Lattice Vibration Spectra of Aluminum Nitride

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The reflectivity and transmission spectra of aluminum nitride have been measured using unpolarized radiation in the wavelength region 2 to 30 μ. The dielectric parameters and the zone-center ($k\simeq 0$) optical-mode energies [transverse (TO) and longitudinal (LO)] have been calculated from the reflectivity measurements using dispersion theory. The values obtained are TO=82.7 meV (666.7 cm^{-1}), LO=113.6 meV (916.3 cm^{-1}), $\epsilon_\infty=4.84$, and $\epsilon_0=9.14$. From these data the value calculated for the Szigeti effective charge is $q^*=1.2$. Polarization measurements have revealed a sharp minimum in the reststrahlen band for E parallel to the c axis at $\sim$111.0 meV. Otherwise the reflectivity curves appear identical for both polarizations. Thirteen absorption bands have been observed on the high-energy side of the reflectivity band. A tentative interpretation is proposed in which these bands are considered to be due to combinations of six representative phonon branches at or near the Brillouin-zone boundary ($\mathbf{k}\simeq\mathbf{k}_{\max}$). The phonon energies resulting from this interpretation are LO=91.4, $\text{TO}_1=82.5$, $\text{TO}_2=78.1$, LA=62.9, $\text{TA}_1=55.3$, and $\text{TA}_2=50.9$ meV.

I. INTRODUCTION

The growth of AlN single crystals has been investigated by several workers.[1–6] Almost all methods involve subliming AlN in an atmosphere of pure nitrogen at temperatures between 1450 and 2050°C. Very pure sintered AlN may be used as the starting material[1,2]; alternatively the AlN is produced *in situ* by vaporizing the metal[3,4] or one of its salts.[5,6] The pure material is water white and crystallizes in the hexagonal wurtzite structure[3] with unit-cell dimensions $a_0=3.111$ Å, $c_0=4.980$ Å. The blue color observed[7,8] when the crystals are grown in a carbon furnace has been attributed to the presence of aluminum oxycarbide Al_2OC which is isomorphous with aluminum nitride.[9] The growth habit of the crystals depends on the temperature of formation[1,3] and the degree of supersaturation in the gaseous phase[4]; whiskers are obtained at $\sim$1500, hexagonal prisms at $\sim$1850 and flat platelets at $\sim$2000°C. The latter crystals are the most suitable for optical measurements, and are so oriented that the c axis lies in the surface of the large faces which are perpendicular to $1\bar{2}10$ direction.[2] Many of the crystals produced in this way are amber or pale brown in color. It has been observed that the position of the uv absorption edge apparently moves to lower energies after heating the crystals for several hours in an argon atmosphere at 1100°C.[10] This absorption which has a long tail stretching into the blue end of the visible spectrum is thought to be caused by nitrogen vacancies,[10] and could be responsible for the amber coloration observed. The dependence of the position of the uv absorption edge on the nitrogen vacancy concentration would also account for the large range of values (3.8–6.0 eV) quoted in the literature for the band gap of AlN.[2,11–14] Recent measurements by Edwards *et al.*, indicate that the absorption edge is at 5.9±0.2 eV.[2] From detailed absorption and photoconductivity measurements Pastrňák has concluded that the direct energy gap (i.e., at $\mathbf{k}\simeq 0$) is $\sim$6.0 eV, and that while the origin of the absorption in the region 4 to 6 eV is not clear, it seems more probable that this is due to indirect transitions rather than transitions via impurity states.[14]

In the present series of measurements the infrared absorption and reflectivity have been determined using crystals obtained from three different sources. Preliminary measurements were made using crystals grown at the Allen Clark Research Center of the Plessey Company. These were flat platelets about 0.25 mm square and 0.025 mm thick, which have been designated "series *E*." Several multiphonon absorption bands were observed, and the position of the reststrahlen reflectivity band located. The small crystal size, however, necessitated the use of strongly convergent light for the reflectivity measurements, and consequently the results did not lend themselves to detailed analysis. The absorption measurements were confirmed using "series *W*" crystals grown at the Physics Department of the University College of North Wales.[2] These were typically 1.0×1.0×0.1 mm in linear dimensions although some platelets were much thinner, again about 0.025 mm. The specimens used to measure the reflectivity at near normal incidence were grown by the Pechiney Company, France. Most of these crystals, "series *F*,"

