Optical Properties of 21R SiC: Absorption and Luminescence

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Measurements from 4.2 to 300°K show that the absorption edge of 21R SiC is due to phonon-assisted transitions which create excitons. The exciton energy gap is 2.853 eV at 4.2°K. A region of anomalous absorption is found. The luminescence at 6°K is due to excitons bound to nitrogen atoms (Lampert complexes). The binding energies, measured for six of the seven inequivalent nitrogen atoms, range from 10 to 40 meV. Applicability of the Haynes rule is discussed. A number of phonon energies are obtained from the luminescence spectrum, which is simpler than expected for a high polytype. Comparisons with other SiC polytypes are given throughout.

I. INTRODUCTION

SOME 40 polytypes of SiC have been found which differ only in the stacking order of close-packed planes of atoms. They all have tetrahedral bonding, and they are semiconductors with a considerable range of energy gaps.[1] One of the less common polytypes is 21R (space group R3m).[2] It was discovered by Thibault[3] and its atomic arrangement was established by the x-ray work of Ramsdell.[4] Some room-temperature optical-absorption measurements, showing the absorption edge, but no structure, were made by Lipson.[5] We have given a preliminary report of the low-temperature photoluminescence of nitrogen-exciton complexes.[6]

In this paper we report the luminescence in Sec. III, absorption at low temperatures in Sec. IV, and in Sec. V we discuss possible positions of the conduction-band minima, using a large zone to facilitate comparisons with other polytypes. We compare results with those previously obtained in similar measurements on the simpler SiC polytypes, namely, cubic,[1] 4H,[7] 6H,[8] and 15R.[9]

The luminescence spectrum proves to be less complex than expected for a crystal with 14 atoms per unit cell. We measure the "principal" phonon energies, which are found to be close to those of other SiC polytypes. Binding energies of excitons to nitrogen atoms are measured for six of the seven inequivalent nitrogen sites. These energies have an unusually wide range (from 10 to

40 meV). It is argued that the Haynes rule is unlikely to be valid in this case.

Optical absorption at the edge is shown to be phonon-assisted, with an exciton energy gap of 2.852 eV at 77°K. Some measurements of the temperature dependence of the gap are reported. The absorption spectrum is similar in many respects to those of other SiC polytypes. However, a region of anomalous absorption is found. One may ask if this is due to the unusually complex neighborhood in which the conduction band minima are thought to be located.

II. POLYTYPE GROWTH AND IDENTIFICATION

Several crystals of 21R SiC were grown from relatively pure silicon and carbon by vapor transport,[10] in furnace runs which produced mostly 6H SiC. In most cases the crystals were partly 21R, partly 6H and/or 15R. The reason for the appearance of 21R polytype is not known, but it is usually assumed that the growth of uncommon polytypes is due to the presence of suitable screw dislocations.[11] Such dislocations may be formed accidentally in the initial growth stages.

Seven crystals from various runs were selected because of a characteristic luminescence spectrum, and the crystals were then identified as 21R by x-ray analysis. The active impurity was identified as nitrogen by observing the spectra in mixed crystals of 21R with 6H or 15R; the spectrum due to nitrogen in the latter polytypes is known. The samples used for obtaining the experimental data were either pure 21R specimens, or were prepared by grinding off, or by covering up, the 6H and 15R portions.

Our photoluminescence and absorption measurements were made in the same way as for other SiC polytypes, and the experimental procedures have already been described.[1,8]

III. LOW-TEMPERATURE LUMINESCENCE

We have reported the exciton photoluminescence of several SiC polytypes, viz., cubic, 4H, 15R, and 6H. In cubic[1] and 4H SiC[7] the spectra are due to excitons bound

[1] W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. 133, A1163 (1964).

[2] We use the Ramsdell notation. Other designations for this polytype are *Type IV* (Thibault), *hkkhkkk* (Jagodzinski), and (34)₃ (Zhdanov). The common *ABC* notation is awkward for high polytypes. For 21R it is *ABCABACBCABCBACABCACB*. For a discussion of SiC polytypes and notations see A. R. Verma, *Crystal Growth and Dislocations* (Butterworths Scientific Publications, Ltd., London, 1953), Chap. 7.

[3] N. W. Thibault, Am. Mineralogist 29, 249, 327 (1944).

[4] L. S. Ramsdell, Am. Mineralogist 29, 431 (1944). In this paper, Ramsdell uses the old designation, *Type IV*.

