# Pressure dependence of the optical-absorption edge of cubic boron nitride

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The optical-absorption edge of zinc-blende-structure boron nitride has been measured at high pressure to 1.8 GPa using a sapphire-anvil cell. The effect of pressure on the minimum band gap is found to be 6.0 meV/GPa, which is greater than twice the value found in recent *ab initio* calculations.

The cubic form of boron nitride (c-BN) is very similar to diamond. The two materials have fascinating properties such as extreme hardness, high thermal conductivity, and high melting point.[1] They have band gaps which are wide and indirect. There is, however, a small difference in the band structures. The indirect transition in c-BN is from the $\Gamma$ point of the valence band to the $X$ point of the conduction band,[2-8] whereas it is from $\Gamma$ to $\Delta$ [or $(0.7-0.8)X$] in diamond.[9-11]

We have reported from an optical-absorption-edge measurement that the indirect gap of diamond increases with increasing pressure.[12] The coefficient of the increase, 6.0 meV/GPa, is in close agreement with first-principles calculations,[10,13] but on the other hand is opposite in sign to those of the group-IV elements, silicon and germanium.[14]

Viewed from the similarity of the properties between c-BN and diamond, it is intuitively expected that c-BN would also show a positive pressure coefficient for the energy gap. Indeed, Zunger and Freeman[2] using the linear combination of atomic orbitals method, have given a value of 2 meV/GPa for the pressure dependence of the energy gap between $\Gamma_{15}$ and $X_1$. With a pseudopotential approach, Van Camp, Van Doren, and Devreese[5,15] have obtained values between 2.5 and 2.6 meV/GPa for the pressure coefficient for the same energy gap. Also, Wentzcovitch, Chang, and Cohen,[3] from a pseudopotential calculation, have obtained a positive pressure coefficient for the indirect energy gap.

We have extended our study on diamond[12] towards c-BN. The c-BN crystals grown at high pressure by a temperature gradient method[16] were, in most cases, triangular platelets with the crystallographic (100) plane parallel to the plate. Spectroscopic data of the crystals taken at ambient conditions were reported earlier.[17] For the samples to be studied, platelets approximately 200 $\mu$m across and 100 $\mu$m thick were chosen from as-grown crystals. Each sample was pressurized in a gasketed sapphire-anvil cell.[18]

The sample arrangement and the system for the absorption-edge measurement were basically the same as in the earlier study[12] except for the pressure-transmitting medium employed. After testing a variety of liquids it turned out that water was best transparent to near-

ultraviolet radiation, the region of interest. Although water freezes at around 1 GPa into ice VI and this crystalline phase, in turn, transforms into ice VII at 2 GPa, $H_2O$ remains a medium that is able to transmit quite a hydrostatic pressure.[19] Thus, water was employed for the pressure-transmitting medium. The pressure generated was measured by the shift of the fluorescence line of ruby[20] which was incorporated into the sample space. A total of 26 measurements were made at room temperature on five different samples.

Figure 1 shows typical examples of transmittance data. The transmittance of the c-BN sample was obtained by reference to a measurement when the sample space was filled only with water. There appear two bents in the transmittance data at each pressure. Of the two, the bent shown by the arrow is better defined and hence is taken as the absorption edge. The absorption edge appearing at 197.6 nm at ambient pressure shifts towards shorter wavelength as the pressure is elevated.

The transmittance at each pressure was converted to the absorption coefficient. Figure 2 shows the absorption coefficient plotted against the photon energy. There are again two bents, around 6.26 and 6.28 eV, on the curves. In correspondence with Fig. 1, the bent at higher energy
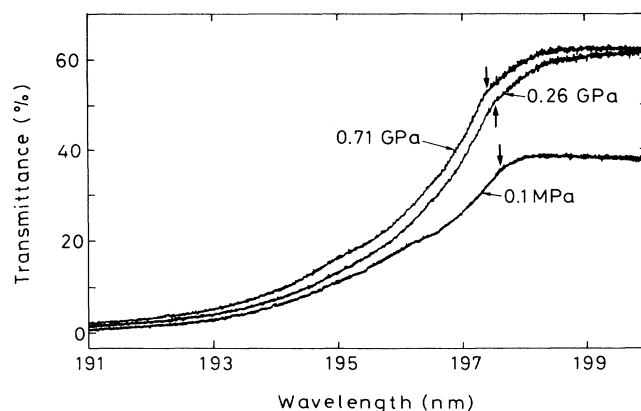