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were malformed hexagonal prisms about 1.5 cm long and 2–3 mm in width, and were similar to those used previously to investigate the optical and electrical properties.[11]

A number of fairly strong intrinsic absorption bands have been observed, on the high-energy side of the fundamental one-phonon lattice absorption, in the range 120 to 200 meV together with a weaker absorption band at 245 meV. It is generally considered that these absorption maxima originate from multiple-phonon combinations involving the interaction of an infrared photon with two or three lattice phonons and are due to singularities in the phonon frequency distribution. For two-phonon combinations these singularities arise from critical points in the Brillouin zone where $(\partial/\partial\mathbf{k})(\omega_1+\omega_2)=0$. This condition often occurs at $\mathbf{k}=\mathbf{k}_{\max}$,[15] where $\partial\omega_1/\partial\mathbf{k}$ and $\partial\omega_2/\partial\mathbf{k}$ are separately equal to zero. However, critical points may occur well inside the zone if the condition that $(\partial/\partial\mathbf{k})(\omega_1+\omega_2)=0$ is satisfied over a sufficiently large interval $\Delta\mathbf{k}$.[16] The combination bands associated with the zone-boundary phonons may be associated with a single critical point. Equally, the bands may arise from combinations of several sets of phonons at different critical points. It is rarely possible to decide unambiguously, purely from the infrared absorption data, which of these possibilities is more likely, and the assignment of particular phonons to particular critical points usually has to await neutron-scattering data. In the absence of neutron data or more detailed optical measurements, the infrared data are generally interpreted in terms of four, five, or six unassigned characteristic phonon frequencies.

Multiphonon combination bands have been reported for a number of III–V compounds.[17–20] In InSb [17] and AlSb [18] these have been interpreted in terms of four characteristic phonon frequencies, and for GaP [19] and GaAs [20] five frequencies have been used. For II-VI compounds having the hexagonal wurtzite structure, six phonon energies have been used to account for the observed absorption bands,[21] but for hexagonal SiC[22] the combination bands have been fitted by four phonon energies.

Aluminum nitride is the only III-V compound available at present, in a form suitable for optical measurements, which has the hexagonal wurtzite structure. The lattice bands are similar to those reported for SiC,[22] but the presence of additional structure requires, as with the II-VI wurtzite compounds, six phonon energies to completely describe the system. The infrared absorption spectrum of AlN from 2 to 16 μ, using the KBr disk technique, has been previously reported.[23] Some structure is apparent in the two-phonon region, but the results do not appear to bear much similarity to the data obtained from single crystals.

Since the hexagonal wurtzite structure has four atoms per unit cell, there are nine optical and three acoustic modes at $\mathbf{k}\simeq 0$. The three acoustic branches are essentially zero at $\mathbf{k}\simeq 0$ and only three of the nine optical modes are infrared active. The separations of nearest and next-nearest neighbors are almost the same parallel or perpendicular to the c axis, and the separation of the two transverse-optical branches is usually very small at $\mathbf{k}\simeq 0$. The difference in reflectivity measured for the two different polarizations is generally only slight[24,25] and if unpolarized radiation is used one observes the average value and the data can be adequately interpreted in terms of a single classical oscillator. This approach is useful where small crystal size precludes detailed polarization studies. The zone center ($\mathbf{k}\simeq 0$) longitudinal optical (LO) and transverse optical (TO) frequencies are determined from the reflectivity data using classical dispersion theory (Kramers-Krönig relations). The refractive index n and extinction coefficient k at frequency ω for a dielectric with a single resonance frequency can be written in terms of a complex reflectivity

$$\rho(\omega)=\frac{n-ik-1}{n-ik+1}=r(\omega)e^{i\theta(\omega)}\,,$$

Where $\theta(\omega)$ is the phase shift of the reflected electric field with respect to the incident field and $[r(\omega)]^2$ is the reflectivity measured at normal incidence. The phase shift is given by the dispersion integral

$$\theta(\omega)=\frac{2\omega}{\pi}\int_0^\infty\frac{\ln r(\omega')-\ln r(\omega)}{\omega^2-\omega'^2}d\omega'\,.$$

