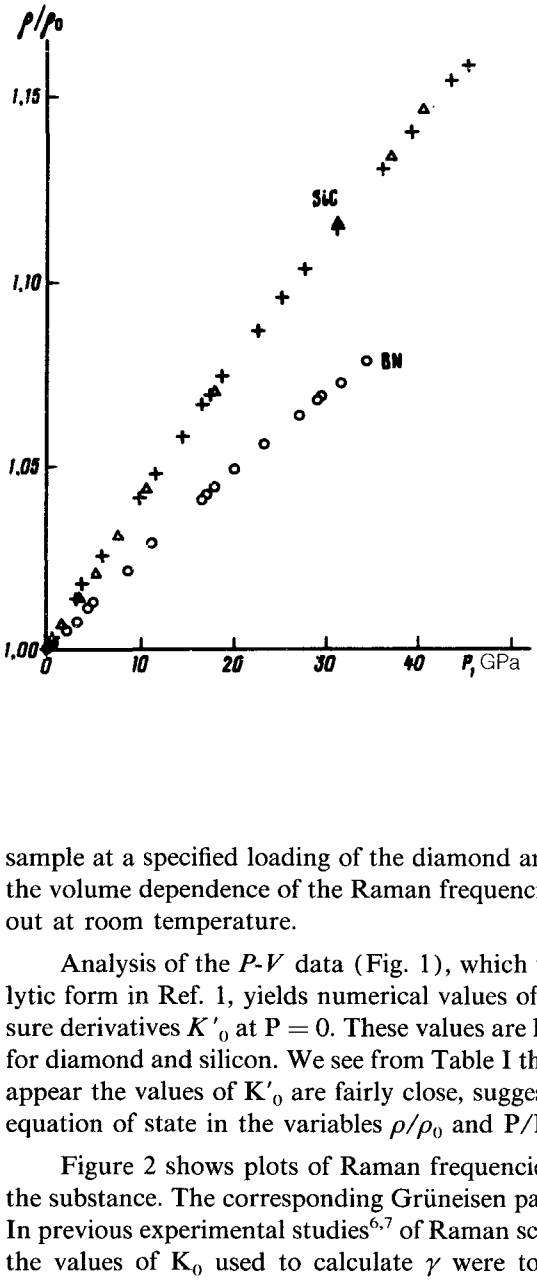

FIG. 1. A plot of density versus pressure for SiC and BN. + —Forward evolution; Δ—backward evolution (SiC); O—forward evolution (BN).

sample at a specified loading of the diamond anvils, allowing us to directly determine the volume dependence of the Raman frequencies. All the measurements were carried out at room temperature.

Analysis of the P-V data (Fig. 1), which were presented in the appropriate analytic form in Ref. 1, yields numerical values of the bulk moduli K_0 and of their pressure derivatives K'_0 at $P = 0$. These values are listed in Table I, along with K_0 and K'_0 for diamond and silicon. We see from Table I that the row in which C, BN, SiC, and Si appear the values of K'_0 are fairly close, suggesting that for them there is a universal equation of state in the variables ρ/ρ_0 and P/K_0.

Figure 2 shows plots of Raman frequencies versus the degree of compression of the substance. The corresponding Grüneisen parameters at $P = 0$ are listed in Table I. In previous experimental studies[6,7] of Raman scattering in BN and SiC under pressure, the values of K_0 used to calculate γ were too high, yielding higher values of the Grüneisen parameters than those obtained by us.

We recall that in polar crystals of the class we are studying the LTO(Γ) mode splits because of the existence of long-range Coulomb forces. This splitting can be described in terms of the "effective" charge e^*.[8] Accordingly, the difference in the behavior of $\nu_{LO}(\rho)$ and $\nu_{TO}(\rho)$ for BN and SiC (Fig. 2) is attributable to the difference in $e^*(\rho)$ (Ref. 6). In our comparative analysis we will use the average optical

TABLE I. Bulk moduli, their pressure derivatives, and the Grüneisen parameters for C, BN, SiC, and Si.

