Infrared Absorption in SiC Polytypes

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A strong residual ray absorption is observed in SiC. In most polytypes, additional one-phonon absorption lines are permitted by group-theoretical selection rules, but such lines have not been reported. A procedure is now outlined that makes it possible to classify all the additional weak lines, and to identify three of them reported in previously published work. Two are lines at 62 and 110 meV in 6*H* SiC; the third is a 70-meV line in 15*R*. The classification procedure can also be used for Raman lines. On making what appear to be reasonable assumptions, one can estimate the energies of infrared and Raman lines in any SiC polytype. The high anisotropy of the weak modes in these uniaxial crystals is discussed.

I. INTRODUCTION

IT has been shown that SiC has a strong residual ray absorption, with frequency and strength only weakly dependent on polytype.[1] In the uniaxial polytypes there is also a weak dependence on the polarization direction of the light.[2] For all polytypes, except cubic and 2*H*, group-theoretical selection rules permit additional one-phonon absorption lines, eight in 6*H* SiC, many more in some polytypes. In order to discuss and classify these additional allowed but unreported lines, we use the concept of a standard large zone for all SiC polytypes. With the aid of this concept we are able to identify three weak observed lines as fundamental lattice lines.

The additional lines are expected to be weak, but strongly dependent on the polarization direction of the light. They are weak because their dipole moments result from the very small Si or C site differences permitted by the polytype stacking arrangements, a distant neighbor effect.[3] Their polarization dependence may be 100 times that of the principal infrared line because these modes have anisotropic intracell motion along or perpendicular to the *c* axis, i.e., of the bond-stretching or bond-bending type. The additional infrared or Raman-active modes are therefore best described as "axial" or "planar"; an axial mode, for example, may be either longitudinal or transverse, or mixed, depending on the propagation direction.

Spitzer *et al.* found it necessary to use both a strong and a weak oscillator to fit reflectivity data for the 6*H* extraordinary ray.[2] The axial lattice mode responsible for the weak infrared activity can now be identified. Ellis and Moss have recently reported weak infrared absorption of unknown origin in 6*H* and 15*R* polytypes.[4] Their two lines can also be classified and identified as fundamental lattice modes. The identification requires the use of an approximate large-zone phonon spectrum, which can be drawn with the use of previous experimental data.

There is reason to believe that in the axial direction of the large zone a common phonon spectrum can be used (as a good approximation) for all SiC polytypes. The approximate energies of infrared and Raman lines in various polytypes can then be predicted. Further absorption and Raman measurements are needed to test the common spectrum concept.

Some aspects of large zones and of anisotropy in uniaxial crystals are discussed next in Sec. II. Their significance for SiC polytypes is first illustrated by considering the phonon spectrum for the simple 2*H* structure in Sec. III. The observed weak absorption lines in 6*H* and 15*R* polytypes are identified in Sec. IV, and their energies are found to be consistent with the common spectrum concept.

II. GENERAL CONSIDERATIONS

A. Phonons in Uniaxial Crystals

The energy of a long-wavelength optical mode has a complex dependence on polarization and propagation directions in a uniaxial crystal.[5] It is a function of the interplay between *a*, the long-range electric field, and *b*, crystal anisotropy, a function that simplifies for the two limiting cases considered by Loudon,[5] $a \gg b$, and $b \gg a$. In the former case the vibrations are longitudinal or transverse.[6] In the latter the modes may be called axial or planar, because the atomic motions are primarily along or perpendicular to the *c* axis.[6]

All SiC polytypes have a strong infrared-active mode in which the Si and C sublattices vibrate against each other, creating a strong electric field which makes the longitudinal frequency considerably higher than the transverse. This simple vibration has low anisotropy,[2] hence $a \gg b$. All other optical modes, in various polytypes,[7] generate only very weak fields, a result of the very small site inequivalencies. On the other hand, they have intracell motions that are highly anisotropic (Sec. II C), hence for these modes $b \gg a$. Thus, SiC optical modes belong to one of the two limiting cases considered by Loudon, no intermediate case being found.