This integral is readily evaluated if the reflectivity is known over a frequency range $\omega_1<\omega<\omega_2$ outside of which the reflectivity is essentially constant.[26] The values of n and k are then determined by the relations

$$n=(1-r^2)/(1+r^2-2r\cos\theta)\,,$$

$$k=2r\sin\theta/(1+r^2-2r\cos\theta)\,,$$

and the real and imaginary dielectric constants are given

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by

$$\epsilon' = n^2 - k^{\gamma 2},$$
$$\epsilon'' = 2nk.$$

The resonance frequency (TO) is then located at the conductivity maximum $(2nk\omega)_{\mathrm{max}}$,[27] and the LO frequency occurs where $\epsilon' = 0$.[28]

II. EXPERIMENTAL

A. Transmission Measurements

The maximum absorption coefficient in the two-phonon combination band (6 to 11 μ) is approximately 10^3 cm^{-1}; therefore, the optimum crystal thickness is ~25 μ giving ~10% minimum transmission. Measurements were made at room temperature using a Perkin-Elmer model 99 double-pass monochromator with NaCl optics and thermocouple detector, the second pass being internally chopped at 13 cps.

An infrared microscope attachment designed by Norris[29] was used which had an image-reduction ratio of ~10:1, giving an intermediate image size about 2×0.2 mm. A single series E crystal ~0.25 mm square positioned at the intermediate focus therefore utilizes about 10% of the available energy from the Nernst filament. The microscope and monochromator were continuously flushed with dry nitrogen during measurements to minimize the effect of atmospheric water-vapor absorption. Unfortunately this unwanted absorption could not be completely eliminated in these single-beam measurements. Signals proportional to the transmitted and incident light intensities I_t and I_0 were obtained with a strip chart recorder at suitable gain settings, with and without the specimen in position, respectively. The ratio of the signal amplitudes was obtained point by point and arbitrarily normalized to $I_t/I_0 = 100\%$ for $\lambda \leq 5.5$ μ. The transmission spectrum for crystal AN265E8 is shown in Fig. 1; the dotted portion is uncertain because of a small amount of residual atmospheric water-vapor absorption. The assignment of the absorption bands is discussed in Sec. IV. The positions of the weaker bands were confirmed at a later date using the series W crystals which, because of their larger area, enabled the spectrum to be run at a much improved signal-to-noise ratio. In order to confirm that none of the structure observed was due to electronic transitions, the absorption spectrum of one crystal was measured at liquid-air temperature. (Electronic transitions would be expected to sharpen up markedly between 300 and 80°K, particularly in this spectral region.) The specimen was mounted in a specially designed crysotat with KRS-5 windows which could be positioned at the intermediate focus of the infrared microscope. Difficulty was experienced with low-temperature measurements because the peak of the room-temperature blackbody radiation lies in the spectral region being investigated, and the zero offset produced by the spectrometer "seeing" the cooled specimen mount instead of ambient objects was comparable with the signal transmitted by the specimen. However, bearing this limitation in mind, no significant change in the spectrum was observable at 80°K, which suggests that all the detected absorption peaks are due to phonon combinations.