Substance	K_0, GPA	K'_0	γ_i^0	$(\partial\gamma_i/\partial(\rho/\rho_0))^{2)}_{\rho=\rho_0}$
C	442 ± 3 [a]	4,0 ± 0,7 [a]	0.97 ± 0,01 (*LTO*) [b]	0 (*LTO*) [b]
BN	382 ± 3 [c]	4,5 ± 0,2 [c]	0.91 ± 0,01 (*LO*) [c]	0 (*LO*) [c]
	363 [d]	3,5 [d]	1,188 ± 0,002 (*TO*) [c]	0 (*TO*) [c]
	369 ± 14 [d]	4,0 ± 0,2 [d]	0,93*	0*
SiC	227 ± 3 [c]	4,1 ± 0,1 [c]	1,091 ± 0,007 (*LO*) [c]	− 0,37 ± 0,13 (*LO*) [c]
	212 [e]	3,7 [e]	1,102 ± 0,002 (*TO*) [c]	0 (*TO*) [c]
	224 [e]		1,07*	− 0,34*
Si	97,9 ± 0,2 [f]	4.16 [f]	0,98 ± 0,06 (*LTO*) [g]	− 1,12 ± 0,08 (*LTO*) [g]

a—Data of Ref. 2; b—data of Ref. 1; c—our data; d—data of Ref. 3; e—data of Ref. 4; f—data of Ref. 5; g—our calculations based on the data of Ref. 9; *—our calculations for the frequency $\bar{\nu}_{\mathrm{LTO}}$ which does not have a Coulomb component (see the text).

frequency without the Coulomb component. This frequency, according to Ref. 9, is given by

$$\bar{\nu}^2_{LTO} \equiv \frac{k}{\mu} = \frac{\epsilon_\infty \nu^2_{LO} + 2\nu^2_{TO}}{\epsilon_\infty + 2},$$

where k is the non-Coulomb strength constant corresponding to the given mode. μ is the reduced mass, and ε_∞ is the rf dielectric constant.

The results of the calculations are shown in Figs. 2 and 3 and in Table I. As can be seen, $\bar{\gamma}_{\mathrm{LTO}}$ for BN is virtually independent of the density, consistent with the "diamond" behavior,[1] while the behavior of $\bar{\gamma}_{\mathrm{LTO}}$ for SiC links this substance with silicon.

It can be said about this result that a decrease in the rate at which $\nu_{\mathrm{LT}(\Gamma)}$ increases in silicon precedes the phase transition and may be an indication of the loss of stability, along with the experimentally established pressure-induced softening of TA(X), TA(L), and TA(Σ) phonons.[10]

The strength constants, which determine the LTO oscillation frequencies, actuate the combined contribution from the central and noncentral interactions. The latter contribution clearly determines the specific features of the behavior of phonon frequencies in silicon.[8,11]

