

Normal Modes in Hexagonal Boron Nitride

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Pyrolytic boron nitride, a rather anisotropic material among the III-V compounds, has been investigated in reflection and transmission, using polarized infrared radiation in the spectral range from 100 cm^{-1} to 3000 cm^{-1} . The reflection spectra have been analyzed by means of a Kramers-Kronig analysis and a classical oscillator fit. The results indicate one infrared active lattice mode for in-plane motion of the particles and one for out-of-plane motion, in accordance with the boron-nitride structure reported by Pease and the resulting group-theoretical selection rules. In addition, one Raman line has been found corresponding to a lattice mode for in-plane motion. Furthermore, the absorption spectrum exhibits several minor peaks which are probably due to 2-phonon combination processes.

I. INTRODUCTION

IN its hexagonal form, boron nitride is a particularly interesting material among the III-V compounds, as many of these materials crystallize in the isotropic-cubic zinc-blende structure.¹ Others crystallize in the hexagonal-wurtzite structure¹ where there is essentially a change of symmetry only in comparison to the zinc-blende structure, and the distances of nearest and next-nearest neighbors are almost the same parallel or perpendicular to the c axis. Thus the lattice-vibrational properties of the wurtzite-structure compounds are only slightly anisotropic.² While BN in its cubic form is similar to diamond, the hexagonal form is similar to graphite, with a hexagonal-layer structure. Therefore, its properties should be highly anisotropic.

II. STRUCTURE OF HEXAGONAL BN

The structure of hexagonal BN has been investigated with x rays in the past by Hassel³ and Brager⁴ and more recently by Pease.⁵ All investigators agree that the hexagonal unit cell is bimolecular and that the structure consists of layers of flat B_3N_3 hexagons with an interplanar spacing of $\frac{1}{2}c$. However, there is some disagreement concerning the packing of the layers. Hassel and Brager reported a structure with B ions and N ions at sites occupied by carbon atoms in graphite. One of the possible graphite-like structures for BN is shown in Fig. 1. The ionic sites in the unit cell can be written as

follows:

$$\begin{aligned} \text{B: } & 0; & \frac{1}{3}(\mathbf{a}_1 + 2\mathbf{a}_2) + \frac{1}{2}\mathbf{a}_3 \\ \text{N: } & \frac{1}{3}(\mathbf{a}_1 + 2\mathbf{a}_2); & \frac{1}{2}\mathbf{a}_3, \end{aligned}$$

where a_1 , a_2 , and a_3 are the lattice vectors. The point group of this lattice (BN No. 1) and other graphite-like structures is D_{3h} . The only other possible structure was reported by Pease and has a packing of the layers as shown in Fig. 2. In this case the ionic sites in the unit cell can be written

$$\begin{aligned} \text{B: } & +\frac{1}{3}(\mathbf{a}_1 + 2\mathbf{a}_2) + \frac{1}{4}\mathbf{a}_3; & -\frac{1}{3}(\mathbf{a}_1 + 2\mathbf{a}_2) - \frac{1}{4}\mathbf{a}_3 \\ \text{N: } & -\frac{1}{3}(\mathbf{a}_1 + 2\mathbf{a}_2) + \frac{1}{4}\mathbf{a}_3; & +\frac{1}{3}(\mathbf{a}_1 + 2\mathbf{a}_2) - \frac{1}{4}\mathbf{a}_3. \end{aligned}$$

The point group of this lattice (BN No. 2) is $D_{6h} = D_{3h} \times C_2$. Some of the symmetry operations are connected with nonprimitive translations.

Although the results of Pease seem to be more accurate, the data of the optical investigation will be

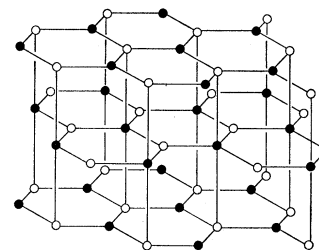


FIG. 1. One of the possible graphite-like structures of BN (BN No. 1).