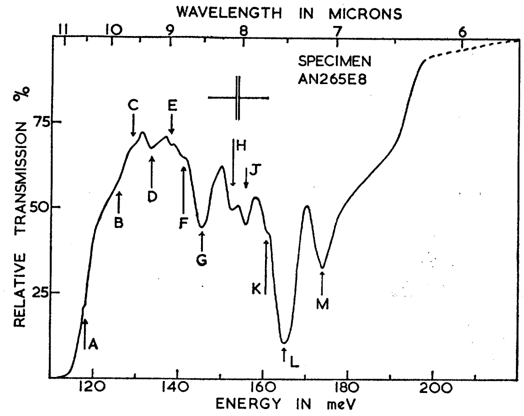

FIG. 1. Absorption bands in the two-phonon combination region. The assignment of the peaks is discussed in Sec. IV.

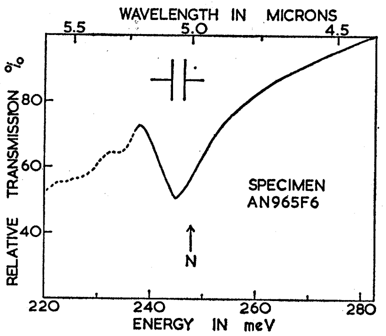

FIG. 2. Three-phonon combination region.

The three-phonon combinations are relatively weak, and many of them occur in the atmospheric water-vapor absorption region, making measurements unreliable. Using a series F crystal about 2 mm thick, however, the 3TO peak has been located. The spectrum for crystal AN965F6 is shown in Fig. 2. As before, the wavelength at which I_t/I_0 has been set at 100% has been arbitrarily chosen ($\lambda \leq 4.4$ μ in this case) and the dotted portion of the spectrum is uncertain.

B. Reflectivity Measurements

The reflectivity spectra in strongly convergent light have been compared for the series E, F, and W crystals from 8–15 μ and found to be identical. The method of adapting the infrared microscope for measuring the reflectivity of very small samples is described else-

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where.[30] As the angle between the propagation vector and the c axis of a uniaxial crystal is decreased from 90°, the width of the reststrahlen band decreases markedly for the extraordinary ray, the long-wavelength side of the band moving to shorter wavelengths.[31] For unpolarized strongly convergent light, therefore, it is expected that the reflectivity spectrum will be distorted at longer wavelengths. A typical reflectivity spectrum, obtained from a row of four series E crystals, mounted in a suitable nonreflecting medium, with their surfaces coplanar[30] is shown in Fig. 3. (Four crystals are used to obtain a measurable signal in regions where the reflectivity is low.)

For measurements of the reflectivity near normal incidence, the largest of the series F crystals, AN965F2, was ground and polished to give a suitably large surface area, the final polish being 0.5-μ alumina. The resulting specimen had dimensions $\sim 8\times 2\times 0.5$ mm and the c axis approximately parallel to the front surface. Measurements of the reflectivity before and after polishing showed no detectable difference, and so no chemical etching was attempted. The reflectivity was measured at $\sim 10°$ off normal from 2–15 μ using the Perkin-Elmer monochromator with NaCl optics. The long-wavelength tail from 14 to 28 μ was measured on an Ebert grating spectrometer which was evacuated to eliminate atmospheric absorption.[32] The measured reflectivity was compared point by point with a freshly aluminized mirror, the reflectivity of which was assumed to be 100% over the range of wavelengths covered. The small crystal size and the necessity for using two spectrometers to cover the entire spectrum made quantitative polarization studies impracticable. However, measurements with radiation polarized parallel and perpendicular to the c axis indicate that, with one exception to be mentioned below, the reflectivity is practically the same for both polarizations. This justifies using only two parameters to describe the reststrahlen band. It should be noted that one might expect a shift in the position of the long-wavelength boundary of the reststrhalen band of $\sim 2\%$ from one polarization to the other because of the slight anisotropy of the hexagonal wurtzite structure. However, since this is precisely the region where it was necessary to change spectrometers, such a shift would go undetected. The complete spectrum for unpolarized radiation is shown in Fig. 4. It will be noted that in addition to the main reststrahlen band there is some weak structure at $\sim 11\ \mu$. This structure has been found to be polarization-dependent, and the reflectivity from 10 to 12 μ is shown in more detail in Fig. 5 for radiation polarized parallel and perpendicular to the c axis. It is then apparent that the observed structure is due to a sharp minimum at ~ 111.0 meV for E parallel to the c axis.