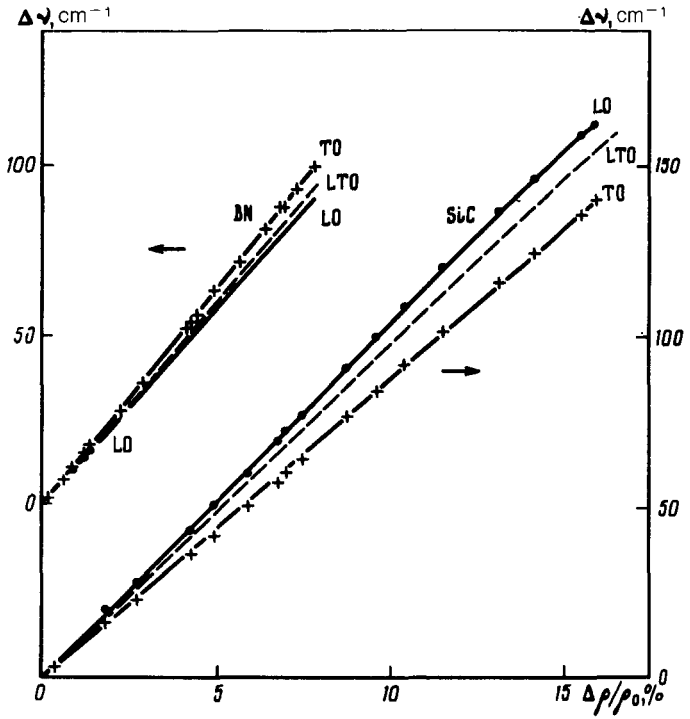

FIG. 2. The Raman frequencies of Bn and SiC versus the degree of compression. At $P=0$, $\nu_{TO}=1055.8$ cm^{-1}, and $\nu_{LO}=1306.3$ cm^{-1} for BN; $\nu_{TO}=795.9$ cm^{-1} and $\nu_{LO}=972.9$ cm^{-1} for SiC. In calculating $\tilde{\nu}_{LTO}(\rho)$ for BN and SiC it was assumed that $\partial \ln \varepsilon_\infty / \partial \ln \rho = -0.6$ (Ref. 6). Furthermore, since the LO(Γ) mode of BN was studied in a narrow range (see the text proper), we had to calculate $\nu_{LO}(\rho)$ outside this range using the relation[8] $\nu_{LO}^2 = [4\pi(e^*)^2/\mu\Omega\varepsilon_\infty] + \nu_{TO}^2$, where Ω is the unit-cell volume. In this calculation we worked from an experimentally established conclusion that the effective charge e^* of borazon depends linearly on the degree of compression only slightly (according to our data, $\gamma_{e^*} = -0.51$; according to the calculation of Ref. 6, $\gamma_{e^*} = -0.67$).

Diamond, whose exceptional stability at high pressures has been determined by direct experiments, gives us, on the other hand, a fundamentally different example of the behavior of $\nu_{LTO(\Gamma)}$.

We emphasize in this connection that an unusually large stability region of diamond is the result, according to the theory advanced by Yin and Cohen,[12] of the absence of p electrons in the ion core of carbon.

The results of our experiments, which characterize the behavior of $\nu_{LTO(\Gamma)}$ of the isoelectronic analog of diamond—borazon, and of the "intermediate" substance—β-SiC, suggest that there is a definite relationship between the stability of the substance,

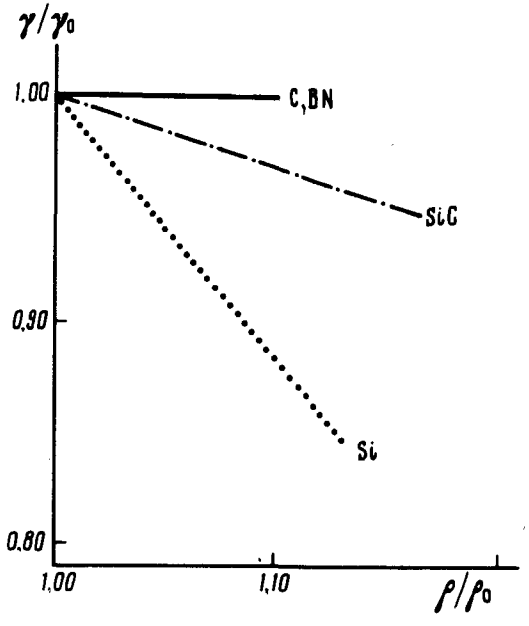

FIG. 3. Dependence of $\gamma_{\text{LTO}}(\Gamma)$ on the degree of compression for diamond, BN, SiC, and Si. The results for $\bar{\gamma}_{\text{LTO}}(\Gamma) = \partial \ln \bar{\nu}_{\text{LTO}} / \partial \ln \rho$ are given for BN and SiC (see the text).

the volume dependence of the Raman frequencies, and the electronic structure of the ion core of the particles that form the crystal.

[1)]Here and elsewhere the average Grüneisen parameter is taken to mean the quantity $\bar{\gamma}_{\text{LTO}} = -d\ln\bar{\nu}_{\text{LTO}}/d\ln V$, where ν_{LTO} is the frequency in which the Coulomb component is missing (see the text proper).
[2)]It is easy to show that at $\gamma_i^0 \sim 1$ we have $[\partial\gamma_i/\partial(\rho/\rho_0)_{\rho=\rho_0}] \sim [\partial^2(\nu_i/\nu_i^0)/\partial(\rho/\rho_0)^2]\ \rho=\rho_0$.

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