[1] W. G. Spitzer, D. A. Kleinman, and C. J. Frosch, Phys. Rev. **113**, 133 (1959).
[2] W. G. Spitzer, D. A. Kleinman, and D. Walsh, Phys. Rev. **113**, 127 (1959).
[3] Lyle Patrick, Phys. Rev. **127**, 1878 (1962).
[4] B. Ellis and T. S. Moss, Proc. Roy. Soc. (London) **299**, 393 (1967). The absorption strength is about 100 cm^{-1} in 6*H*, 150 cm^{-1} in 15*R*.
[5] R. Loudon, Advan. Phys. **13**, 423 (1964).
[6] The terminology is exact for propagation in a symmetry direction, approximate in a general direction.
[7] The common uniaxial polytypes belong to one of two space groups, $P6_3mc$ (hexagonal), or $R3m$ (rhombohedral).

TABLE I. Some SiC polytypes with information pertinent to infrared absorption and the construction of a standard large zone. The special values of the reduced momentum $x=q/q_{\max}$ are those equivalent to $q=0$ in the Brillouin zone.

Ramsdell symbol	Atoms per unit cell	Infrared lines	Special values of x
3*C* (cubic)	2	2 (equal)	0
2*H*	4	2	0, 1
4*H*	8	6	0, 0.5, 1
6*H*	12	10	0, 0.33, 0.67, 1
15*R*	10	18	0, 0.4, 0.8
21*R*	14	26	0, 0.29, 0.57, 0.86

Modes classified as axial or planar have energies that depend very little on whether they are longitudinal or transverse. Hence, an infrared absorption line may be observed for the extraordinary ray at a frequency almost identical with that of a longitudinal phonon for the ordinary ray.[8] This has led to some misinterpretation of experimental results. The concepts involved are best illustrated by using a standard large zone for all polytypes.

B. Large Zones for SiC Polytypes

The small structural differences of SiC polytypes produce correspondingly small differences in most physical properties. In particular, the phonon spectra of all polytypes are expected to be similar in many respects. However, the polytypes have various numbers of atoms per unit cell, hence various numbers of phonon branches in the Brillouin zone (BZ). This difficulty is avoided by using, for all polytypes, a standard large zone (LZ) which extends in the axial direction to $N\pi/c$, where N is the number of close-packed layers in the polytype stacking sequence[9] (the number that appears in the Ramsdell symbol, e.g., 6 in 6*H*), and c is the length of the unit cell (also proportional to N). This LZ has three "acoustic" and three "optic" branches for any polytype, and the energy discontinuities[10] that exist within the LZ are so small that they may be neglected here. The differences between polytypes are now reflected in the number and positions of these discontinuities.

The momentum vectors of all infrared-active phonons lie on the LZ axis, and we assume that the phonon spectrum in this direction is the same for all polytypes. Points of this common spectrum accessible to absorption measurements have pseudomomentum vectors q that reduce to zero (almost) in the BZ scheme. These points are different for different polytypes, and their reduced momentum values $x=q/q_{\max}$ are shown in Table I for the simplest polytypes. In all polytypes the absorption is expected to be strong and nearly isotropic for the residual ray at $x=0$, but weak and anisotropic for the more complex modes that correspond to other values of x. The use of infrared or Raman data from enough polytypes should make it possible to test the assumption of a common spectrum by plotting it.

C. Anisotropy

Consider a SiC polytype in which an infrared-active mode at $q=0$ in the BZ has a propagation vector of $2n\pi/c$ in the axial direction of the LZ, corresponding to a wavelength of c/n, where n is an integer. From the BZ point of view this is a long-wavelength mode, but with additional intracell motion. A comparison of the wave from both BZ and LZ points of view shows that the intracell motion is either axial or planar, of the bond-stretching or bond-bending type, respectively.

The axial direction in uniaxial polytypes corresponds closely to a ⟨111⟩ direction in cubic crystals, and one can use the known phonon-dispersion curves in Ge,[11] Si,[12] and diamond[13] to estimate the SiC anisotropy. The ratio of longitudinal to transverse energies for the [111] acoustic branches in Ge and Si is about 3, in diamond about 2. A similar ratio of axial to planar energies might therefore be expected for the acoustic branches in the SiC LZ.[14] Some of these acoustic LZ modes are infrared-active optical modes in the BZ scheme. Thus, in SiC polytypes, one might expect some very large differences in absorption frequencies between the extraordinary ray (which excites a transverse axial mode) and the ordinary ray (which excites a transverse planar mode).

