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# Dynamical Charge and Force Constant Calculations in c-BN under Pressure

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A combination of an adjusted pseudopotential method and the bond-orbital model of Harrison was used to derive the polarity and the force constants of cubic boron nitride (c-BN) under pressure up to 900 kbar. The results show that the hybrid covalent energy dominates at high pressure and the transverse effective charge changes by less than 3.3% between normal condition and 900 kbar. The idea of taking the free-atom term values and the  $1/d^2$  formulae for the covalent energy is not a good approximation to estimate the variation of the transverse effective charge under pressure. In fact, this approximation overestimates the relative variation to 10.2% in the same range of pressure.

## 1. Introduction

Boron nitride (BN) is a chemically and thermally stable, highly insulating material. It is currently known to exist in several crystal structures. The most common structures being the zinc-blende structure (or cubic BN), a layered structure similar to graphite (g-BN), and a wurtzite-type structure (w-BN). Cubic BN is especially a hard material and has other potential applications. In fact c-BN is a promising material for use as hightemperature, wear-resistant, hard solid lubricant as well as a protective insulating film on semiconductors under a variety of harsh environmental conditions. However, the physical properties of c-BN when subjected to external perturbations such as high pressures and high temperatures are scarcely known [1, 2]. The material has been investigated by Raman scattering in a large range of temperatures up to 1600 K [1] where it was found that, in this range, Born's transverse effective charge changes by less than 2.5%. It was also found that the relatively small change in the frequency of the Raman modes of c-BN indicates that the material retains its strong mechanical properties at high temperature and hence indicates its suitability for high-temperature applications. Under a hydrostatic pressure less than 100 kbar [2] (1 kbar= $10^8$  Pa), it was reported that the effective charge is almost independent of the volume.

The purpose of this work is to increase our understanding regarding the high pressure properties of this material and how to deal with them when this material is supposed to retain its mechanical properties under such pressure. We have investigated the effect of volume compression on Born's transverse effective charge (the dynamical

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charge), the polarity, and the force constants in c-BN up to a pressure of 900 kbar. To our knowledge the elastic constants are not yet measured due to the non-availability of thin film single crystal c-BN material. In fact, ultrasonic velocity measurement techniques, which determine the elastic constants, required high quality crystalline c-BN material.

### 2. Theoretical Background

The transverse effective charge is a fundamental quantity in the lattice dynamics of ionic solids and it is manifested in the observed splitting of the optical mode frequencies in partially ionic III-V and II-VI compound semiconductors. The transverse effective charge  $e_{\rm T}^*$  and its volume dependence are calculated using the simple semi-empirical bond-orbital model (BOM) of Harrison and Ciraci [3]

$$e_{\rm T}^* = -\Delta Z + \frac{20}{3} \ \alpha_{\rm p} - \frac{8}{3} \ \alpha_{\rm p}^3 \,. \tag{1}$$

Here the term  $\Delta Z$  is half the difference in core charges between anion and cation  $(\Delta Z = 1 \text{ for III-V compounds})$  and  $\alpha_p$  is the polarity of the bond (or ionicity parameter). It measures the excess number of electrons placed on the anion from each bond.  $\alpha_p$  is expressed following Harrison's equation [4]

$$\alpha_{\rm p} = \frac{V_3}{\left(V_2^2 + V_3^2\right)^{1/2}} , \qquad (2)$$

where  $V_2$  is the hybrid covalent energy, which is approximated in the following way:  $V_2 = -\eta_{\sigma} \hbar^2 / (md^2)$ , where  $d = (\sqrt{3}/4) a$  is the nearest-neighbor distance and  $\eta_{\sigma}$  is the dimensionless universal Harrison parameter [4].

