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RAMAN SCATTERING FROM TWO-PHONON EXCITATIONS AND FROM NITROGEN ELECTRONIC IMPURITY LEVELS IN CUBIC SILICON CARBIDE

presented by

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Bу

Philip Allen Gaubis

AN ABSTRACT OF A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

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RAMAN SCATTERING FROM TWO-PHONON EXCITATIONS AND FROM NITROGEN ELECTRONIC IMPURITY LEVELS IN CUBIC SILICON CARBIDE

By

Philip Allen Gaubis

The two-phonon Raman spectra and nitrogen donor electronic Raman spectra of the 3C polytype (zinc-blende) of SiC are presented. 3C SiC is a IV-IV semiconductor having an indirect gap of 2.4 eV with a conduction band minimum at X. The nitrogen impurity concentrations of both samples used in this study are found to be well below the Mott transition.

The Γ_1 component of the two-phonon spectra is the dominant component. A number of spectral features are identified and assigned to critical point overtones and combinations, including overtones due to critical points TA(Σ) at 476 cm⁻¹ and TO(Σ) at 737 cm⁻¹, which had not previously been measured. No difference combination scattering is observed, in accord with intensity estimates for difference combination bands in 3C SiC. All feature assignments are consistent with theoretical selection rules and previously measured phonon energies. The close

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agreement of branch energies at X with previous luminescence measurements supports the assignment of the conduction band minimum to X. Sample nitrogen concentration, surface damage due to sample preparation, and exciting line wavelength are found to have negligible effects on the second-order spectra. The spectral feature assignments in conjunction with a lattice dynamical calculation are used to perform a critical point analysis, producing a set of critical point sector numbers which satisfy the two- and three-dimensional Morse relations.

The low temperature spectra of both samples show the appearance of a line at 67.5 cm⁻¹ of E symmetry. The thermal behavior, symmetry, concentration dependence, and theoretical intensity estimates strongly favor the identification of this line as a $lS(A_1)+lS(E)$ transition in the valley-orbit split 1S nitrogen donor level. The thermal behavior of this line is investigated from 7°K to 180°Kand indicates that the $lS(A_1)$ level is the true ground state. No other transitions are found, in accord with theoretical intensity estimates for the inter-manifold transition intensities and with the assignment of the conduction band minimum to X.



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CHAPTER I

INTRODUCTION

Silicon carbide is an indirect gap IV-IV semiconductor which can grow in a variety of different polytypes. The 3C or cubic polytype used in this investigation has a zinc-blende structure with two atoms per primitive cell and space group T_d^2 (PT3m). This structure can be visualized as two interpenetrating face-centered cubic lattices, one of silicon and one of carbon, which are separated along one-quarter of a body diagonal. The zinc-blende structure is nothing more than the diamond structure with every other carbon replaced by a silicon. From this point of view, cubic SiC may be considered as a perturbed silicon lattice. SiC is of interest in that it may be considered to exist "between" the purely covalent IV-IV semiconductors (such as silicon and germanium) and the more ionic III-V zinc-blende semiconductors.

This study is concerned with the first observation and analysis of two-phonon Raman host crystal spectra and Raman scattering from nitrogen donor electronic levels in 3C SiC. Since the topics of two-phonon spectra and donor spectra are not closely related, this thesis is organized

into two nearly independent sections. The analysis of the two-phonon spectra presented in Chapter II yields detailed information concerning host crystal phonon dispersion curves, including a set of dispersion curve critical points. Nitrogen donor Raman spectra are reported in Chapter III and discussed in terms of effective mass theory (EMT) as it applies to weakly bound donor electrons. Relevant background is included in each chapter. Group theory is employed where possible, as it often gives clearer insight than brute force calculation. Many of the experimental and theoretical details of this study are deferred to the Appendices. The remainder of this section includes a very brief description of the Raman effect and its experimental utility.