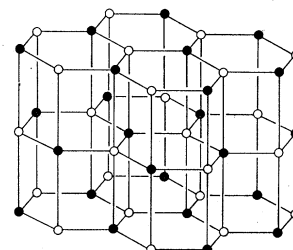


FIG. 2. The structure of BN reported by Pease (Ref. 5) (BN No. 2).

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¹ Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1960), Vol. I, Chap. III.

² W. G. Spitzer, D. A. Kleinman, and D. Walsh, *Phys. Rev.* **113**, 127 (1959); T. Deutsch, *J. Appl. Phys.* **33**, 751 (1952).

³ O. Hassel, *Norsk Geol. Tidsskr.* **9**, 258 (1926).

⁴ A. Brager, *Acta Physicochim. U.R.S.S.* **7**, 699 (1937); **11**, 617 (1939).

⁵ R. S. Pease, *Acta Cryst.* **5**, 536 (1952).

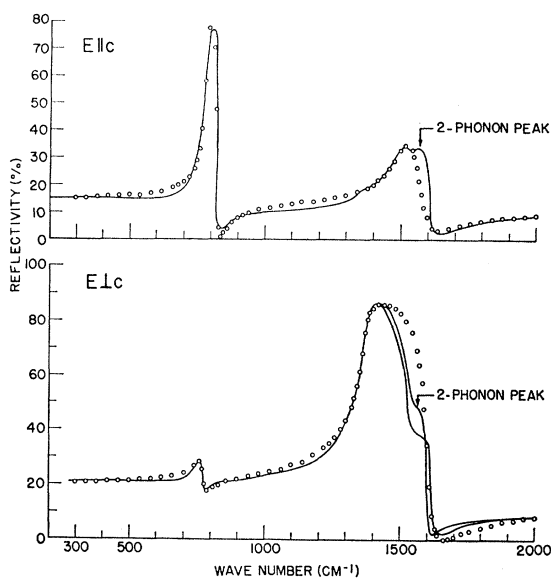


FIG. 3. Reflectivity of BN for both directions of polarization, experimental data (solid line) and computed by means of classical dispersion formula (circles).

discussed in terms of both structures in connection with group-theoretical considerations. The important difference between the two structures is the center of symmetry in BN No. 2.

According to the lattice parameters given by Pease,⁵ the nearest neighbors' distances are $a/\sqrt{3} \approx 1.44$ Å in the hexagonal plane and $c/\sqrt{2} \approx 3.33$ Å parallel to the c axis. From this and from the fact that in analogy to graphite the ions are probably more tightly bound in the plane than perpendicular to the plane, there is to be expected a relatively large splitting between in-plane and out-of-plane lattice vibrations, larger than the splitting between longitudinal and transverse modes due to Coulomb forces.

III. INFRARED AND RAMAN SPECTRA

For the optical measurements, various samples of pyrolytic boron nitride were investigated. X-ray studies of these have confirmed the results of Pease⁵ with respect to the structure of BN, but the x-ray studies have shown also that the samples were polycrystalline with some preferential orientation of the c axis. The angular deviation of the basal planes from the c direction has a distribution function with a halfwidth of about 30° .

The reflectivity of hexagonal BN has been measured throughout the infrared spectral region from 300 to 2000 cm^{-1} and the absorption coefficient from 100 to 3500 cm^{-1} . All these measurements were performed with linearly polarized light, with E parallel and perpendicular to the c axis of the crystal. The instruments used were a Perkin-Elmer spectrophotometer, Model 521, with a reflection attachment for the reflectivity meas-

urements, and for the region 100 cm^{-1} to 300 cm^{-1} a Michelson-type Fourier spectrophotometer.