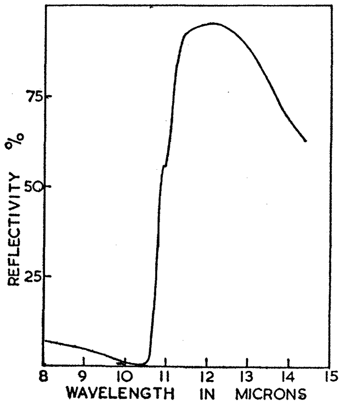

Fig. 3. Reflectivity from series E crystals in strongly convergent light.

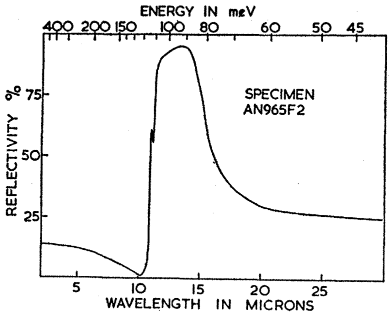

Fig. 4. Complete reflectivity spectrum measured at near normal incidence using unpolarized radiation.

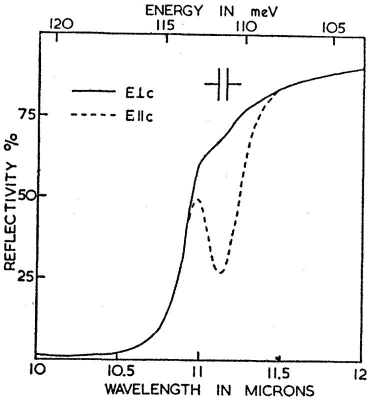

Fig. 5. Reflectivity spectrum from 10 to 12 μ for $E\|$ and $E\perp$ to the c axis.

An attempt has also been made to measure the reflectivity of thin films of AlN deposited on a quartz substrate.[33] These films have been successfully used to investigate the uv absorption edge,[14] but exhibited no measurable reflectivity in the infrared, the spectrum obtained being indistinguishable from that obtained from the quartz substrate. It is therefore assumed that the properties of these thin films are not typical of the bulk crystalline material in this wavelength region.

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III. ANALYSIS OF REFLECTIVITY DATA

The zone-center values of LO and TO effectively form the limits of the reststrahlen band.[31] For reasons already discussed, the long-wavelength side of the band moves to shorter wavelengths when strongly convergent light is used. The reflectivity data of Fig. 3 therefore suggest $\lambda_{\mathrm{LO}}\sim 10.8\ \mu$ and $\lambda_{\mathrm{TO}}>13.5\ \mu$, i.e., the zone-center phonon energies are LO$\sim$115 and TO$<$92 meV.

The optical parameters n, k, ϵ', and ϵ'' have been calculated from the reflectivity measured at normal incidence with unpolarized radiation. The relatively insignificant feature at $\sim 11\ \mu$ has been ignored for the purposes of this calculation. The Kramers-Krönig analysis was performed on the University of London I.C.T. Atlas computer, and the results are shown in Fig. 6. The conductivity maximum $(2nk\omega)_{\max}$ occurs at 14.97 μ (82.7 meV) and the real dielectric constant ϵ' is zero at 10.91 μ (113.6 meV). These are, respectively, the TO and LO energies at $\mathbf{k}\simeq 0$. The imaginary dielectric constant ϵ'' is also a maximum very near 14.97 μ.