III. PHONON SPECTRUM IN THE LARGE ZONE

The application of the large zone concept to the classification of infrared and Raman lines is first illustrated for the simplest uniaxial polytype, namely 2*H*, with wurtzite structure. There are no additional infrared active modes for 2*H*, but the description is easily extended to other hexagonal polytypes (space group $P6_3mc$) and, with minor changes, also to the rhombohedral polytypes (space group $R3m$). Experimental information on phonon energies in SiC polytypes is then reviewed before going on to the identification of observed lines in Sec. IV.

A. Polytype 2*H*

A recent paper[15] on 2*H* SiC gives a description of the phonon spectrum along the LZ axis, with a derivation

[8] We use the terms ordinary ray and extraordinary ray for light with electric vector perpendicular and parallel to the c axis, respectively. Light absorption excites only transverse phonons, but longitudinal phonons may be observed in Raman scattering.

[9] The use of a LZ for 33*R* SiC is described in Sec. XV of W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. **139**, A1262 (1965).

[10] The corresponding x-ray reflections are not observed.

[11] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

[12] G. Dolling, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 2, p. 37.

[13] J. L. Warren, R. G. Wenzel, and J. L. Yarnell, in *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1965), Vol. 1, p. 361.

[14] The terminology is discussed in more detail in Sec. III A.

[15] Lyle Patrick, D. R. Hamilton, and W. J. Choyke, Phys. Rev. **143**, 526 (1966).

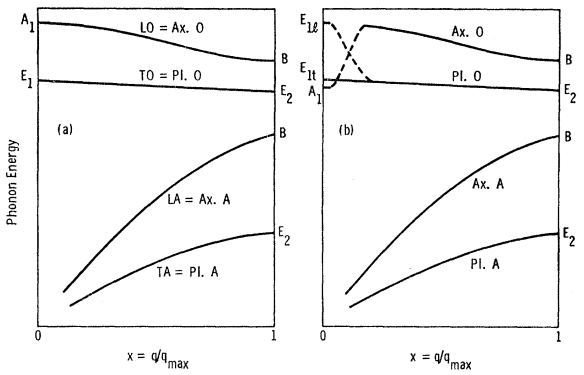

FIG. 1. Schematic phonon spectrum in the large zone. The values of x at which infrared or Raman phonons appear are shown in Table I. Polytype $2H$ is considered here, with phonon representations at $x=0$ and $x=1$. An absorbed photon determines the phonon propagation direction, to which the structure near $x=0$ is sensitive. Thus, separate drawings are shown for absorption of (a) the ordinary ray, and (b) the extraordinary ray. Abbreviations are L—longitudinal, T—transverse, A—acoustic, O—optic, Ax—axial, and Pl—planar.

of the representations. The labeling of the representations Γ_1, Γ_4, Γ_5, and Γ_6, is now changed to A_1, B, E_1, and E_2, to conform with the notation of Ref. 5 and with that of recent Raman work on ZnO[16] and CdS.[17] The sum modes A_1 and E_1 are infrared active, the difference modes B and E_2 are not.

In Fig. 1 we write $x=q/q_{\max}$, where $q_{\max}=2\pi/c$ for $2H$, and we observe that $x=0$ and $x=1$ both correspond to $q=0$ in the BZ scheme. When the propagation vector is along the axis of the LZ, axial phonons are longitudinal and planar phonons are transverse. No difficulties arise for phonons that interact with the ordinary ray, even when the small photon momentum is taken into account, because the photon momentum is also directed along the c axis. The appropriate schematic phonon spectrum is that of Fig. 1(a), and the common notation (TA, LA, TO, and LO) is satisfactory. At $x=0$ the planar E_1 is transverse and doubly degenerate. The axial A_1 is longitudinal and higher in energy than E_1 because of the long-range Coulomb field.

For the extraordinary ray, considered in Fig. 1(b), special attention must be given to the two points $x=0$ and $x=1$ for which $q=0$ in the BZ. At these points the photon momentum has an added significance because it determines the phonon propagation direction, which now is perpendicular to the axis, so that an axial vibration is transverse. Thus, in going from $x=0$ to $x=1$, the axial branch is first transverse, then longitudinal (approximately), and then once more transverse. The line traced by the propagation vector in the LZ is slightly off axis, i.e., it represents a small value of q perpendicular added to a variable q parallel to the axis. Although an axial phonon branch is approximately longitudinal nearly everywhere, it is transverse, for the extraordinary ray, at points accessible[18] to infrared measurements. It is important to label it "axial," because "longitudinal" would imply an absence of infrared absorption.

