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Strain-induced shifts of the infrared-active phonon of cubic boron nitride

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Recent calculations by Fahy [Phys. Rev. B **51**, 12 873 (1995)] have produced values of strain coefficients for the infrared-active phonon of cubic BN. We discuss these results and show that they are not fully consistent. Furthermore, we comment on their general trends in comparison with other crystals of the diamond–zinc-blende family. [S0163-1829(96)02546-5]

I. INTRODUCTION

In a recent paper[1] Fahy has reported *ab initio* total energy calculations of the splittings of the TO(Γ) phonons of cubic BN under hydrostatic and uniaxial strains of specific geometries. While the calculated hydrostatic dependence leads to a Grüneisen parameter $\gamma=1.13$, in agreement with experimental data,[2] the calculated dependence on shear strain was found to be much larger than that for other materials of the diamond–zinc-blende family.[3–7] This has been recently attributed to numerical errors.[8] The corrected values,[8] based on calculations for the two independent irreducible traceless strains and called the group A results from now on, are in line with the systematics of the family. On the other hand, the results obtained under the assumption of uniaxial strains with components *only* along either [111] or [110], called the group B results from now on, are shown here to be inconsistent with those of group A.

The purpose of this paper is, first, to obtain values for the TO phonon deformation potentials (PDP's) using the group A and B results and to show that the two sets are inconsistent with each other, and second to comment on the trends of these results in comparison with other diamond–zinc-blende crystals. In addition, we obtain a reliable value for the TO-mode Grüneisen parameter by combining group B results and experimental information. This work concerns only TO phonons. For simplicity, we omit the TO label throughout.

II. MODE GRÜNEISEN PARAMETER

The mode Grüneisen parameter can be written in one of the following forms:[3–5]

$$\gamma=-\frac{d\ln\omega}{d\ln V}=-\frac{\Delta\Omega_h}{3\varepsilon_h\omega_0}=-\frac{(\widetilde{K}_{11}+2\widetilde{K}_{12})}{6}, \tag{1}$$

where V is the crystal volume, ω_0 the strain-free TO phonon frequency, ε_h the isotropic (hydrostatic) strain, $\Delta\Omega_h$ the shift of ω_0 caused by ε_h, and $\widetilde{K}_{11}$ and $\widetilde{K}_{12}$ two of the three TO PDP's, normalized to ω_0^2 (Ref. 9). The group B calculations[8] lead to $\Delta\Omega_h=-36$ cm^{-1} for $\varepsilon_h=+0.01$ and $\omega_0=1063$ cm^{-1} (Ref. 1). (No such information can be obtained from group A calculations.) Equation (1) then yields $\gamma=1.13$, which agrees rather well with the experimental value 1.19 ± 0.08.[10]

This indicates that the ε_h calculation given above was not affected by whatever errors occurred in Ref. 1.[8] Accordingly, the value

$$\widetilde{K}_{11}+2\widetilde{K}_{12}=-6.8 \tag{2}$$

is an acceptable one and we shall use it in the following sections.

III. GROUP A RESULTS

A uniaxial strain (ε) along [001], [110] or [111] only (i.e., with no lateral deformation) can be written as follows:

$$\left.\begin{array}{r}\boldsymbol{\varepsilon}_{001}\\ \boldsymbol{\varepsilon}_{110}\\ \boldsymbol{\varepsilon}_{111}\end{array}\right\}=\varepsilon\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix} \tag{3a}$$

$$=\frac{\varepsilon}{3}\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+\frac{\varepsilon}{3}\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&2\end{pmatrix}, \tag{3b}$$

For the present purpose we assume that $\boldsymbol{\varepsilon}_{001}$ refers to the system $S{:}x_1\|[100]$, $x_2\|[010]$, $\underline{x_3}\|[001]$, $\boldsymbol{\varepsilon}_{110}$ to the rotated system $S'{:}x_1'\|[001]$, $x_2'\|[\underline{1}10]$, $\underline{x_3'}\|[110]$, and $\boldsymbol{\varepsilon}_{111}$ to the rotated system $S''{:}x_1''\|[112]$, $x_2''\|[110]$, $x_3''\|[111]$. The first matrix in Eq. (3b) corresponds to the hydrostatic component of the applied strain, the second to the shear (traceless) component.