[5] H. G. Lipson (private communication).

[6] W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Bull. Am. Phys. Soc. 9, 270 (1964).

[7] Lyle Patrick, W. J. Choyke, and D. R. Hamilton Phys. Rev. 137, A1515 (1965).

[8] W. J. Choyke and Lyle Patrick, Phys. Rev. 127, 1868 (1962).

[9] Lyle Patrick, D. R. Hamilton, and W. J. Choyke, Phys. Rev. 132, 2023 (1963).

[10] D. R. Hamilton, J. Electrochem. Soc. 105, 735 (1958).

[11] R. S. Mitchell, Z. Krist. 109, 1 (1957). See also A. R. Verma, Ref. 2.

FIG. 1. Luminescence spectrum, at 6°K, of four-particle nitrogen-exciton complexes in 21R SiC. P, Q, R, S, T, and U are six no-phonon lines due to complexes at six of the seven inequivalent nitrogen sites. Exciton binding energies at these sites are measured by the displacements of the lines from $E_{Gx}=2.853$ eV. Other labeled lines, which occur in groups of three, are one-phonon lines of the P, Q, and R series, and the phonon energies are indicated in meV. Similar, but weaker, lines of the S, T, and U series are present, but unmarked.
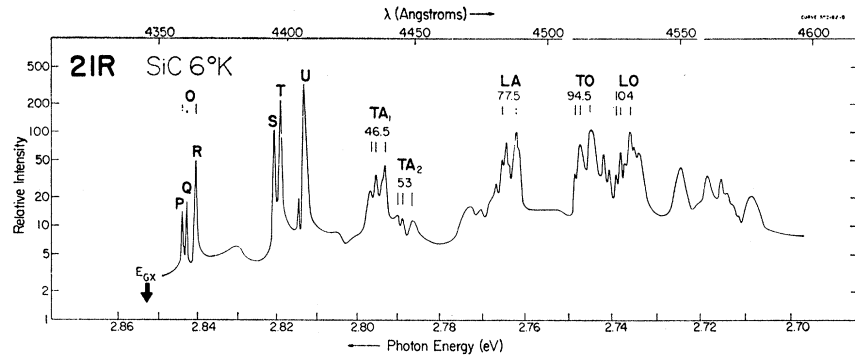
to neutral nitrogen atoms (forming four-particle Lampert[12] complexes which decay with photon and phonon emission). In 15R[9] and 6H[8] SiC such spectra are again observed, and, in addition, some quite different spectra due to excitons bound to ionized nitrogen (three-particle Lampert complexes).[13] Observation of both kinds of spectra makes it possible to deduce the donor ionization energies for nitrogen.[9] In 21R SiC only four-particle nitrogen-exciton complexes are observed.[14]

There is a tendency for the spectra to get more complex as the number of atoms per unit cell increases from two in cubic SiC to eight in 4H, ten in 15R, and twelve in 6H. There are 14 atoms per unit cell in 21R, hence 42 phonon branches, and there are seven inequivalent carbon sites at which nitrogen atoms may be substituted. Thus, there could be seven series of lines, each series having as many as 43 lines, including the no-phonon line.

Surprisingly, the observed 21R spectrum is not particularly complex, as Fig. 1 shows. There are six no-phonon lines whose displacements in energy from the exciton energy gap (marked E_{Gx})[15] give us the binding energies listed under E_{4x} in the first column of Table I. The seventh expected line is not observed. There is a weak line near U, but its relative intensity varies from sample to sample, indicating that it is not due to nitrogen (it may be due to aluminum). The nitrogen atoms are almost certainly distributed over the seven sites. It is possible that the binding energy is very small at one site, but a spectrum taken at 1.6°K still does not show the seventh line.[16]

The six observed no-phonon lines fall into two groups of three. The weakly bound complexes, P, Q, and R have weaker no-phonon lines, but have larger total emission,[17] and they give rise to the strongest lines in the part of the spectrum which is due to phonon-assisted transitions. The set of three lines, due to P, Q, and R, is identified in Fig. 1 at each recurrence. The displacements from the no-phonon lines measure the phonon energies, which are indicated in Fig. 1, and listed in the second column of Table I.