The Raman process may be more descriptively referred to as inelastic light scattering, wherein the incident light exchanges energy with a sample concurrent with a transition between quantum levels in the sample. The energy of the scattered light will be shifted by an amount equal to the difference in energy of the quantum levels involved in the transition. The scattered light will be shifted toward the violet if it gains energy during the interaction, and toward the red if it loses energy. The violet shifted light is referred to as anti-Stokes scattering while the red shifted light is called Stokes scattering. (All spectra throughout

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this study are Stokes spectra, with energy scales representing the energy shift between the incident and scattered light.)

The scattered light intensity of a Raman process is quite weak (typically 10^{-8} to 10^{-12} of the incident intensity), and early experiments suffered from the lack of suitably intense, narrow band sources. Lasers are ideal sources for Raman spectroscopy, having highly monochromatic outputs of several watts, and are directly responsible for the widespread use of Raman techniques.

A great variety of phenomena in semiconductors have been studied using Raman scattering, including one-phonon processes (called first-order scattering), two-phonon processes (called second-order scattering), donor and acceptor impurity levels, magnons, plasmons, defect modes, single-particle excitations, impurity-induced scattering, resonant processes, LO-plasmon coupling, and others. This list is by no means complete, and is intended only to show the broad applicability of Raman techniques to semiconductor studies.

Infrared absorption spectra and Raman spectra can be complementary in the sense that selection rules are often different. For example, in materials with inversion symmetry, where parity is a good quantum number, only oddparity transitions are infrared-active. Conversely, in

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such systems only even-parity transitions are Raman-active, so Raman and absorption spectra are strictly complementary. In addition, Raman techniques can easily detect transitions of energy as low as ~1 meV, which lie in an experimentally difficult region for absorption techniques.

CHAPTER II

TWO-PHONON RAMAN SPECTRA OF 3C SiC

A. Background

This chapter presents the two-phonon (second-order) Raman spectra of 3C SiC, an identification of spectral features, and a critical point analysis of lattice dispersion curves. Several theoretical topics require development before the observed spectra can be interpreted. In this section, a preliminary overview of Raman scattering from lattice vibrations is presented, followed by a description of previous measurements of phonon energies in 3C SiC.

In one-phonon or first-order Stokes Raman scattering, an incident photon of wavevector \vec{k}_1 creates a phonon of wavevector \vec{k}_p and is scattered with wavevector \vec{k}_s . Wavevector conservation requires that $\vec{k}_1 - \vec{k}_s = \vec{k}_p$. In a typical semiconductor, the wavevector of visible light is of order 10^5 cm⁻¹ (depending on the dielectric constant of the crystal) while the width of the Brillouin zone is of order 10^8 cm⁻¹. Thus the only phonons which can participate in first-order Raman scattering have a wavevector very near the center of the Brillouin zone and are therefore referred to as "zone-center" or " $\vec{k}=0$ " phonons.

This scattering process can be roughly visualized in a semiclassical fashion. Given a crystal having polarizability tensor \tilde{P} and incident field \tilde{E} , an oscillating dipole moment $\vec{M} = \tilde{P} \cdot \vec{E}$ is established in the crystal. This moment reradiates the incident beam, producing elastic Rayleigh scattering. However, as the nuclei move, the electrons follow adiabatically, and the polarizability changes. It is the change of electronic polarizability with nuclear motion that gives rise to Raman scattering. Thus, the moment \tilde{M} contains "sidebands" formed from the product of the incident field and the phonon-modulated polarizability tensor.

This qualitative description can be put in more formal terms. Raman cross sections for first-order scattering can be expressed using straightforward perturbation theory. The process involves three steps: a photonelectron interaction, an electron-lattice interaction, and a scattered photon-electron interaction. The resulting expressions¹ involve double sums over (usualy unknown) electronic states in the crystal. In order to obtain useful expressions for the cross section, one resorts to the "polarizability approximation"² by making the following assumptions:

 Vibronic states are written as simple products of electron and phonon states, with the nuclear

coordinates appearing as parameters in the electron states (adiabatic approximation).

b. The incident and scattered light are of much higher energy than the phonon states. In other words, the crystal polarization is largely electronic in character. For visible light, this is typically a quite good approximation.