The reflection spectra exhibit two restrahlen bands for each direction of polarization, one connected with a strong infrared active lattice mode and the other connected with a weaker one (see Fig. 3). The results of a Kramers-Kronig analysis show this more explicitly [see Fig. 4(a) and 4(b)]. Furthermore, the spectra were analyzed by means of an optimum fit with a classical dispersion formula which was used in the following form

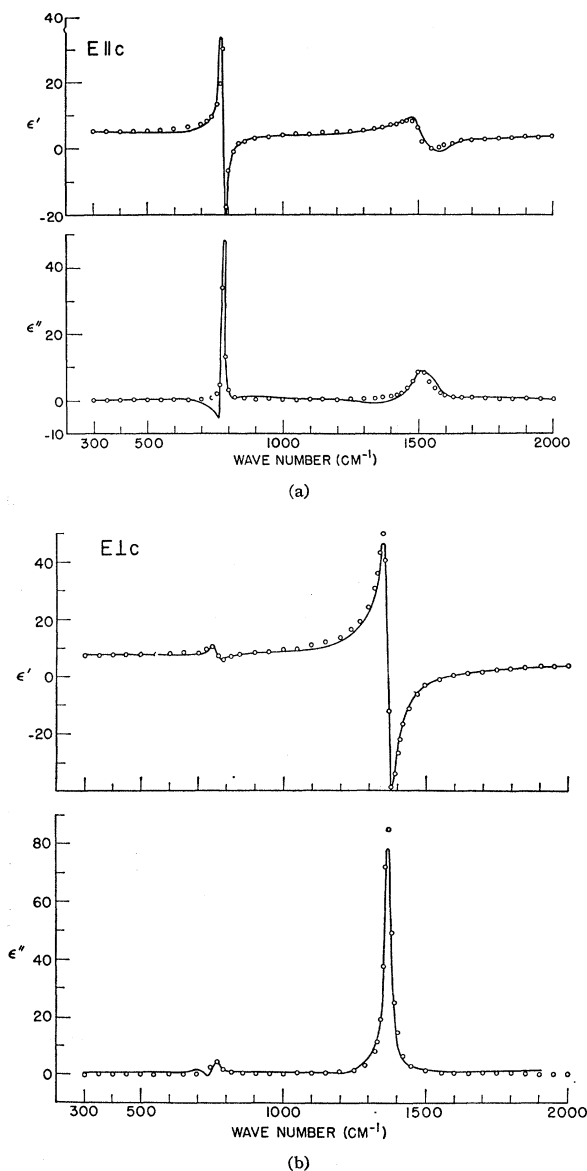


FIG. 4. (a) Real and imaginary part of the dielectric constant of BN for $E \parallel c$ as determined by Kramers-Kronig analysis (solid line) and computed by means of classical dispersion formula (circles). (b) Real and imaginary part of the dielectric constant of BN for $E \perp c$ as determined by Kramers-Kronig analysis (solid line) and computed by means of classical dispersion formula (circles).

for each direction of polarization separately:

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_\infty + \frac{s_1^2}{\omega_1^2 - \omega^2 + i\omega\gamma_1} + \frac{s_2^2}{\omega_2^2 - \omega^2 + i\omega\gamma_2}, \quad (1)$$

where ϵ_∞ is the optical dielectric constant, ω is the fre-

quency of incident light, and s_ν^2 , ω_ν , and γ_ν are the oscillator strength, the eigenfrequency, and the damping constant of normal mode ν , respectively. The best fit was obtained with the following values of the constants in Eq. (1):

$E \parallel c$:

$$\begin{aligned} \epsilon_\infty &= 4.10, & \epsilon_0 &= 5.09, & s_1^2 &= 3.26 \times 10^5 \text{ cm}^{-2}, & \gamma_1 &= 8.0 \text{ cm}^{-1}, \\ \omega_{l1} &= 783 \text{ cm}^{-1}, & \omega_{l1} &= 828 \text{ cm}^{-1}, & s_2^2 &= 1.04 \times 10^6 \text{ cm}^{-2}, & \gamma_2 &= 80.0 \text{ cm}^{-1}, \\ \omega_{l2} &= 1510 \text{ cm}^{-1}, & \omega_{l2} &= 1595 \text{ cm}^{-1}, & & & & \end{aligned}$$