The strain-induced phonon frequency shifts are obtained from the corresponding secular equation for the equivalent Hamiltonian, which for the triply degenerate phonons of cubic crystals considered here has the form[3–6,11]

$$\begin{vmatrix}K_{1j}\varepsilon_j-\lambda & K_{6j}\varepsilon_j & K_{5j}\varepsilon_j\\ K_{6j}\varepsilon_j & K_{2j}\varepsilon_j-\lambda & K_{4j}\varepsilon_j\\ K_{5j}\varepsilon_j & K_{4j}\varepsilon_j & K_{3j}\varepsilon_j-\lambda\end{vmatrix}=0, \tag{4}$$

where summation over j is implied, and

$$\lambda_\sigma\simeq 2\omega_0\Delta\Omega_\sigma \qquad \sigma=1,2,3, \tag{5}$$

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designates the three eigenvalues, i.e., the frequency shifts $\Delta\Omega_\sigma=\Omega_\sigma-\omega_0$. All K_{ij} and ε_j components are given in suppressed index notation,[12] and are referred to the same system of axes.[11]

According to group *A* results of Ref. 8 and (3b), a uniaxial traceless strain $2\boldsymbol{\varepsilon}/3=0.01$ along [001] ([111]) causes a shift of -5 (-26) cm^{-1} for TO modes polarized along the strain. We will extract from these values the PDP's of the TO phonons. The cases $\boldsymbol{\varepsilon}_{001}$ and $\boldsymbol{\varepsilon}_{111}$ are discussed separately.

(i) For $\boldsymbol{\varepsilon}_{001}$ the secular equation (4) becomes *diagonal* in the *S* system. After inserting the traceless strain Eq. (3b) into Eq. (4) we obtain for the eigenvalue corresponding to x_3

$$\lambda_3=(K_{11}-K_{12})2\varepsilon/3. \tag{6a}$$

where the primeless PDP's refer to the system *S*. Therefore,

$$\Delta\Omega_3=\frac{2\varepsilon}{3}\,\frac{\widetilde{K}_{11}-\widetilde{K}_{12}}{2}\omega_0. \tag{6b}$$

Setting $2\varepsilon/3=0.01$, $\Delta\Omega_3=-5\ \mathrm{cm}^{-1}$ in Eq. (6b) yields[8]

$$\frac{\widetilde{K}_{11}-\widetilde{K}_{12}}{2}=-0.47. \tag{7}$$

From Eqs. (2) and (7) we find the normalized PDP's for the TO phonon,

$$\widetilde{K}_{11}=-2.90,\quad \widetilde{K}_{12}=-1.95. \tag{8}$$

(ii) For $\boldsymbol{\varepsilon}_{111}$, the traceless strain and the secular equation have the same form as before provided it is referred to the coordinate system S''. The eigenvalue corresponding to x''_3 is

$$\lambda_3=(K''_{31}+K''_{32})(-\varepsilon/3)+2K''_{33}\varepsilon/3=2\omega_0\Delta\Omega_3, \tag{9}$$

with[11,13]

$$K''_{31}=K''_{32}=(K_{11}+2K_{12}-2K_{44})/3, \tag{10a}$$

$$K''_{33}=(K_{11}+2K_{12}+4K_{44})/3. \tag{10b}$$

Finally,

$$\Delta\Omega_3=2\varepsilon\omega_0\widetilde{K}_{44}/3, \tag{11}$$

and, after setting $2\varepsilon/3=0.01$, $\Delta\Omega_3=-26\ \mathrm{cm}^{-1}$,

$$\widetilde{K}_{44}=-2.45. \tag{12}$$

This completes the derivation of PDP's for the TO phonon from the results of group *A*.

IV. GROUP *B* RESULTS

According to Ref. 8, a strain of the form (3a) with $\varepsilon=+0.01$ along [111] ([110]) causes a shift of -29 (-13) cm^{-1} for TO modes polarized along [111] ([001]), namely, for the phonon component parallel (perpendicular) to the strain axis.