 $V_3$ , the hybrid polar energy which gives the ionic contribution to the effective gap, is given by

$$V_3 = \frac{1}{2} \left( \varepsilon_{\rm h}^{\rm c} - \varepsilon_{\rm h}^{\rm a} \right),\tag{3}$$

where  $\varepsilon_{\rm h}^{\rm c}$  and  $\varepsilon_{\rm h}^{\rm a}$  are averages of the cation and anion hybrid energy, respectively,

$$\varepsilon_{\rm h}^{\rm c} = \frac{1}{4} \left( \varepsilon_{\rm s}^{\rm c} + 3\varepsilon_{\rm p}^{\rm c} \right), \qquad \varepsilon_{\rm h}^{\rm a} = \frac{1}{4} \left( \varepsilon_{\rm s}^{\rm a} + 3\varepsilon_{\rm p}^{\rm a} \right), \tag{4}$$

where  $\varepsilon_{s}^{c}$ ,  $\varepsilon_{p}^{c}$ ,  $\varepsilon_{s}^{a}$ , and  $\varepsilon_{p}^{a}$  are the free-atom energies for s and p states for cation and anion, respectively [5]. Unfortunately, if we try to calculate the dependence of the polarity on lattice compression and thereafter the force constants under pressure, we encounter the difficulty that the free-atom term values are not available and henceforth the ionic contribution is unknown. The failure will also be evident when using the dependence of the polarity on lattice compression as given by [4]

$$\frac{\partial \alpha_{\rm p}}{\partial (\Delta a/a)} = 2\alpha (1 - \alpha_{\rm p}^2) \,. \tag{5}$$

In this relation the compression dependence of the ionic contribution to the effective gap, which enters in the definition of  $a_p$ , is completely neglected. To overcome this problem in the BOM, the polarity  $a_p$  is determined using an empirical model [6]. By simply computing the right polarity of the material at equilibrium volume and its variation as the pressure increases more considerably, we are able to find all the derived properties as

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accurate as possible. The polarity  $\alpha_p$  is expressed in terms of the ionicity  $f_i$  [7] which is the main key to determine the physical properties of interest in this paper.

$$1 - f_{\rm i}^2 = (1 - \alpha_{\rm p}^2)^{3/2}, \tag{6}$$

where  $f_i$  is taken as the square root of the Phillips ionicity, whereas according to [6], this ionicity is evaluated from the valence electronic charge density which is computed using an adjusted pseudopotential method [8, 9]. Table 1 gives the experimental direct and indirect transitions used in our adjusted pseudopotential method for c-BN. The best set of form factors obtained and used to compute the charge density are given in Table 2. The experimental lattice constant of this material is also reported.

The total valence charge density distribution is computed using the two-point scheme of Chadi and Cohen [14],

$$\varrho_{\mathbf{n}}(\mathbf{r}) = \sum_{\mathbf{k}} e \left| \boldsymbol{\Psi}_{n\mathbf{k}}(\mathbf{r}) \right|^2,\tag{7}$$

where n is the index of the energy eigenvalue associated with the state **k**. The valence charge density distribution profile along the bond direction  $\langle 111 \rangle$  was used to calculate the ionicity  $f_1$  using an empirical formula [6], where the total area integration over the total valence charge density is divided into two parts with respect to the bond center,

$$f_{\rm i} = \left[S_{\rm A}/(S_{\rm A} + \lambda S_{\rm C})\right]^{\lambda},\tag{8}$$

Table 1

Experimental optical transitions used to adjust the pseudopotential data of c-BN (energies in eV)

| $\Gamma^v_{15} \to X^c_1$ | $L_1^{\mathbf{v}} \to \Gamma_{15}^{\mathbf{v}}$ | $\Gamma_1^{\mathbf{v}} \to K_1^{\mathbf{v}}$ | $\Gamma^{\rm v}_{15} \to \Gamma^{\rm c}_1$ |  |
|---------------------------|---|--|--|--|
| 6.10 [10]                 | 13.50 [11]                                      | 5.20 [11]                                    | 14.5 [12]                                  |  |

#### Table 2

Parameters used in the calculation of the electronic structure and the charge density of c-BN (the form factors are given in Ry)

| a (Å)      | $V_{\rm s}~(G^2=3)$ | V <sub>s</sub> (8) | $V_{\rm s}$ (11) | $V_{\rm A}$ (3) | V <sub>A</sub> (4) | V <sub>A</sub> (11) |
|------------|---------------------|--------------------|------------------|-----------------|--------------------|---------------------|
| 3.615 [13] | -0.4672             | 0.0312             | 0.3905           | 0.3292          | 0.1250             | 0.0251              |