$E \perp c$:

$$\begin{aligned} \epsilon_\infty &= 4.95, & \epsilon_0 &= 7.04, & s_1^2 &= 1.23 \times 10^5 \text{ cm}^{-2}, & \gamma_1 &= 35.0 \text{ cm}^{-1}, \\ \omega_{l1} &= 767 \text{ cm}^{-1}, & \omega_{l1} &= 778 \text{ cm}^{-1}, & s_2^2 &= 3.49 \times 10^6 \text{ cm}^{-2}, & \gamma_2 &= 29.0 \text{ cm}^{-1}, \\ \omega_{l2} &= 1367 \text{ cm}^{-1}, & \omega_{l2} &= 1610 \text{ cm}^{-1}, & & & & \end{aligned}$$

The longitudinal frequencies $\omega_{l\nu}$ of the various lattice modes were derived from the poles of the complex dielectric constant of the classical oscillator fit.⁶ These values agree quite well with the high-frequency cutoff of the corresponding reststrahlen band. The static dielectric constant ϵ_0 was computed by means of Eq. (1) with the data given above.

The Raman scattering of boron nitride was measured with a Carey Model 81 instrument from 150 to 2000 cm^{-1} frequency shift in the Stokes region. The sample was oriented with the c axis parallel to the direction of propagation of the scattered light. One Raman line was found with $\omega_{\text{Raman}} = 1370 \text{ cm}^{-1}$ and $\gamma_{\text{Raman}} = 30 \text{ cm}^{-1}$, where γ_{Raman} is the halfwidth of the line (see Fig. 5). This line is ascribed to first order Raman effect. There

was no indication of second order Raman peaks in the experimental results.

The absorption spectrum of BN exhibits major peaks near the infrared active eigenfrequencies, as determined from the reflection spectra (see Figs. 6 and 7). Furthermore, there are some minor peaks which are probably due to a high density of 2-phonon processes at 210, 500, 820, 920, and 2600 cm^{-1} . The 2-phonon peaks are more

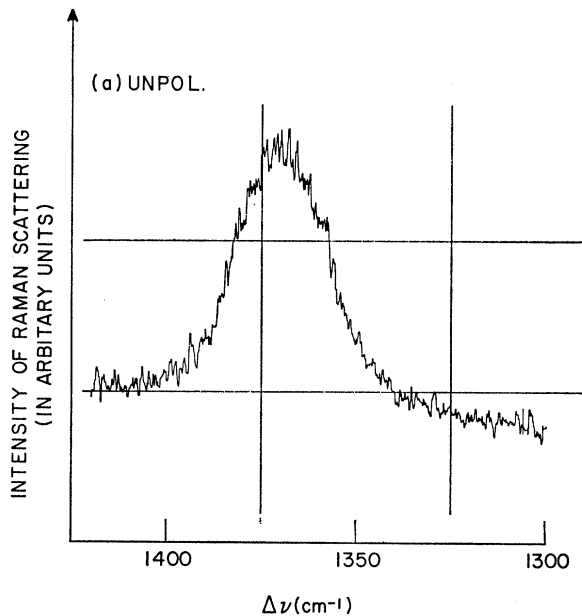


FIG. 5. Raman spectrum of hexagonal BN.

⁶ A. S. Barker, Jr., Phys. Rev. 136, A1290 (1964).

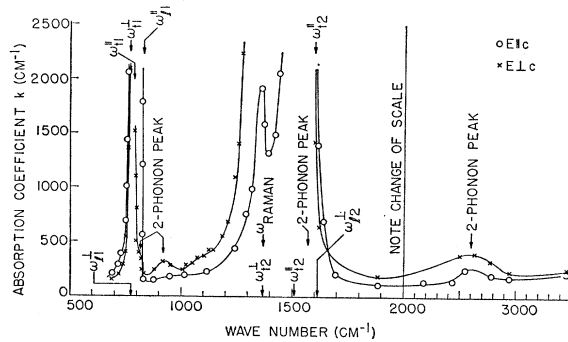


FIG. 6. Absorption coefficient of hexagonal BN from 600 to 3000 cm^{-1} for $E \parallel c$ (x's) and $E \perp c$ (o's). The arrows indicate also the frequencies determined from reflectivity and Raman data.