The calculated values for the optical parameters below $\lambda=5\ \mu$ are rather uncertain because of experimental inaccuracies. However, if we assume the high-frequency dielectric constant ϵ_∞ to be the square of the refractive index measured in the visible, then taking $n_\infty=2.2$ as the average of the values for the ordinary and extraordinary rays at $\lambda=5500$ Å[34] gives $\epsilon_\infty=4.84$. The value of the low-frequency dielectric constant ϵ_0 can then be calculated from the Lyddane-Sachs-Teller relation[35]:

$$\epsilon_0=(\omega_L/\omega_T)^2\epsilon_\infty\,.$$

Substitution of the appropriate values gives $\epsilon_0=9.14$. This agrees well with the value $\epsilon_0'=9.1$ calculated from the reflectivity data. Taylor and Lenie have measured the dielectric constant for hot-pressed aluminum nitride which was $\sim$96% pure and $\sim$98% of theoretical density.[3] They obtained the value $\epsilon'=8.5$ at $\sim 10^{10}$ cps. The agreement with the optical data is therefore quite good although the latter, being measured on a single crystal, are probably more significant.

The Szigeti effective charge has been calculated using the formula given by Mitra and Marshall[15]

$$q^*=2\pi\nu_T\left(\frac{\epsilon_0-\epsilon_\infty}{4\pi}\right)^{1/2}\frac{3}{\epsilon_\infty+2}\,\frac{(\mu v_a)^{1/2}}{e},$$

where ν_T is the $\mathbf{k}\simeq 0$ transverse optical frequency (cps), v_a is the unit-cell volume, μ is the reduced ionic mass $M_{\mathrm{Al}}M_{\mathrm{N}}/(M_{\mathrm{Al}}+M_{\mathrm{N}})$, and e is the electronic charge. Using the values of the lattice constants given by Taylor and Lenie[3] the calculated value is

$$q^*=1.2\,.$$

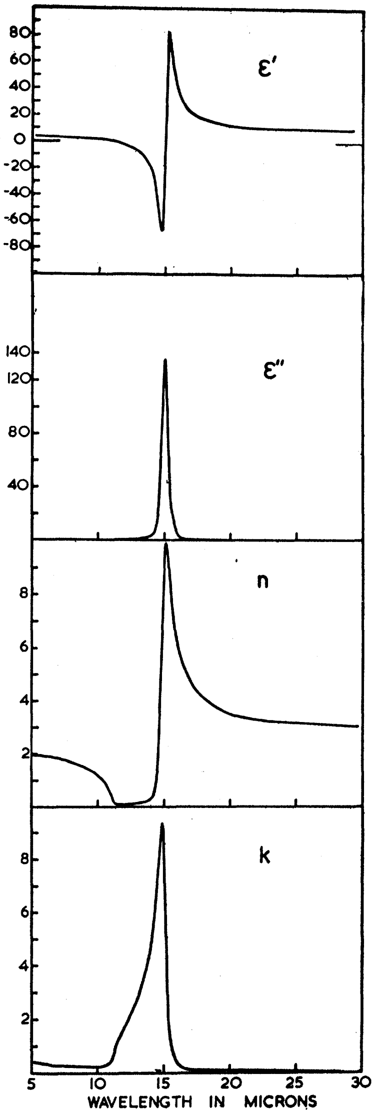

FIG. 6. Optical parameters calculated from reflectivity data.

IV. ANALYSIS OF TRANSMISSION DATA

It has been stressed in Sec. I that in the absence of neutron-scattering data any phonon assignment derived purely from the infrared data must necessarily be tenative. However, the major features of the spectrum can be identified with reasonable certainty although the symmetry direction cannot be specified. For compounds in which the effective charge is large ($q^*\gtrsim 1$) the transverse optical phonon branch TO shows little dispersion, and the energy of the longitudinal optical branch LO is greater than TO, thoughout the Brillouin zone.[15] Hence in the two-phonon combination band we expect to find a $2TO$ absorption peak close to 2×82.7 meV ($=2\times TO$ at $\mathbf{k}\simeq 0$). This immediately identifies the peak L at 165.0 meV (Fig. 1), giving $TO=82.5$ meV. The next peak M at higher energy is presumably $LO+TO$ giving $LO=91.4$ meV. As in SiC[22] the $2LO$ combination is ill

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TABLE I. Comparison of observed and assigned summation band energies using $LO=91.4$, $TO_1=82.5$, $TO_2=78.1$, $LA=62.9$, $TA_1=55.3$, and $TA_2=50.9$ meV.