With these assumptions, the intensity of Stokes first-order scattering from a specific phonon becomes

$$I_{\text{Stokes}} \propto |\vec{e}_{i} \cdot \langle o|\tilde{P}|v_{f} \rangle \cdot \vec{e}_{s}|^{2}(n_{f}+1)$$
(1)

where \tilde{P} is the polarizability tensor, $|o\rangle$ and $|v_{f}\rangle$ are the ground and excited vibrational states, respectively, and \vec{e}_{1} and \vec{e}_{s} are the polarization vectors of the incident and scattered light. The term n_{f} +1, where n_{f} is the Bose population factor, results from the thermal average over initial states. A knowledge of the dependence of (1) on \vec{e}_{1} and \vec{e}_{s} for a given $|v_{f}\rangle$, known as "selection rules," may be obtained from group theoretical arguments. Selection rules will be discussed in depth in a following section.

The traditional means of obtaining detailed information on lattice dynamics is through neutron scattering. This technique, while quite powerful, requires large single-crystal samples (on the order of several cm).

To date, it has not been possible to grow single crystals of 3C SiC this large, thus precluding neutron studies. Raman scattering provides the most complete information available concerning the lattice dynamics of crystals that are inherently too small for neutron studies.

Phonon energies of 3C SiC at several high-symmetry points in the Brillouin zone have been measured previously with a variety of techniques, including polytype analysis, luminescence measurements, and first-order Raman scattering. These techniques are now described.

SiC can exist in a number of different polytypes which are all very similar in structure, differing mainly in the stacking sequence of hexagonal planes along the (111) or C axis (group label A. Subsequent group labels, to be defined later, follow Reference 7). As the number of planes in the stacking sequence varies, so also does the size of the unit cell along the C axis. As the unit cell size increases, the Brillouin zone size decreases. For example, if the unit cell is doubled in size, the Brillouin zone is folded in half. Modes that were at the zone edge before the folding now become zone-center modes and therefore Raman active. It is then possible to obtain (approximately) phonon energies along A in 3C SiC by examining the Raman spectra of other polytypes. It is not obvious a-priori that such a technique should work at all. Its success depends on

the extent to which one may consider variations in stacking sequences as small perturbations on the structure of the 3C polytype. This technique has been successfully applied to SiC,³ and provides not only a fairly complete determination of the 3C dispersion curves along Λ , but the phonon energies at the point L as well.

Luminescence studies⁴ of 3C SiC have revealed an indirect gap of 2.4 eV as measured from the conduction band minimum at X. The location of the conduction band minimum is fortunate in that the indirect phonon-assisted transitions observed in the luminescence spectra permit a determination of the phonon energies at X point.

The zone-center optic phonons (at F) are strongly Raman active and have been determined from first-order Raman spectra.³ Two-phonon absorption bands, also observed in 3C SiC,⁵ were quite weak, allowing only very tentative identification of a few spectral features.

The previous experimental measurements of phonon energies at Γ , X, and L are listed in Table 1. These previous measurements at Γ , X, L, and along Λ have been the only input to lattice dynamical calculations of 3C SiC. A satisfactory assessment of model calculations cannot be made without more extensive experimental input.

Branch	Г (Ref. 3)	X (Ref. 4)	L (Ref. 3)
ТА		373	266
LA		640	610
то	796	761	766
LO	975	829	838

Table 1. Experimental lattice energies (cm^{-1})

B. Phonon Symmetries

The space group of 3C SiC is $T_d^2(F\overline{4}3m)$. This group is symmorphic, having an associated point group T_d . There are two atoms per primitive cell, giving rise to six normal modes, three optic and three acoustic. The wavevector of visible light is typically several orders of magnitude smaller than the size of the Brillouin zone. Due to wavevector conservation, the phonons which can participate in first-order scattering are very nearly at the zone center. To the extent that these wavevectors can be considered as zero (typically a very good approximation), the zone-center modes must transform as representations of the full point group T_d .