(i) The strain $\boldsymbol{\varepsilon}_{111}$ exhibits in the S'' system only a nonvanishing $x''_3x''_3$ component. The singlet, vibrating along [111], has the eigenvalue

$$\lambda_3=K''_{33}\varepsilon=2\omega_0\Delta\Omega_3, \tag{13a}$$

where K''_{33} is given by Eq. (10b). Then

$$\Delta\Omega_3=\varepsilon\omega_0(\widetilde{K}_{11}+2\widetilde{K}_{12}+4\widetilde{K}_{44})/6. \tag{13b}$$

Setting $\gamma=1.13$, $\varepsilon=0.01$, and $\Delta\Omega_3=-29\ \mathrm{cm}^{-1}$ we find from Eqs. (13b) and (2)

$$\widetilde{K}_{44}=\frac{3}{2}\left(\gamma+\frac{\Delta\Omega_3}{\varepsilon\omega_0}\right)=-2.4. \tag{14}$$

This value agrees with that in Eq. (12).

(ii) The strain $\boldsymbol{\varepsilon}_{110}$ exhibits only the $x'_3x'_3$ component in the S' system. Again the secular equation is diagonal but the degeneracy is now completely removed,

$$\lambda_1=\varepsilon K'_{13},\ \text{eigenvector}\|x'_1, \tag{15a}$$

$$\lambda_2=\varepsilon K'_{23},\ \text{eigenvector}\|x'_2, \tag{15b}$$

$$\lambda_3=\varepsilon K'_{33},\ \text{eigenvector}\|x'_3. \tag{15c}$$

We are only interested in λ_1. Since[13] $K'_{13}=K_{12}$,

$$\Delta\Omega_1=\varepsilon\omega_0\widetilde{K}_{12}/2. \tag{16}$$

Setting $\varepsilon=0.01$ and $\Delta\Omega_1=-13\ \mathrm{cm}^{-1}$ we find from Eqs. (14) and (2)

$$\widetilde{K}_{11}=-1.9\quad \widetilde{K}_{12}=-2.4, \tag{17}$$

and, therefore,

$$\frac{\widetilde{K}_{11}-\widetilde{K}_{12}}{2}=+0.27. \tag{18}$$

We see that the group *B* values Eqs. (17) and (18) differ in magnitude, and Eq. (18) even in sign, from the corresponding results of group *A*, i.e., Eqs. (8) and (7), respectively. This discrepancy reflects lack of internal consistency of the corrected results reported in Ref. 8. The change in sign is understood as follows: If we express $(\widetilde{K}_{11}-\widetilde{K}_{12})/2$ in terms of the slope $\Delta\Omega_1$ we find, using Eqs. (16) and (2),

$$\frac{\widetilde{K}_{11}-\widetilde{K}_{12}}{2}\simeq-3\left(\gamma+\frac{\Delta\Omega_1}{\varepsilon\omega_0}\right)=-0.28\Delta\Omega_1-3.39. \tag{19}$$

This expression reverses sign at $\Delta\Omega_1\approx-12\ \mathrm{cm}^{-1}$; thus, even minor computational noise is sufficient to reverse the sign of Eq. (19) if $\Delta\Omega_1$ happens to be in the vicinity of 12 cm^{-1}, as in the present case.

The above discrepancies may be due to the choice of special points for the sampling of the charge in the BZ which is likely to be different for every strain configuration. More special points should reduce the differences. The number of plane waves used may also play a role. We feel that the results of group *A* based on Ref. 8, i.e., those in Eqs. (7), (8), and (12), follow closer the general trends of the diamond–zinc-blende family, as discussed next, and include them in Table I. Fahy also believes that his group *A* results are more reliable than those in group *B*.[14]

TABLE I. Dimensionless coefficients reflecting the strain-induced singlet-doublet splitting of TO modes for several diamond and zinc-blende semiconductors.

	Diamond [a]	BN [b]	Si [c]	Ge [d]	GaAs [e]
$\frac{\tilde{K}_{11}-\tilde{K}_{12}}{2}$	-0.50	-0.47	$+0.23$	$+0.23$	$+0.15$
$\tilde{K}_{44}$	-1.20	-2.45	-0.70	-0.90	-0.90

[a] From Ref. 3.
[b] Present results based on group *A* data of Ref. 8.
[c] From Ref. 4.
[d] From Ref. 6.
[e] From Ref. 5.