For the extraordinary ray [Fig. 1(b)] the consequences of the axial transverse motion at $x=0$ are quite different from those at $x=1$. At $x=0$ the modes have low anisotropy; A_1 is assumed to lie lowest,[19] as it does in $6H$. The planar E_1 is now split by the strong long-range field into the transverse E_{1t} and the longitudinal E_{1l}. At $x=1$, however, the opposite field and anisotropy conditions are valid. E_2 is not split, because the long-range field vanishes for this infrared-inactive mode, and B remains high, as in Fig. 1(a), because anisotropy keeps the axial mode high (on our assumption).

The broken lines in Fig. 1(b) show how the representations join up. The crossing of the phonon branches near $x=0$ is a result of the strong longitudinal long-range field and low anisotropy of the residual ray phonon, and occurs at no other value of x. This crossing occurs very much closer to $x=0$ than shown, the photon momentum being extremely small on the scale of our drawing.[20]

The LZ acoustic branches have a set of representations identical to those of the optic branches. The modes at $x=0$ are truly acoustic, and are therefore not labeled, but those at $x=1$ are optic modes in the BZ scheme. Thus, $2H$ SiC has two E_2 modes, both active in Raman scattering.

Some of the more complex SiC polytypes have many values of $x=q/q_{\max}$ that are equivalent to $q=0$ in the BZ, and they have additional modes with the infrared active representations A_1 and E_1. Before considering these we will review the experimental work on phonon energies in order to place some limits on the energies of the various branches.

B. Phonon Energies

The strong residual ray absorption determines phonon energies at $x=0$ in the LZ.[2] Other phonon energies, in various polytypes, are obtained in luminescence measurements[21] and in two-phonon infrared absorption.[22] The latter gives an indication of LZ zone boundary values, but not necessarily of phonons on the symmetry axis. The phonons found in luminescence are known *not* to represent points on the symmetry axis, for they are linked to the conduction-band minima, which lie off axis. Nevertheless, these phonons fall into

[16] T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. **142**, 570 (1966).
[17] B. Tell, T. C. Damen, and S. P. S. Porto, Phys. Rev. **144**, 771 (1966).
[18] Using the concept of a common phonon spectrum, different points of the spectrum are accessible for different polytypes.
[19] Reference 2 shows a separation of about 1 meV for $6H$ SiC, with A_1 below E_1.
[20] Still closer to $x=0$, the photon-phonon interaction results in other structure, as indicated by Loudon in Ref. 5, Fig. 2.
[21] W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. **133**, A1163 (1964), Table I, and SiC papers listed in Ref. 15.
[22] Lyle Patrick and W. J. Choyke, Phys. Rev. **123**, 813 (1961).

TABLE II. Approximate phonon energy ranges deduced from previous experimental work. The previous notation, in column 1, is misleading for infrared absorption, and is replaced, on the large zone axis, by the notation of column 2. Abbreviations are T—transverse, L—longitudinal, A—acoustic, and O—optic.

Previous notation	Present notation	Energy range (meV)
TA	Planar A	0– 50
LA	Axial A	0– 80
TO	Planar O	90–100
LO	Axial O	100–120

well-defined groups whose limits help to identify the one-phonon infrared absorption lines.

Unfortunately, the phonons previously reported were considered to be quasitransverse or quasilongitudinal, and the LZ branches were labeled TA, LA, TO, and LO. These labels lead to no difficulty for the ordinary ray absorption, but are misleading for the extraordinary ray. Along the axial direction of the LZ, the only direction we are now interested in, the phonon branches are adequately described by the substitution of "axial" for "longitudinal" and "planar" for "transverse." These notations are listed in Table II, and energy limits, as suggested by previous work, are shown in the last column.

IV. IDENTIFICATION OF WEAK ABSORPTION LINES

The simplest SiC polytypes with additional infrared absorption lines are $4H$, $6H$, and $15R$, which we now consider. There is experimental evidence of weak infrared absorption lines in the latter two, and it is now possible to classify three observed lines according to the LZ phonon branch and the value of $x=q/q_{\max}$.