For later purposes, the symmetry properties of modes at several high-symmetry points in the Brillouin zone will be needed. For any given \vec{k} in the zone, there will be a set

of symmetry operations from the space group T_d^2 which leave that \vec{k} vector unaltered. This set of operations will form a subgroup of the original space group and is referred to as the group of the wavevector.⁶ Each such group will have associated representations and a character table which will characterize the symmetry of modes with that wavevector. Parmenter⁷ has conducted such an analysis for zinc-blende. Figure 1 contains a sketch of the Brillouin zone adopted by Parmenter, Γ character table, and wavevector groups of specific points. Subsequent notation in this chapter follows Figure 1.

If the atomic displacement representation of the zone-center modes are reduced into representation of Γ , the result is $2\Gamma_{15}$. That is, the zone-center acoustic and optic modes are triply-degenerate, and belong to representation Γ_{15} . In ionic crystals, however, there is a long-range electrostatic field associated with the longitudinal optic modes (see Reference 1). This field lifts the degeneracy of the optic branches, leaving a singly-degenerate longitudinal optic (LO) mode higher in energy than the doubly-degenerate transverse optic (TO) mode. It is for this reason that two lines appear in the first-order Raman spectrum of 3C SiC rather than one (as in silicon).



r(T _d)	E	C2	с ₃	JC4	JC2	
^г 1	1	1	1	1	1	$x^{2}+y^{2}+z^{2}$
г2	1	1	1	-1	-1	
r ₁₂	2	2	-1	0	0	$\sqrt{3}(x^2-y^2), 3z^2-r^2$
^г 15	3	-1	0	-1	1	xy,yz,zx;z,x,y
г ₂₅	3	-1	0	1	-1	
						1

POINT	WAVEVECTOR GROUP
Δ	C ₂₁₇ (2mm)
Λ,L	C _{3v} (3m)
Σ	C ₅ (m)
К	C (m)
Х	D_{2d} ($\overline{4}2m$)
W	s4(4)

Figure 1. Brillouin zone of 3C SiC and wavevector groups.

C. First-Order Polarization Selection Rules

Experimentally, the apparatus used to perform Raman spectroscopy can easily be arranged to analyze the polarization selection rules of a spectral feature (see Appendix A). In this section, the origin of selection rules for first-order (zone-center) scattering are discussed as well as the extra considerations required for zinc-blende crystals with LO-TO splitting.

Within the context of the polarizability approximation, the Stokes intensity is given by (1). As with any tensor, the individual elements of \tilde{P} must transform as products of coordinates (XX. YY. etc.). This implies that one can find linear combinations of the elements of \tilde{P} which transform like representations of F. These combinations are obtained directly from an examination of the basis functions included with common character tables. The (zone-center) normal modes of the crystal will also belong to certain representations of the point group of the crystal. Using a general group theoretical result,⁶ the matrix element in (1), $\langle o | \tilde{P} | v_{f} \rangle$, will vanish unless \tilde{P} and $|v_{f}\rangle$ have parts belonging to the same representation of the point group (the ground state is taken as totally symmetric). In other words, the only normal modes which can participate in first-order scattering are

ones belonging to a representation contained in the decomposition of the polarizability tensor.

The polarizability tensor, which is modulated by the normal modes, may be expanded in terms of normal mode coordinates Q,

$$\tilde{P} = \tilde{P}_{o} + \sum_{\Gamma,j} \frac{\partial \tilde{P}}{\partial Q(\Gamma_{j})} \Big|_{o}^{Q(\Gamma_{j})} + \dots$$
(2)

where j denotes the partners of a given representation Γ . The first term gives rise to Rayleigh (elastic) scattering, the second term to first-order Raman scattering. In order that (2) be an equality, the second term must have the same transformation properties under all group operations as \tilde{P} . Therefore, the sum over Γ includes only those representations which are contained in the reduction of the polarizability tensor consistent with the general selection rules above. (The zero order polarizability tensor $\tilde{P}_{_{O}}$ must be invariant under all point group operations of the crystal.) One demands that the interaction energy, $\vec{E}_i \cdot \tilde{P} \cdot \vec{E}_s$ (\vec{E}_i and \vec{E}_s are incident and scattered electric fields), be invariant under all group operations of the crystal. Since normal coordinates belonging to different representations do not mix under group operations, the invariance of $\vec{E}_i \cdot \tilde{P} \cdot \vec{E}_s$ requires that for each Γ_i ,

$$\vec{E}_{i} \cdot \frac{\partial \vec{P}}{\partial Q(\Gamma_{j})} | \cdot \vec{E}_{s}$$

transforms identically to $\mathbb{Q}(\Gamma_j)$ (so that their product will contain the totally symmetric representation). The tensors

are commonly referred to as Raman tensors, and may be determined by inspection of the character table basis functions. (A listing of Raman tensors for all crystal classes appears in Reference 1.)