V. DISCUSSION

The trends of the PDP values for various members of the diamond–zinc-blende family are best described by the dimensionless parameters $(\tilde{K}_{11}-\tilde{K}_{12})/2$ and $\tilde{K}_{44}$ which reflect the singlet-doublet splittings under traceless uniaxial strains along [001] and [111], respectively. In Table I we give these values for various materials and include the present BN results based on the group *A* data of Ref. 8.

The values of the BN parameters agree in sign and magnitude with those found for diamond but show systematic differences to those of Ge, Si, and GaAs. The latter, however, are similar to the results found for other zinc-blende-type semiconductors.[6,7] The purpose of this discussion is to provide a simple physical understanding for the systematics of the parameters of Table I.

In Ref. 4 these parameters have been related to harmonic and anharmonic valence force field constants [see Eq. (6) of Ref. 4]. We rewrite these equations keeping only the largest (negative) anharmonic terms $\overline{\gamma}$ (bond stretch-stretch-stretch term) and $\overline{\varepsilon}$ (bond stretch-bend-bend term):

$$\tilde{K}_{44} \simeq 1 + \frac{4a_0\overline{\gamma}(1-\zeta)}{\omega_0^2\mu}, \qquad \frac{\tilde{K}_{11}-\tilde{K}_{12}}{2} \simeq 1 + \frac{8a_0\overline{\varepsilon}}{\omega_0^2\mu}, \tag{20}$$

where ζ is the internal strain parameter, a_0 the lattice constant, and μ the reduced mass of a primitive cell. Inclusion of additional anharmonic terms in Eqs. (20) does not alter our qualitative conclusions.

A comparison of the diamond and silicon data of Ref. 4 yields the scaling behavior $|\overline{\gamma}| \propto a_0^{-2.9}$ and $|\overline{\varepsilon}| \propto a_0^{-6.5}$ while it is known from Ref. 15 that $\omega_0^2\mu \propto a_0^{-3}$. We thus rewrite Eqs. (20) as

$$\tilde{K}_{44} \simeq 1 - Ra_0^{+1.1}(1-\zeta), \qquad \frac{\tilde{K}_{11}-\tilde{K}_{12}}{2} = 1 - Qa_0^{-2.5}, \tag{21}$$

where R and Q are positive and should be constant for all members of the family. They represent the anharmonicity of the valence forces while the unit terms in the right-hand side of Eqs. (20) and (21), independent of the anharmonic parameters, are geometric contributions due to the changes in bond angles induced by the strain. The signs in Table I are determined by the balance between geometric and anharmonic terms in Eqs. (20) and (21).

It is known that for diamond[4] and for BN[16] $\zeta \simeq 0.12$ while for all other group IV and III-V materials which do not contain C, B, or N (first row in the periodic table) $\zeta = 0.55$. This striking difference arises from the strong covalency of the bond between first-row elements, which implies bond-bending and bond-stretching harmonic force constants of the same order, while for the other materials bond-bending are much smaller than bond-stretching parameters. With these arguments it is easy to see from Eq. (21) that the anharmonic term in $\tilde{K}_{44}$ varies little from material to material [changes in $(1-\zeta)$ compensate the changes in $a_0^{1.1}$]. Because it is known to be negative for diamond, we conclude that the anharmonic terms overcompensate the positive geometric term in all cases listed in Table I, and give rise to negative values of $\tilde{K}_{44}$, with a magnitude larger for diamond and BN than for materials not involving first-row elements.

In the case of $(\tilde{K}_{11}-\tilde{K}_{12})/2$, because of the strong dependence on a_0 in Eq. (21), the anharmonic terms may or may not dominate over the geometric term and the sign can be negative or positive. In C and BN the anharmonic terms dominate, making this coefficient negative. On these grounds, we reject the positive value $+0.27$ reached in Eq. (18) from the group *B* data. However, for the other materials, with a much larger a_0, the anharmonic term is not able to overcompensate the geometric term and $(\tilde{K}_{11}-\tilde{K}_{12})/2$ remains positive.

It would be appropriate to calculate the LO phonon PDP's of BN, since they are different than the TO PDP's, in general. It would also be of great interest to investigate materials involving one element of the first and one of the second or third row, such as BP ($\zeta = 0.31$ according to Ref. 16); they should display a behavior intermediate to that shown by (C, BN) and (Ge, Si, GaAs) in Table I.

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