A. Polytype 4H

There were two drawings in Fig. 1 to show the differences, at $x=0$, between absorption of the ordinary and extraordinary rays. For a consideration of the *weak* infrared absorption, in any polytype, the structure near $x=0$ may be omitted, and a single drawing suffices for both polarization directions, provided one remembers that the accessible axial modes are transverse for the extraordinary ray.

The LZ phonon spectrum for $4H$ SiC is shown in Fig. 2(a), with vertical lines indicating long-wavelength modes at $x=0$, 0.5, and 1. All hexagonal polytypes have the same symmetry as $2H$, and it can be shown by the method of Ref. 15 that a polytype NH (N is 2, 4, 6, etc.) has phonon representations $N(A_1+B+E_1+E_2)$, i.e., the multiplicity of a representation simply increases in proportion to the number in the Ramsdell symbol.[23]

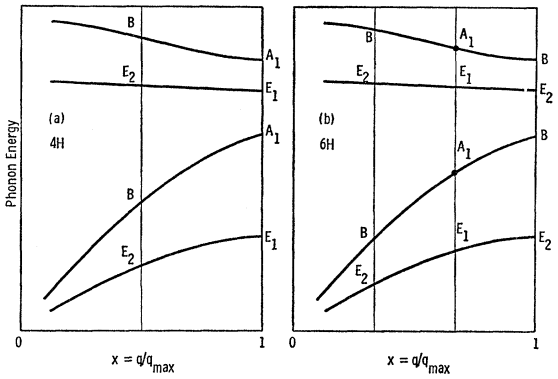

FIG. 2. Schematic phonon spectrum in the large zone, with vertical lines and phonon representations appropriate to (a) $4H$, and (b) $6H$. The phonon branches, in ascending order, are planar A, axial A, planar O, and axial O, as in Fig. 1(b). The ordinary and extraordinary ray differences near $x=0$ are omitted. In infrared absorption planar modes are excited by the ordinary ray, axial modes by the extraordinary ray. Experimentally observed infrared lines in $6H$ SiC are identified by the filled circles on the axial branches at $x=0.67$. The measured phonon energies are 62 and 110 MeV.

Along the LZ axial branches A_1 and B modes alternate at the special values of x shown in Table I, and E_1 and E_2 likewise alternate along the planar branches. Figure 2(a) shows that $4H$ SiC has additional infrared-active modes A_1 and E_1 at $x=1$, but these have not yet been observed. The axial A_1 would be observed in absorption of the extraordinary ray, the planar E_1 in absorption of the ordinary ray. The two E_1 modes at $x=1$ split into longitudinal and transverse for propagation perpendicular to the c axis, but this is not indicated in Fig. 2(a) because one can predict that the fields generated by these modes will produce only negligible splitting.

B. Polytype 6H

Figure 2(b) shows that long-wavelength modes occur at $x=0$, 0.33, 0.67, and 1 in $6H$ SiC, with the additional infrared-active modes at 0.67. In making a classical oscillator fit to reflection data for the $6H$ extraordinary ray, Spitzer *et al.*[2] found it necessary to use both a strong oscillator and a weak one, with energies of about 98 and 110 meV, respectively. The use of Fig. 2(b) and Table II indicates that the weak infrared activity is due to an A_1 mode on the axial optical branch at $x=0.67$. There are small energy discontinuities (not shown) at all the vertical lines *within* the LZ, hence one might observe a splitting into two A_1 lines at $x=0.67$, but these lines could only be resolved if the energy discontinuity were large enough.

Recently Ellis and Moss[4] found a weak infrared absorption at about 62 meV for the extraordinary ray. Again, Fig. 2(b) and Table II show that this should be assigned to an A_1 mode on the axial acoustic branch

[23] The number of values of x in Table I does not increase as fast as the Ramsdell number, but double sets of representations appear at all *internal* boundaries, i.e., at all x values except 0 and 1. There are small energy discontinuities (not shown) at such values of x, hence each representation occurs twice. The number of infrared-active modes is also shown in this table. For $4H$ polytype, for example, this number is obtained as follows; (24 total) − (12 forbidden − (3 acoustic) − (3 longitudinal) = (6 infrared).