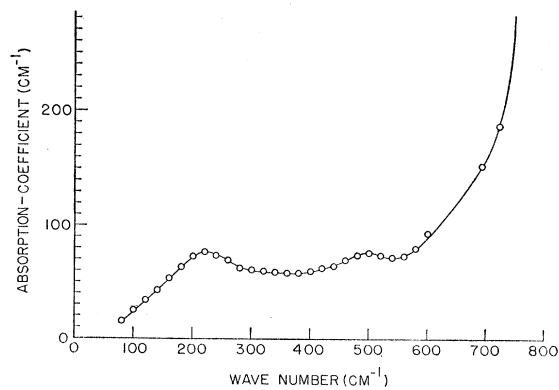


FIG. 7. Absorption coefficient of hexagonal BN for $E \perp c$ from 100 to 600 cm^{-1} .

pronounced for $E \perp c$ than for $E \parallel c$. An additional absorption peak arises for $E \parallel c$ at the Raman frequency reported in the foregoing section. This peak is probably due to the interaction of the Raman mode with the nearby infrared active mode (cf. dispersion formula with interaction damping⁷). A further 2-phonon peak has been found in the reflection spectra (see Fig. 3) for both directions of polarization at 1540 cm^{-1} . However, our experimental results do not indicate the irregularities of the absorption coefficient near 300 cm^{-1} reported by Li and Lepie.⁸

In addition to these data, the static dielectric constant has been determined independently at a frequency of 1 Mc/sec by capacity measurements. The values obtained, $\epsilon_0 = 5.06$ for $E \parallel c$ and $\epsilon_0 = 6.85$ for $E \perp c$, agree quite well with those deduced from the reflectivity in the far infrared spectral region. In performing the measurements of the dielectric constant, it was found that the obtained value depends on whether or not the sample was exposed to the water vapor of the air. The values given above were obtained with dried samples.

IV. GROUP-THEORETICAL CONSIDERATIONS

In this section the species of the normal modes of lattice vibrations and the resulting selection rules^{9,10} are given for the two BN lattices and compared to the experimental results.

The irreducible representations for the normal modes near $\mathbf{k}=0$ for BN No. 1 (without inversion symmetry) are

3 acoustical modes	$E' + A_2''$
6 infrared active and Raman active optical modes	$3E'$
3 infrared active optical modes	$3A_2''$.

If the three reststrahlen bands corresponding to the infrared active modes are well separated and far apart in the reflection spectrum, the six Raman lines will appear in pairs of two, since the longitudinal optical modes are also Raman active but not infrared active.¹¹

The irreducible representation for the normal modes near $k=0$ for BN No. 2 (with inversion symmetry) are

3 acoustical modes	$A_{2u} + E_{1u}$
3 infrared active optical modes	$A_{2u} + E_{1u}$
4 Raman active optical modes	$2E_{2g}$
2 inactive optical modes	$2B_{1g}$.

Under these conditions there should be, in the experimental results, only one reststrahlen band for each direction of polarization and two single Raman lines.