These concepts are now illustrated for zinc-blende. The decomposition of the polarizability tensor for zincblende and associated Raman tensors, obtained with the aid of the T_d point group character table of Figure 1, are shown in Table 2. The Raman tensors within a given representation are determined up to an overall multiplicative constant. Since the decomposition of \tilde{P} includes only representations Γ_1 , Γ_{12} , and Γ_{15} , only modes belonging to these representations can be Raman active. The phonon polarization direction associated with each Γ_{15} Raman tensor is indicated in Table 2. This phonon polarization vector indicates the relative displacement of the two sub-lattices of the crystal at zero wavevector in zinc-blende.

The utility of these Raman matrices is that they allow a determination of the symmetry of observed spectral features. Denoting the Raman tensors as $\tilde{R}(\Gamma_4)$, the

Representation	Basis function	Polarizability components
rl	x ² +y ² +z ²	P _{xx} +P _{yy} +P _{zz}
r ₁₂	$\sqrt{3}(x^2-y^2)$, $2z^2-x^2-y^2$	√3(P _{xx} -P _{yy}), ^{2P} zz ^{-P} xx ^{-P} yy
r ₁₅	xy,yz,zx	P _{xy} , P _{yz} , P _{zx}
RAMAN TENSORS:		
$r_{1}; a \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix}$	0 0 1_	
$\Gamma_{12}; b \begin{bmatrix} \sqrt{3} & 0 \\ 0 & -\sqrt{3} \\ 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}; b \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}$	
$r_{15}; c \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 1 \\ 0 \\ \mathbf{x} \end{bmatrix}; \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix};$	$ c \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}_{\mathbf{Z}} $

Table 2. Decomposition of the polarizability tensor and Raman tensors for point group ${\rm T}_{\hat{d}}$

Note: x, y, z denote phonon polarization directions.



intensity of a mode belonging to a particular representation Γ is given by

$$I(\Gamma) \propto \sum_{j} |\vec{e}_{1} \cdot \tilde{R}(\Gamma_{j}) \cdot \vec{e}_{s}|^{2}, \qquad (3)$$

where \vec{e}_1 and \vec{e}_s are unit polarization vectors of the incident and scattered light. A standard notation has been adopted which completely describes the experimental geometry of a given spectrum. This notation is

$$\vec{k}_{i}(\vec{e}_{i},\vec{e}_{s})\vec{k}_{s},$$

where \vec{k}_1 and \vec{k}_s are wavevectors of incident and scattered light, respectively. For example, the notation $\overline{X}(YZ)X$ indicates incident light propagating in the direction -xwith $\vec{e}_1 || y$, and scattered light propagating in the direction x with $\vec{e}_s || z$. (This geometry is called "back scattering" for obvious reasons.) This notation is employed throughout. A glance at Table 2 shows that only modes of Γ_{15} symmetry will be observable in this geometry. Thus, experimental geometries can be selected such that only modes having a desired symmetry will appear.
D. LO and TO Phonon Selection Rules