The phonon energies of Table I are very close to those of six other polytypes, and attributed to phonons which conserve crystal momentum for conduction-band minima at the large zone boundary.[18] We do not resolve spectral lines due to emission of any of the many other phonons having the same $\mathbf{k}$ vector in the Brillouin zone, or differing by a reciprocal lattice translation in the large zone scheme. Such phonons were clearly resolved in 4H, 6H, and 15R SiC, but appear to be very weak in 21R, contributing only to the unresolved background. Thus, the 21R spectrum does not have the complexity one might have expected. A similar simplification is observed also in 33R SiC.[19]

TABLE I. Energies obtained from Fig. 1. E_{4x} is the energy which binds an exciton to a nitrogen atom at one of the six inequivalent sites (of a possible seven). E_p is one of the principal phonon energies. All energies are in meV.

E_{4x}		E_p	
P	10.0	TA$_1$	46.5
Q	11.2	TA$_2$	53
R	13.4	LA	77.5
S	32.7	TO	94.5
T	34.2	LO	104
U	40.0		

[12] M. A. Lampert, Phys. Rev. Letters 1, 450 (1958).
[13] D. R. Hamilton, W. J. Choyke, and Lyle Patrick, Phys. Rev. 131, 127 (1963). This reference uses ⊕ and ⊙ for three- and four-particle complexes, a convenient notation when both are present. Lampert's notation is ⊕+− and ⊕+−−.
[14] A possible reason for the absence of three-particle complexes is given by W. J. Choyke, Lyle Patrick, and D. R. Hamilton, in Physics of Semiconductors (Dunod Cie., Paris, 1964).
[15] The exciton energy gap E_{Gx} is the usual energy gap E_G minus the still unknown energy which binds the hole and the electron in exciton formation. We obtain E_{Gx} from the absorption measurements of Sec. IV.
[16] Most spectra were taken with the samples not immersed in the helium. Under uv irradiation, the sample then reaches a temperature of approximately 6°K, as indicated in Fig. 1.

[17] These correlations for E_{4x} were also observed in other polytypes, and are discussed in Ref. 8, Sec. D.
[18] Reference 1, Table I, gives the values for three polytypes. TA$_2$ was first identified as belonging to the second TA branch in 4H SiC (Ref. 7), but phonons of this energy were also reported for 6H and 15R (Ref. 9, Table I). They were listed under LA in Ref. 9, but probably are TA$_2$.
[19] W. J. Choyke, D. R. Hamilton, and Lyle Patrick (unpublished).

Most of the other lines in Fig. 1, including the prominent unmarked lines at the right, belong to the S, T, and U series. They are not as strong as the P, Q, and R lines, but yield the same phonon energies. There are also a few weak lines whose assignment is in doubt.

At somewhat higher temperatures ($\approx 20°$K) the spectra of the weakly bound complexes (P, Q, and R) disappear, but those of the S, T, and U complexes remain. Additional lines can then be seen due to thermally excited states of these complexes. The additional lines increase in relative intensity with increasing temperature. They indicate that there is an excited state 4.8 meV higher in energy than the ground state for S, T, and U. This is the same energy separation measured in $4H$, $6H$, and $15R$ polytypes, and attributed to the presence of a second valence band, split off by the spin-orbit interaction. The exact position of the second valence band also depends to some extent on the crystal-field splitting.[20] Thus, the constancy of the 4.8-meV separation in four polytypes is further evidence of the similarity in valence band structure (at $\mathbf{k}=0$). Differences in polytype semiconductor properties are probably largely due to differences in the positions of the conduction-band minima. Such differences are most easily visualized by a comparison of large zones (see Sec. V).

From the luminescence of exciton complexes in silicon, Haynes[21] found the rule $E_{4x} \approx 0.1 E_i$ for all shallow donors (E_i is the donor ionization energy). The Haynes rule has been reported to hold also for donors in II–VI compounds (with a proportionality constant of 0.2).[22] If we were to apply this rule to the nitrogen donors in $21R$ SiC we would conclude that values of E_i vary by a factor of 4 (see Table I). However, we found that the Haynes rule does not work well for $6H$ and $15R$ SiC.[23] In those polytypes the variation in E_i is of the order of 50%, which is a more probable variation for $21R$ also.

It is possible that the validity of the Haynes rule in silicon and II–VI compounds is related to the fact that in those materials the donor ionization energies differ because of departures from the effective-mass approximation within the central cell.[24] For SiC polytypes the variation of nitrogen ionization energies appears to be due to an entirely different cause, namely, the Kohn-Luttinger interference effect.[25]

IV. ABSORPTION

The samples used for absorption had light paths of 0.4, 0.6, and 1.44 mm. Polarized light was used, with $E \| c$ or $E \perp c$, but only the $E \perp c$ curve is shown, because

the structure is more distinct for this polarization (as in other polytypes). The absorption edge of $21R$ SiC is similar in most respects to those previously reported for other polytypes, but it has an anomalous region discussed below.