Now, in the infrared investigations we have found two active modes for each direction of polarization, a strong one and a weaker one. ($\omega_{i1} = 783 \text{ cm}^{-1}$ and $\omega_{i2} = 1510 \text{ cm}^{-1}$ for $E \parallel c$, and $\omega_{i2} = 1367 \text{ cm}^{-1}$ and $\omega_{i1} = 767 \text{ cm}^{-1}$ for $E \perp c$.) Though it could be that there is a third mode for each direction which has not been found, the results cannot be explained for the model BN-1 which has no inversion symmetry. The highly anisotropic structure of boron nitride requires highly anisotropic normal modes. Therefore, the modes with slightly different frequencies ($\omega_{i1} = 783 \text{ cm}^{-1}$ for $E \parallel c$ and $\omega_{i1} = 767 \text{ cm}^{-1}$ for $E \perp c$, $\omega_{i2} = 1367 \text{ cm}^{-1}$ for $E \perp c$ and $\omega_{i2} = 1510 \text{ cm}^{-1}$ for $E \parallel c$) have to be considered as one normal mode of the lattice. The weaker modes in the infrared spectra (767 cm^{-1} for $E \perp c$ and 1510 cm^{-1} for $E \parallel c$) are then probably due to the misorientation in our polycrystalline sample. The small shift in their frequencies, as compared to the stronger modes, may be due to the angular dependence of the extraordinary waves.

Only one line was found in the Raman spectrum, and no indication of a line was seen in the vicinity of the longitudinal frequency measured in the infrared. However, a small polarizability in the longitudinal direction and the geometry of our system (which may cause a wide range of phonon frequencies) could result in this band's not being observed. No additional Raman line was found in our spectra, and the question about this second frequency, which should be present in BN, will be discussed later.

From both the infrared (I. R.) and Raman data, it appears that a sample with a symmetry center (i.e., BN-2) fits the results best, but the model BN-1 cannot be entirely eliminated on the basis of our present Raman results.

V. THE NORMAL MODES OF BN

If we assume that the eigenfrequencies connected with the strong reststrahlen bands in the reflectivity represent the true eigenfrequencies of the lattice modes, we can list the following normal modes near $\mathbf{k}=0$:

- (a) In plane:
 $\omega_{i1} = 1367 \text{ cm}^{-1}$, $\omega_{i1} = 1610 \text{ cm}^{-1}$ (I.R.)
 $\omega_{i2} = 1370 \text{ cm}^{-1}$, (Raman).
- (b) Out of plane:
 $\omega_{i3} = 783 \text{ cm}^{-1}$, $\omega_{i3} = 828 \text{ cm}^{-1}$ (I.R.).

In order to discuss the accidental degeneracy of ω_{i1} and ω_{i2} , and the question of the second Raman frequency, a simple lattice model for the in-plane motion of the particles was calculated. The forces assumed were a spring with constant force P between nearest neighbors in the plane and a weak interaction with

⁷ A. S. Barker, Jr., and J. J. Hopfield, Phys. Rev. **135**, A1732 (1964).

⁸ P. C. Li and M. P. Lepie, J. Am. Ceram. Soc. **48**, 277 (1965).

⁹ G. F. Koster, Solid State Phys. **5**, 173 (1957).

¹⁰ E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955).

¹¹ R. Loudon, Advan. Phys. **13**, 423 (1964).

force constant B between adjacent planes. The Coulomb forces in this polar lattice were neglected completely. The eigenfrequencies for in-plane motion with $k \approx 0$ according to this model are

$$\begin{aligned} \omega_1^2 &= 0 && \text{(acoustical modes),} \\ \omega_2^2 &= 2(P+B)\left(\frac{1}{m_B} + \frac{1}{m_N}\right) && \text{(I.R.-active),} \\ \omega_{3,4}^2 &= (P+B)\left(\frac{1}{m_B} + \frac{1}{m_N}\right) \\ &\quad \pm \left[(P+B)^2 \left(\frac{1}{m_B} - \frac{1}{m_N}\right)^2 \right. \\ &\quad \left. + (4/m_B m_N)(P-B)^2 \right]^{1/2} && \text{(Raman-active).} \end{aligned}$$