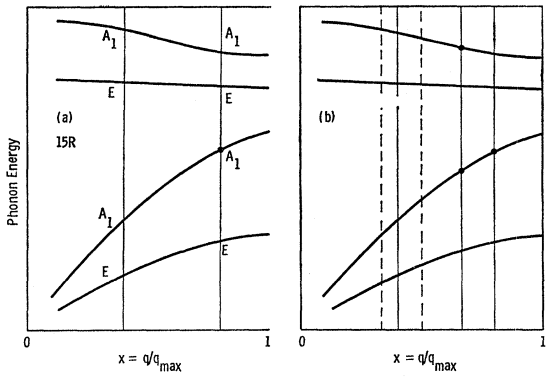

FIG. 3. Schematic phonon spectrum in the large zone. The vertical lines and representations appropriate to $15R$ are shown in (a), with a filled circle indicating the identified axial acoustic mode at $x=0.8$. Part (b) is a composite of $4H$, $6H$, and $15R$, in which vertical lines have been drawn at all the special values of x for the three polytypes, enough to plot the common spectrum in some detail when experimental data is available. Broken lines indicate Raman scattering only, solid lines both Raman and infrared. The three identified experimental points are indicated by filled circles.

at $x=0.67$. Again, two lines could in principle be observed, but have not been resolved. Both the 62 and 110 meV lines have also been observed in Raman scattering.[24] Our assignment of these two points is shown by the filled circles in Fig. 2(b).

For the ordinary ray the active modes are E_1, and the ordinary residual ray is due to the E_1 at $x=0$. The additional weak E_1 lie on the planar branches at 0.67. The optic E_1 might show up as fine structure in measurements of the ordinary residual ray, but there is no indication of it in the data of Spitzer *et al.*[2] The planar acoustic E_1 is expected to be much lower in energy than the axial acoustic A_1, and no doubt lies far beyond the range of the Ellis and Moss measurements.[4]

C. Polytype 15*R*

Figure 3(a) shows that long-wavelength modes occur in $15R$ SiC at $x=0$, 0.4, and 0.8 (not at $x=1$). The symmetry of $15R$ is only C_{3v}, and one can show that a rhombohedral polytype with Ramsdell symbol NR has phonon representations $(\frac{2}{3}N)(A_1+E)$, all infrared and Raman active except the one truly acoustic set of A_1+E. Thus, infrared- and Raman-active A_1 and E modes are found at all the vertical lines of Fig. 3(a).

Ellis and Moss[4] reported a weak absorption line at about 70 meV. Since it has a larger energy than the similar $6H$ line the obvious place for it is at $x=0.8$ on the axial acoustic branch. Its energy relative to that of the $6H$ line appears to be consistent with the common spectrum concept. The other acoustic A_1, at $x=0.4$, no doubt falls beyond the range of the Ellis and Moss measurements, as do the two E modes on the planar acoustic branch (observable in the ordinary ray absorption). There are also infrared-active modes on the optic branches which could show up as fine structure in the residual way reflectivity.

D. Plotting a Common Spectrum

Figure 3(b) is a composite of Figs. 2(a), 2(b), and 3(a), for $4H$, $6H$, and $15R$ polytypes. Values of x at which there are infrared-active modes are shown by solid vertical lines, and values of x at which only Raman activity occurs are shown by broken lines. The three weak identified lines are again shown by filled circles. Infrared and Raman data for these three polytypes should enable one to plot the common spectrum in some detail, if it exists, or to note any discrepancies. The absence of splitting in the three identified lines seems to indicate that the discontinuities within the LZ can indeed be neglected.

More complex polytypes have still more values of x accessible to infrared and Raman measurements, but some of the lines would no doubt be extremely weak, and too many lines could make identification more difficult. However, $21R$ and $33R$ polytypes may provide useful experimental data.

Again, we repeat that the schematic common phonon spectrum has been simplified by the omission of those things considered unimportant for the identification of the weak infrared or Raman lines. Omitted are (1) structure near $x=0$, important only for the strong residual ray; (2) small energy discontinuities within the LZ at the positions of the vertical lines; (3) splitting of weak hexagonal E_1 modes and rhombohedral E modes into longitudinal and transverse; and (4) differences due to polytype structural differences. The second and third items may show up as line-splittings in careful experimental work; (2) might be seen in infrared or Raman measurements, (3) in Raman scattering only.

[24] D. W. Feldman (private communication).