The absorption is due to phonon-assisted transitions which produce excitons, and at $77°$K only the transitions with phonon *emission* are observed. In Fig. 2 we have plotted the square root of the absorption coefficient ($\alpha^{1/2}$) against photon energy, as is usually done for indirect transitions. Such a plot becomes linear at higher photon energies. However, in the exciton region there is a portion for each phonon with α^2 proportional to $E - E_{Gx} - E_p$, where E is the photon energy, and E_p the phonon energy.[26] In $21R$ SiC there are 42 phonons which conserve crystal momentum in the creation of excitons. With increasing photon energy an additional absorption threshold is possible each time the emission of another of these phonons becomes energetically possible. However, the structure due to most of the 42 phonons, if present, is not resolved. The *observed* structure is due to the "principal" phonons listed in Table I, except that TA_2 is not resolved, and TO is poorly resolved.

Measurable absorption begins with the emission of the 46.5-meV phonon (TA_1). Our transmission measurements are normalized to unity at that point, hence there is no tail in the absorption curve which would merely represent uncertainty in our data. The phonon energies used to put in the arrows in Fig. 2 are those obtained from the luminescence.[27]
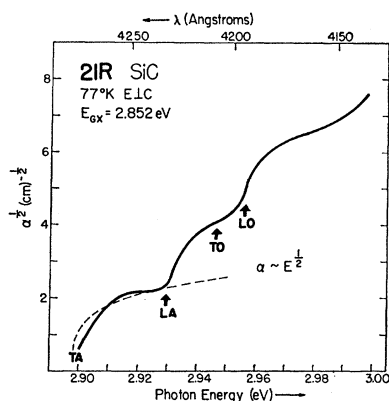

Fig. 2. Absorption edge of $21R$ SiC for polarized light, with $E \perp c$. The plot of $\alpha^{1/2}$ against photon energy is conventional for indirect transitions. At $77°$K only the phonon *emission* part of the spectrum is significant. Arrows mark thresholds for the indicated phonons. A theoretical curve, for spherical bands, is shown by the dashed line (for a single phonon). The experimental curve is anomalously flat in the neighborhood of 2.92 eV.

[20] A similar situation exists in CdS, and has been discussed by J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).
[21] J. R. Haynes, Phys. Rev. Letters **4**, 361 (1960).
[22] R. E. Halsted and M. Aven, Bull. Am. Phys. Soc. **9**, 631 (1964).
[23] Reference 9, Table II.
[24] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 257.
[25] Lyle Patrick, Phys. Rev. (to be published).

[26] T. P. McLean, in *Progress in Semiconductors* (Heywood and Company, Ltd., London, 1960), Vol. 5, p. 55.
[27] Phonon energies can be measured from the optical-absorption spectrum alone, by observing also the *phonon-absorption* part of the spectrum (at higher temperatures). The accuracy is poor, and experience with other SiC polytypes has shown us that the same energies are obtained from the luminescence measurements.

FIG. 3. Temperature dependence of the exciton energy gap, obtained by observing the sharp LA absorption threshold at four temperatures.
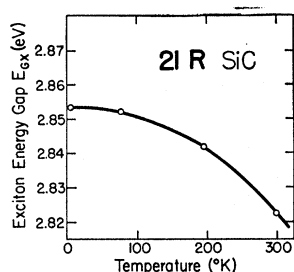
The phonons responsible for the structure in the 21R absorption edge are the same (almost) as those giving the structure in the 6H and 15R absorption edges. Thus, the three absorption edges can be very nearly superimposed after the appropriate energy shifts and changes of scale. This was done for 6H and 15R in Fig. 11 of Ref. 9. If 21R is compared in this way with 6H and 15R, its absorption intensity is found to be very close to that of 6H, and almost three times that of 15R.[28]

The comparison with 6H and 15R absorption edges also reveals that the 21R structure is sharper, contrary to what might have been expected for a high polytype. The edge due to emission of the LA phonon at 2.93 eV is particularly sharp, and it is still quite distinct at room temperature. It provides an accurate means of measuring the temperature dependence of the exciton energy gap E_{Gx}. We show E_{Gx} at four temperatures in Fig. 3.