Obviously for $B \ll P$ we have $\omega_2^2 \approx \omega_3^2$. On the other hand, ω_4^2 depends strongly on B and will be very low compared to the other optical frequencies. The eigenvectors show this behavior more clearly:

$$\begin{array}{l} \omega_1: E_{1u} \\ \text{(acoustical modes)} \end{array} \quad \begin{array}{l} B \rightarrow \quad N \rightarrow \\ N \rightarrow \quad B \rightarrow \\ B \rightarrow \quad \leftarrow N \end{array}$$

$$\begin{array}{l} \omega_2: E_{1u} \\ \text{(infrared active)} \end{array} \quad \begin{array}{l} \leftarrow N \quad B \rightarrow \\ B \rightarrow \quad \leftarrow N \end{array}$$

$$\begin{array}{l} \omega_3: E_{2g} \\ \text{(Raman active)} \end{array} \quad \begin{array}{l} N \rightarrow \quad \leftarrow B \\ B \rightarrow \quad N \rightarrow \end{array}$$

$$\begin{array}{l} \omega_4: E_{2g} \\ \text{(Raman active)} \end{array} \quad \begin{array}{l} \leftarrow N \quad \leftarrow B. \end{array}$$

Though the model is somewhat oversimplified, our experimental results agree qualitatively with the conclusions from these considerations for the limit of very small interaction between the planes. Thus the conclusion may be justified that these forces are indeed small, and the second Raman line will have a rather low frequency ($< 150 \text{ cm}^{-1}$) as it could not be found under the conditions of a relatively broad Raleigh line ($\sim 200 \text{ cm}^{-1}$). With better samples and a laser as the Raman source, it might be possible to find this line.

Because of the lack of sufficient information about the two completely inactive modes, a similar analysis cannot be made for the out-of-plane vibrations. A comparison can be made of the present results to those obtained with cubic BN.¹² The infrared eigenfrequency of the cubic form is $\omega_0 = 1045 \text{ cm}^{-1}$ which is intermediate to the in-plane and out-of-plane infrared active eigenfrequencies of hexagonal BN.

¹² R. Marshall, S. S. Mitra, P. J. Gielisse, J. N. Plendl, and L. C. Mansur, *Bull. Am. Phys. Soc.* **10**, 370 (1965).

TABLE I. Assignment to the 2-phonon peaks.

Observed 2-phonon peaks (cm^{-1})	Assignment ^a
2600	$A+B$
1540	$A+D, A+E, B+D, B+E$
920	$C+D, C+E$
820	$C+F, C+G$
500	$D+E$ or $C-D, C-E$
210	$F+G$ or difference process

^a $A, B = 1300 \text{ cm}^{-1}$; $C = 680 \text{ cm}^{-1}$; $D, E = 240 \text{ cm}^{-1}$; $F, G \approx 100 \text{ cm}^{-1}$.

The interpretation of 2-phonon peaks is mostly done in terms of averaged phonon frequencies for the edge of the Brillouin zone. The assignments for the peaks at 2600 cm^{-1} , 1540 cm^{-1} , 920 cm^{-1} , and 820 cm^{-1} is more or less straightforward (see Table I). They all are assigned to summation processes, to the combination of two optical phonons of different symmetry corresponding to in-plane motion ($A, B = 1300 \text{ cm}^{-1}$), one optical phonon corresponding to out-of-plane motion ($C = 680 \text{ cm}^{-1}$), and one or more optical or acoustical phonons with lower frequencies ($D, E = 240 \text{ cm}^{-1}$ and $F, G \approx 100 \text{ cm}^{-1}$). If the peaks at 210 cm^{-1} and 500 cm^{-1} are due to summation processes, we have to assume that there are phonons of different branches with an average energy of $240\text{--}250 \text{ cm}^{-1}$, the combination of which would explain the peak near 500 cm^{-1} . The peak at 210 cm^{-1} must be the combination of two acoustical phonons or of one acoustical and one optical phonon with a rather low average frequency of about 100 cm^{-1} . However, the two peaks at 210 and 500 cm^{-1} could also be due to difference processes. For this case, an assignment for the peak at 500 cm^{-1} is listed also in the table, but for the peak at 210 cm^{-1} it is hard to offer a reasonable assignment for reasons of the lack of detailed information about the phonon spectrum as the splitting of two optical branches for in-plane motion at the various critical points of the Brillouin zone.

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