FIG. 1. Transmittance data for cubic BN. We define the absorption edges at the points shown by arrows (see text).
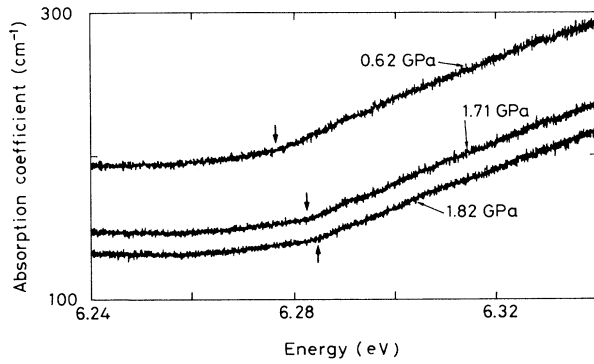
FIG. 2. Absorption coefficient vs photon energy for cubic BN. The energies for the bents, shown by arrows, are defined as the indirect gap energies (see text).

(shown by the arrow) is better defined for the absorption-edge energy.

The absorption-edge energy is plotted in Fig. 3 as a function of pressure. The energy at ambient pressure is about 6.272 eV, a little higher than a previous experimental value (6.1 eV).[17] This arises from the different definition for the absorption edge in the transmittance data. It should be noted that the difference does not give rise to any difference in deriving the pressure coefficient because the shifts of the bents in Figs. 1 and 2 take place almost in a parallel manner. The absorption-edge energy increases linearly with increasing pressure, without showing any discontinuity. The solid line in Fig. 3 is a least-squares fit, which gives a slope of 6.0 meV/GPa.

The absorption-edge energy ($\hbar\omega_{obs}$) is expressed as

$$\hbar\omega_{obs} = E_g - E_{ex} \pm E_p , \tag{1}$$

where $E_g$ is the band gap, $E_{ex}$ the exciton binding energy,
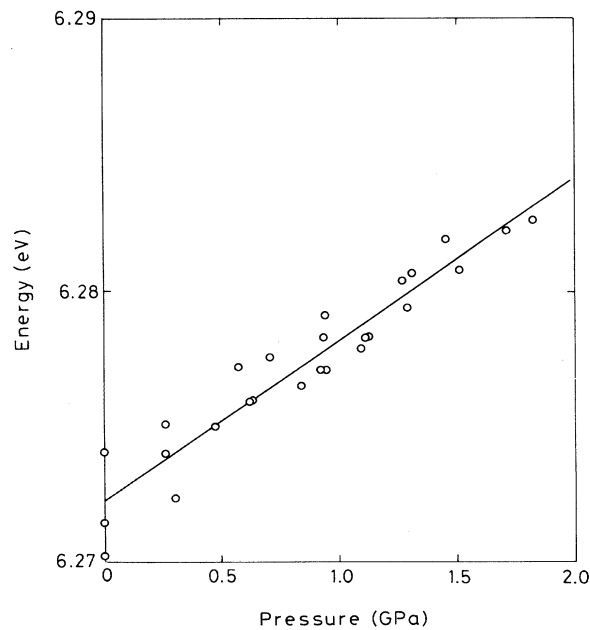


FIG. 3. Plots of energy against pressure.

and $E_p$ the phonon energy. If the pressure dependences of $E_{ex}$ and $E_p$ pertinent to the indirect transition are known, the pressure dependence of $E_g$ in Eq. (1) can be derived. Data for the pressure dependence of the exciton binding energy are not available; we neglect these terms as in the case of diamond.[12] Effect of pressure on the phonon energy can at present be derived only from Raman shift data on the assumption that the pressure coefficient for the phonon energy is the same throughout the reduced Brillouin zone. A coefficient of about 0.4 meV/GPa has been obtained for both the LO and TO modes from Raman-scattering experiments.[21,22] This value is adopted here, although no assignment has been made of the phonon modes responsible for the indirect transition of c-BN. Consequently, we obtain a value of (6.0±0.4) meV/GPa for $dE_g/dP$ of the indirect energy gap. The sign can be positive or negative according to whether the pertinent phonons are emitted or absorbed. The pressure coefficient for the indirect energy gap of c-BN is very similar to that of diamond, 6.0 meV/GPa, which is obtained also for the indirect gap.[12]