Finally, we observe an anomalously flat region, just before the LA edge, in the neighborhood of 2.92 eV. The theoretical curve (for spherical bands)[26] is shown as a dashed line in Fig. 2. Broadening of the structure (probably due to short exciton lifetimes)[29] has been observed in other polytypes, and tends to straighten out the edge, eliminating the structure. The anomalous region is changed in the opposite sense, and we cannot explain it. However, the conduction-band minima may lie in regions which are cut by networks of energy discontinuities, as shown in the next section. This could result in an unusual density-of-states function for the conduction band.

V. LARGE ZONE COMPARISONS

Most SiC polytypes have large unit cells, hence small Brillouin zones (BZs). For band structure comparisons it is desirable to use large, complete zones,[30] such that the volumes of the zones in k space are the same for all polytypes. For a polytype with n silicon and n carbon atoms per unit cell, the proper large zone is one that can be reduced to n BZs. Thus, the cubic and 21R large zones reduce to one and seven BZs, respectively. The

proper axial dimension for the large zone is found to be a constant $N\pi/c$, where N is the number of close-packed layers in the stacking sequence (the number that appears in the Ramsdell symbol), and c is the unit-cell length along the symmetry axis.[31] For comparison with other polytypes, cubic SiC may be regarded as rhombohedral,[32] i.e., as polytype 3R.

The likelihood that the conduction-band minima remain in the mirror planes for all polytypes simplifies a comparison of two polytypes by making it a two-dimensional problem.[7] For 4H SiC, such a comparison located probable positions of the minima, using only an interpretation of the phonon spectrum and the known positions of the minima in cubic SiC.[7] For 21R SiC the data are insufficient to deduce probable minima, but the comparison with cubic SiC is nevertheless a useful one.

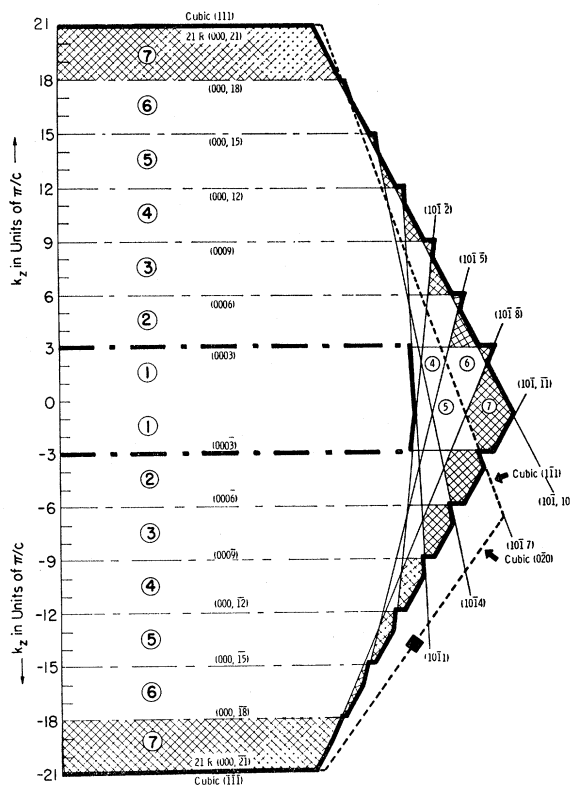For this comparison we refer to Fig. 4. The cubic BZ

FIG. 4. Comparison of cubic Brillouin zone (dashed line) with 21R large zone in a mirror plane. The 21R large zone is a complete two-dimensional zone reducible to seven Brillouin zones (only half the zone is shown in the figure). Energy discontinuities are drawn in and labeled by Bravais-Miller indices. They are of two kinds, horizontal and oblique. The horizontal lines, with the exception of the boundary lines ±(000,21), correspond to extremely weak discontinuities; hence most of the large zone area is free of strong discontinuities. The remaining portion, at the right, is cut by a network of strong energy discontinuities.

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[28] See Ref. 9 for further discussion of intensity differences.

[29] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. 111, 1245 (1958).

[30] A good discussion of large zones is given by H. Jones, in *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960), Chap. 5.

[31] A large zone was used for 15R SiC in Figs. 6 and 7 of Ref. 9. There the axial component of the wave vector (k_c) was given in units of $3\pi/c$, but incorrectly stated to be in units of π/c.

[32] For a discussion of cubic as a special case of rhombohedral, see Ref. 30, p. 55.