### Table 3

Calculated ionicity for c-BN and results from previous works

| ionicity $f_i$ 0.313 0.256 0.383 0.484 |                |                      |                 |               | · · · · · · · · · · · · · · · · · · · |  |
|--|----------------|----------------------|-----------------|---------------|---------------------------------------|--|
| our calcul. $[15]$ $[16]$ $[17]$       | ionicity $f_i$ | 0.313<br>our calcul. | $0.256 \\ [15]$ | 0.383<br>[16] | 0.484<br>[17]                         |  |

# Table 4

Linear and quadratic pressure coefficients of important band gaps for c-BN

|                            | $\mathrm{d}E_{nk}/\mathrm{d}P~(\mathrm{eV/Mbar})$ | $\mathrm{d}^2 E_{nk}/\mathrm{d}P^2~(\mathrm{eV}/\mathrm{Mbar}^2)$ |  |  |
|----------------------------|---|---|--|--|
| $\frac{\Gamma_1^c}{X_1^c}$ | 1.06<br>0.25                                      | -0.21<br>0.08   |  |  |

where  $S_{\rm C}$ ,  $S_{\rm A}$  are the areas of the cation and anion sides, respectively, and  $\lambda$  is a parameter separating the strongly ionic element from the weakly ionic ones.  $\lambda = -1$  and  $S_{\rm C}$ ,  $S_{\rm A}$  are calculated using a parabolic formula with a higher and even number of integration zone.

Table 3 gives the calculated ionicity data together with the results from other published works.

To treat the pressure dependence of  $e_{\rm T}^*$ , the atomic form factors are needed at pressure shifted G values and have to be renormalized to the compressed unit cell volume. We derived a new set of form factors, as the volume changes, by using the adjusted pseudopotential method. Under volume compression, Murnaghan's equation of state [18] is used to convert the pressure to the change of the lattice by taking the measured isothermal bulk modulus at zero pressure  $B_0$  and its pressure derivative  $B'_0$  as 369 GPa and 4.0, respectively [19]. The linear  $dE_{nk}/dP$  and quadratic  $d^2E_{nk}/dP^2$  pressure coefficients of c-BN for direct and indirect band gaps [20] are listed in Table 4. Note that we use the electronic states at the  $\Gamma$  and X points in which the fundamental gaps are defined experimentally. Our calculations of the optical transitions at the L point for different pressures up to 900 kbar give linear and quadratic pressure coefficients of 0.62 and -0.17, respectively.

# 3. Results and Discussion

### 3.1 Dynamical charge

Upon high compression of the crystal to  $0.87 V_0$  corresponding to a pressure of 900 kbar, the charge densities start to decrease in the bonding region and move very slightly towards the interstitial boron site as shown in Fig. 1. This charge flow makes a very small



Fig. 1. Total valence charge density along the direction (111) using the two-point scheme of Chadi and Cohen [14] in c-BN. Solid line normal pressure, dashed line under a pressure of 900 kbar



Fig. 2. Dependence of the transverse effective charge in c-BN on lattice compression and pressure to 900 kbar

decrease of the polarity. The transverse effective charge at equilibrium volume and under pressure is estimated directly from (1). This gives a value of 1.86 which is in good agreement with the experimental value of 1.984 [2]. The results indicate that an evaluated ionicity of 0.313 is more reliable than the small value given by Phillips [15] or the larger values reported in the literature [16, 17]. Fig. 2 displays the dependence of the transverse effective charge in c-BN on lattice compression and pressure. In the case where the polarity is calculated from (2) we simply take the free-atom term values and the  $1/d^2$  formulae for the covalent energy. In order to get a clear picture, the calculated transverse effective charge for  $\Delta a = 0$  is normalized to the experimental value. For a pressure less than 200 kbar, the effective charge decreases very slowly with increasing pressure and the variation is linear with a slope close to unity. The latter is almost identical to the experimental value of 1.01 [2]. However, beyond 200 kbar and up to 900 kbar, a slight sublinearity appears.