In Table I we compare the present experimental results with calculations[2,3,5,7,15] and also with experiments undertaken at ambient pressure.[17,23,24] All the calculations yield positive pressure coefficients for the gap energy, in qualitative agreement with the present experiment. Quantitatively, however, the calculated values for the pressure coefficient are significantly smaller than even half the present experimental value. This is different from the case of diamond in which some of the first-principles calculations[10,13] agree fairly well with experiment.[12] We note, nevertheless, that for diamond the authors of both Refs. 5 and 15 have predicted a pressure coefficient of the energy gap[25] that is in reasonable agreement with experiment.[12]

Comparison between the experiments and calculations in Table I further shows that the energy gap at ambient pressure is either significantly overestimated[2] or underestimated[3,5,15] relative to the experimental values (present result and Refs. 17, 23, and 24). Underestimation also occurs in other calculations[4,6,8] (not shown in Table I) except one[7] that has yielded a gap energy of 6.3 eV, being very close to the experimental values. This again is different from the case of diamond in which the energy gap has been unanimously underestimated relative to experiments (see Ref. 12 and references cited therein).

For the ground-state properties, on the other hand, the theoretical works shown in Table I have achieved really good predictions. The lattice constant computed (between 0.3606 and 0.3674 nm) agrees with experimental value (0.3615 nm) within 1.6%.[3,5,15] Also, the bulk modulus predicted (367 GPa) (Refs. 3 and 5) is in close agreement with a recent experiment (369 GPa).[26] Yet, there is at present no calculation available which can fully describe both the ground-state and electronic properties.

The present study has shown that the band-gap behavior of c-BN under pressure is similar to diamond and is different in sign from that observed in other indirect energy-gap materials.[14] The pressure-induced increase of the energy between the Γ point of the valence

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TABLE I. The indirect energy gap of cubic BN and its pressure coefficient.

| Method | $E_g$ at 0.1 MPa (eV) | $dE_g/dP$ (meV/GPa) | Reference |
|--------|------------------------|----------------------|-----------|
| | Experiment | | |
| Transmittance | $6.27\pm0.02$ | $6.0\pm0.4$ | This study |
| Transmittance, reflectance | $6.1\pm0.2$ | | 17 |
| X-ray emission | $6.0\pm0.5$ | | 23 |
| Transmittance | $6.4\pm0.5$ | | 24 |
| | Calculation | | |
| LCAO[a] | 8.7 | 2 | 2 |
| Pseudopotential | 4.2 | 1.1[b] | 3 |
| Pseudopotential | 4.20 | 2.6 | 5 |
| Pseudopotential | 3.96 | 2.5 | 15 |
| GW approximation | 6.3 | | 7 |

[a]Linear combination of atomic orbital basis.
[b]This value is not explicitly given in Ref. 3. We have obtained this from the 1.1 eV increase in energy with 50% reduction of the volume that is given in Ref. 3 and the equation-of-state data after Ref. 26.

band and the $X$ point of the conduction band of $c$-BN can unequivocally be interpreted by an eventual separation of the two points with increasing pressure. Interpretations for the energy separation are two ways. One envisages the separation by a much more rapid decrease of the valence-band energy relative to the conduction-band energy, while both are decreasing with pressure.[2] The other ascribes the separation to a steeper increase of the conduction-band energy relative to the valence-band energy, while both increase with pressure.[3] Despite the opposite signs for the pressure effects on the pertinent points in the valence and conduction bands, the two theories,[2,3] respectively, derive a positive pressure coefficient for the band-gap energy. In any event, it is

likely that the behavior similar to diamond arises from the absence of the $d$ orbital in the valence state.

In conclusion, the present experiments have revealed that the pressure dependence of the indirect energy gap of $c$-BN is very close to that of diamond. Different from the case of diamond, the pressure coefficient derived from our experiments is much more than twice the existing calculations. Discrepancy is also met in the energy gap at ambient pressure between experimental and computed values, except for that of Surh, Louie, and Cohen.[7]

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