TABLE II. Indices for cubic-zone boundaries appearing in Fig. 4, and the corresponding 21R indices.

Miller	Bravais-Miller	21R
11$\bar{1}$	000$\bar{3}$	000, $\overline{21}$
1$\bar{1}$1	10$\bar{1}$1	10$\bar{1}$7
0$\bar{2}$0	10$\bar{1}$$\bar{2}$	10$\bar{1}$, $\bar{1}$$\bar{4}$
$\bar{1}$1$\bar{1}$	000$\bar{3}$	000, $\overline{21}$

(or large zone) boundaries are shown for half a (10$\bar{1}$) plane by the dashed lines. They are designated by the Miller indices of the corresponding x-ray reflections. They coincide at top and bottom with the large zone boundaries of 21R, just as the cubic (111) x-ray reflections coincide with the 21R (000,21) reflections.[33] The comparison is made more direct by transforming the cubic Miller indices into Bravais-Miller indices[34] as shown in Table II. It is observed that *all* cubic x-ray reflections coincide with *some* of the 21R reflections.[35]

To find a suitable large zone for 21R, all energy discontinuities are drawn in and designated by Bravais-Miller indices in Fig. 4. They are of two types, horizontal and oblique. The dash-dot horizontal lines of the type (000l) indicate some extremely weak discontinuities. The corresponding x-ray reflections have not yet been observed.[36] Thus, most of the 21R large zone is free of strong energy discontinuities.

The oblique lines belong to the set (10$\bar{1}$$l$), and they correspond to the x-ray lines used by Ramsdell to deduce the stacking order of 21R. They form a network

[33] F. G. Smith, Am. Mineralogist **40**, 658 (1955).
[34] We have used the transformation matrix $(0\frac{1}{2}\frac{1}{2}/\frac{1}{2}0\frac{1}{2}/111)$ which is consistent with the obverse orientation for rhombohedral lattices, adopted as standard in the *International Tables for X-Ray Crystallography* (The Kynoch Press, Birmingham, 1952), Vol. 1.
[35] Using Bravais-Miller indices, cubic (*hkl*) reflections correspond to 21R (*hki,7l*) reflections.
[36] The structure factors for these reflections vanish if all planes in the stacking sequence are taken to be equivalent. This is a good approximation, but not exact. The planes are actually inequivalent in the same way that the seven silicon or carbon sites are inequivalent.

which cuts the right-hand portion of the large zone into small segments. In the reduction of the large zone into BZs these segments are translated to complete the seven BZs indicated by the circled numbers.[37] The boundaries of the first BZ are shown by heavier lines, no translations being necessary to complete it. The numbering of the segments is easily done by Jones Rule (i).[38] We have indicated the appropriate numbers for four of the larger segments. The large zone boundary is bordered by segments belonging to the seventh BZ, and they are cross-hatched. The boundary itself is the heavy line, and the (10$\bar{1}$,10) and (10$\bar{1}$,$\bar{1}$$\bar{1}$) energy discontinuities form a large part of it at the right. Discontinuities for which $|l| > 11$ lie entirely outside the large zone and are not shown [for example, (10$\bar{1}$,$\bar{1}$$\bar{4}$) would coincide with the dashed (0$\bar{2}$0) cubic discontinuity as can be seen from Table II].

The presence of the TA$_2$ phonon in the luminescence spectrum shows that the conduction band minima do not lie on the symmetry axis, and the magnitude of the phonons suggests that they lie on the large zone boundary, but the spectrum does not provide further clues as the 4H spectrum did.[7] We therefore use the general arguments of Ref. 7 to suggest that a 21R minimum may be located on the large zone boundary and in the neighborhood of the cubic minimum, which is indicated in Fig. 4 by a black square. There are no critical points in this vicinity due to symmetry alone, hence the minimum is probably determined by the energy discontinuities. There would be six such minima altogether, unless $k_z = -11 \, \pi/c$ exactly, in which case $\mathbf{k}$ and $-\mathbf{k}$ would be equivalent under a reciprocal lattice translation, reducing the number of minima to three.

The band structure would be quite complex in the region suggested for the conduction-band minimum, since it is cut by a network of energy discontinuities. This may possibly be a reason for the absorption anomaly mentioned in the last section.

[37] The reduction is a two-dimensional problem because such translations are also in the mirror plane.
[38] See Ref. 30, p. 188. The similar but easier problem for 4H SiC was done in the same way in Ref. 7.