Observed peak energy (meV)		Assignment	Assigned value (meV)
A	118.2±0.3	$LA+TA_1$	118.2
B	125.8±1.0	$2LA$	125.8
C	130.0±0.5	TO_2+TA_2	129.0
D	133.3±0.2	TO_1+TA_2	133.4
		TO_2+TA_1	133.4
E	137.9±0.3	TO_1+TA_1	137.8
F	140.6±0.5	TO_2+LA	141.0
G	145.5±0.2	TO_1+LA	145.4
H	152.7±0.3	$3TA_2$	152.7
J	155.7±0.2	$LO+LA$	154.4
		$2TO_2$	156.2
K	160.6±0.5	TO_1+TO_2	160.6
L	165.0±0.3	$2TO_1$	165.0
M	173.9±0.2	$LO+TO_1$	173.9
N	245.0±0.5	$3TO_1$	247.5

defined. Following the interpretation used for SiC, for which the absorption spectrum is similar in some respects to that reported here for AlN, the prominent peak *G* at 145.5 meV is given the assignment $TO+LA$, from which the energy of the longitudinal acoustic phonon *LA* is 62.9 meV. The lowest-energy peak *A* at 118.2 meV is then $LA+TA$ which gives the values of the transverse acoustic phonon *TA* as 55.3 meV. (As in other materials, it is assumed that $LA>TA$.)

These four phonon energies do not, however, explain all the features observed. As with the analyses for other wurtzite materials[21] we therefore introduce two additional phonons which we arbitrarily designate TO_2 and TA_2. All the observed absorption peaks of Figs. 1 and 2 can then be satisfactorily explained as shown in Table I using the values $LO=91.4$, $TO_1=82.5$, $TO_2=78.1$, $LA=62.9$, $TA_1=55.3$, and $TA_2=50.9$ meV. This interpretation is examined further in the following section.

V. DISCUSSION

From the reflectivity data the average values of the zone-center optical-phonon energies are calculated to be $LO=113.6$ meV and $TO=82.7$ meV. The values obtained for the dielectric constants $\epsilon_\infty=4.84$ and $\epsilon_0=9.14$ are seen to be consistent with these phonon energies and with the optical and electrical measurements of other workers. The Szigeti effective charge $q^*=1.2$ is the highest that has been reported for a binary compound, but has been shown to be in good agreement with the fraction of ionic binding of ~39% determined from x-ray measurements.[36] The values of $LO\sim115$ meV and $TO<92$ meV determined by inspection from Fig. 3 indicate that a reasonable estimate of the phonon energies (particularly *LO*) can be obtained for materials where only minute samples are available. For cubic crystals there is no long wavelength distortion in convergent light, and *TO* can also be located to within a few percent.

The reflectivity minimum at ~111.0 meV has not been further investigated. However, it has been brought to our attention that minima can occur in the reststrahlen band because of an unspecified two-phonon process resulting from interference between two components of the complex electric susceptibility of the crystal. In hexagonal SiC the minimum observed at 110 meV for $E\|c$[37] is thought to be due to the two-phonon combination $LA+TA$. For AlN the combinations $LA+TA_2$ (113.8 meV) and $2TA_1$ (111.6 meV) are both close to the position of the observed minimum. Although no features corresponding to the combinations TA_1+TA_2 and $2TA_2$ have been observed a two-phonon process of the type indicated is thought to be responsible for the reflectivity minimum at ~111.0 meV.[38]

It has been shown that it is possible to account for the observed multiphonon combination bands using six representative phonon energies. When larger crystals of AlN become available, permitting more detailed measurements, it may prove more realistic to interpret the multiphonon combination spectra in terms of four phonons at each of two critical points. However, it is not anticipated that the phonon energies deduced in this way will differ markedly from those obtained in the analysis above, although the assignments may require slight alteration.

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