The first- and second-order coefficients, b and c, of  $e_{\rm T}^*$  with respect to the relative change in lattice parameter, i.e.

$$e_{\rm T}^{*}(\Delta a/a) = e_{\rm T}^{*}(0) + b(\Delta a/a) + c(\Delta a/a)^{2}$$
(9)

are 1.01 and -2.54, respectively. A simple limitation to first order gives a value of 1.16 which is also in good agreement with the experimental data. Using the BOM the variation of the effective charge has the right sign but is quantitatively wrong. The first-order derivative b = 3.47 indicates a big disagreement with the experimental value. In such situation, the change in the polarity becomes more sensitive to the pressure increase and gives a considerable variation of the transverse effective charge and especially when we try to estimate the force constants not available experimentally. It is well known that the polarity is related to the hybrid covalent and polar (ionic) energies via Harrison's formula (2) and it is not convenient to assume the atomic term values do not change with volume. In the case of tetrahedral compounds for which Harrison's formula is suppossed to be applicable, the ionic contribution should not be kept fixed, otherwise the polarity is still always governed by the hybrid covalent energy. Moreover, if we take into consideration only the term  $1/d^2$  that means that all the considered tetrahedral com-

pounds become more covalent semiconductors as the pressure increases, there is no need to use Phillips' ionicity diagram. In such a way we get only covalent materials and we do not have the right to say such material or another transforms to metallic  $\beta$ -Sn or insulating rocksalt NaCl structure as the pressure increases.

### 3.2 Force constants

The idea to keep the ionic contribution fixed and only choose  $1/d^2$  formulae for the covalent energies brings us to erroneous results about the force constants. For a good estimation of the polarity, which describes the structural modification by means of a quantitative change in the force constants, we used the calculated transverse effective charge as displayed in Fig. 1 together with (1) in order to deduce the right polarity. Using this procedure, an ionicity value of 0.346 instead of 0.313 was assigned to our material under equilibrium volume.

Following the improved description by Baranowski [21] and the covalent and overlap interactions within the bond in tetrahedral compounds, the elastic constants  $C_{11}$  and  $C_{12}$  are given by

$$C_{11} = \frac{\sqrt{3}}{3} \left[ V_2' (1 - \alpha_p^2)^{3/2} \left(3 + \lambda\right) - \frac{3}{4} \left(1 - \alpha_p^2\right)^{1/2} |V_{pp\pi}'| + 2 \times 7.8 \right] \frac{1}{d^5}$$
(10)

and

$$C_{12} = \frac{\sqrt{3}}{6} \left[ V_2' (1 - \alpha_{\rm p}^2)^{3/2} (3 - \lambda) + \frac{3}{4} (1 - \alpha_{\rm p}^2)^{1/2} |V_{\rm pp\pi}'| + 4 \times 7.8 \right] \frac{1}{d^5}$$
(11)

with

$$V_{
m pp\pi}^{\prime}\equiv V_{
m pp\pi}d^{2}=oldsymbol{\eta}_{
m pp\pi}\,rac{\hbar^{2}}{m}\,,$$

where  $\lambda$  and  $\eta_{pp\pi}$  are dimensionless parameters with constant values of 0.738 [21] and -0.81, respectively [22].

The bond-bending force constant  $\beta$  and bond-stretching force constant  $\alpha$  can be obtained by [23]

$$\beta = \frac{d}{\sqrt{3}} \left[ (C_{11} - C_{12}) - 0.053SC_0 \right], \tag{12}$$

$$\alpha = \frac{4d}{\sqrt{3}} \left[ B + 0.355 \ \frac{SC_0}{3} \right] - \frac{1}{3} \ \beta \,, \tag{13}$$

where  $SC_0$  is the Coulomb contribution and B the bulk modulus.

The elastic stiffness constant  $C_{44}$  is also given by [23]

$$C_{44} = \frac{\sqrt{3}}{4d} (\alpha + \beta) - 0.136SC_0 - c\xi^2, \qquad (14)$$

where

$$c = rac{\sqrt{3}}{4d} \,\, (lpha + eta) - 0.266SC_0 \quad ext{and} \quad \xi = c^{-1} \left[ rac{\sqrt{3}}{4d} \,\, (lpha - eta) - 0.294SC_0 
ight].$$

#### Table 5

Bulk material parameters for c-BN. The elastic stiffness constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  are in units of  $10^6 \text{ N/cm}^2$ ,  $V_2$  and  $V_3$  in eV, bond-stretching force constant  $\alpha$  and bond-bending force constant  $\beta$  in units of  $10^{-2} \text{ N/cm}$ 

|   | $C_{11}$  | $C_{12}$   | $C_{44}$  | $V_2$  | $V_3^-$ | α                     | β                    |
|---|---|--|---|--------|---------|-----------------------|----------------------|
| c-BN                                    | 91.44 <sup>a</sup> )<br>71.2 <sup>b</sup> )<br>44.2 <sup>c</sup> )<br>83.1 <sup>d</sup> ) | 41.53 <sup>a</sup> )<br>8.0 <sup>b</sup> )<br>10.7 <sup>c</sup> )<br>42.0 <sup>d</sup> ) | $37.39^{a})$<br>$33.4^{b})$<br>$19.1^{c})$<br>$45.0^{d})$ | 13.6°) | 7.78ª)  | 125.22 <sup>*</sup> ) | 44.37 <sup>a</sup> ) |
| $diamond^{e})$<br>3C-SiC <sup>f</sup> ) | $107.64^{\circ}$<br>36.3  | $12.52^{'}$<br>15.4  | $57.74^{\circ}$ 14.9                                      |        |         |                       |                      |

<sup>a</sup>) This work; <sup>b</sup>) [24]; <sup>c</sup>) [25]; <sup>d</sup>) [26]; <sup>e</sup>) [27]; <sup>f</sup>) [28].

The calculated data at equilibrium volume for c-BN are given in Table 5. As one can see, the agreement between our results and the recent theoretical data is quite good. For a comparative purpose, the elastic constants of diamond and 3C-SiC as hard materials are also presented.

The elastic constants under pressure are easily calculated since they are only dependent on two parameters, i.e., the bond length d and the bond polarity  $\alpha_p$ . The parameter  $V_3$  in Table 5 is deduced from (2). Of special interest is the calculation of  $dV_2/d \ln a$  and  $dV_3/d \ln a$ , which gives values of -27.10 and -10.41, respectively. The results indicate that under volume compression, the hybrid covalent energy increases faster than the hybrid polar energy (see Fig. 3) and this consequently explains the evident covalency trend in c-BN under compression. The behavior of the force constants is best understood by examining the derived parameters  $\alpha$  and  $\beta$  as functions of the ionicity. These two parameters give a quantitative description of the primary trends in the force constants. Our results indicate that both  $\alpha$  and  $\beta$  increase as the ionicity decreases, which makes the material harder. The result suggests that beyond a pressure of 900 kbar and before the phase transition appears, c-BN retains its hardness.



Fig. 3. Dependences of the covalent energy  $(\blacksquare)$  and the polar energy  $(\bigtriangledown)$  in c-BN on lattice compression and pressure up to 900 kbar

# 4. Conclusion

In summary, we have shown that the transverse effective charge in c-BN is not independent of volume and decreases smoothly with pressure up to 900 kbar. A combination of an adjusted pseudopotential method and a bond-orbital model was used to derive the polarity and the force constants of c-BN under considered volumes. The covalency trend under volume compression is well explained by the increase of the hybrid covalent energy comparatively to the hybrid polar one. Our results imply that the transverse effective charge changes by less than 3.3% between normal condition and a pressure of 900 kbar. The idea of taking the free-atom term values and the  $1/d^2$ -formulae for the covalent energy is not a good approximation to estimate the variation of the transverse effective charge under pressure. In fact, this approximation overestimates the relative variation to 10.2% in the same range of pressure.

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