As mentioned previously, the triply-degenerate Γ_{15} zone-center optic modes of the zinc-blende lattice are split by a long-range electrostatic field associated with the LO mode. The resulting singly-degenerate LO mode is higher in energy than the doubly-degenerate TO mode, yielding two spectral lines in the Raman spectrum. The selection rules of each individual line, first obtained by Poulet, 8 require an extension of the group theoretical treatment given above. The assumption is made that the photon wavevectors \vec{k}_i and \vec{k}_s are small but finite, so that the phonon wavevector \vec{k}_{phonon} equals $\vec{k}_{1}-\vec{k}_{e}$ is determined by the directions of the external fields. Consider first the case where the phonon wavevector is parallel to, say, x. Poulet asserts that the Γ_{15} Raman tensor associated with phonons polarized along x describes the LO phonon scattering, while those associated with y and z describe the TO phonon scattering. (Recall that the LO mode has phonon polarization parallel to its wavevector, while the TO mode has phonon polarization perpendicular to its wavevector.) For general phonon wavevectors, one rotates all three $\Gamma_{1,5}$ Raman tensors such that the phonon polarization coordinate associated with any one of them (under the same rotation) is parallel to the phonon wavevector. This "parallel" tensor then describes LO scattering, while the remaining two describe TO scattering. This LO-TO

scattering cannot be treated with conventional group theory since the phonon \vec{k} vector direction, and hence the LO-TO selection rule, is determined by external fields and not by crystal symmetry. This procedure, put forth as a hypothesis by Poulet, accounts very well for observed LO-TO selection rules in zinc-blende crystals.

E. Raman Intensity Matrices

Relation (3) is valid for arbitrary orientations of \vec{e}_1 and \vec{e}_s . It is not convenient to work directly with Raman tensors since (3) must be evaluated for every experimental geometry employed to obtain the expected intensity. If one is willing to restrict the possible polarization vectors to directions along principal axes x, y, or z, only nine possible cases need be considered. These possibilities can be conveniently tabulated by defining intensity matrices (following Poulet) for each set of Raman tensors. The intensity matrix is defined by

$$\Gamma_{\alpha\beta}(\Gamma) \propto \sum_{i} |\vec{e}_{\alpha} \cdot \tilde{R}(\Gamma_{j}) \cdot \vec{e}_{\beta}|^{2}, \alpha, \beta = x, y, z, \qquad (4)$$

where Γ is Γ_1 , Γ_{12} , or Γ_{15} in zinc-blende. LO and TO intensity matrices are similarly defined. However, from the discussion above it is clear that one must specify also the photon wavevectors \vec{k}_1 and \vec{k}_s in order that Poulet's procedure may be carried out.

Selection rules to this point have been discussed under the assumption that the crystal axes and laboratory axes coincide (i.e., Raman tensors and polarization vectors all refer to a common set of axes). Experimentally, it is sometimes more convenient to employ other crystal orientations. For arbitrary crystal orientations, (3) and (4) still apply provided all Raman tensors involved are rotated to coincide with the laboratory system. All intensity matrices and corresponding coordinates employed in this study are listed in Table 3. The backscattering geometry is employed throughout. The unprimed and primed axes both represent laboratory coordinates, indicating different crystal orientations.

$X = (100) = X^{\prime}$ $Y = (010) Y^{\prime} = (01)$	$I(LO) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$	I(TO)= $\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$
$Z = (001) Z' = (0\overline{1})$	$I'(TO) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$I^{(TO)} = \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$
$I(r_{1}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$I(r_{12}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$I(r_{15}) = \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}$
$I^{(r_1)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$I'(r_{12}) = \frac{1}{4} \begin{bmatrix} 4 & 0 & 0 \\ 0 & 1 & 3 \\ 0 & 3 & 1 \end{bmatrix}$	$I^{(r_{15})=\begin{bmatrix} 0 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix}}$

Table 3. Zinc-blende intensity matrices

Appendix B contains a more extensive computer-generated list of zinc-blende intensity matrices for a variety of common experimental geometries, including right-angle scattering.

The discussion of selection rules here is in the context of scattering from crystal phonons. Many of the concepts involved are actually more general, and may be applied to atomic, molecular, and crystal electronic scattering. Briefly, this generality has origin in the fact that Raman processes can often be described by second-order perturbation theory. The cross-section for Raman scattering involves matrix elements of the form $\langle i|\vec{e}, \cdot \vec{r}|m \rangle \langle m|\vec{r} \cdot \vec{e}_{\sigma}|f \rangle$, where i and f denote initial and final quantum states. and m represents a complete set of quantum states.⁶ Because the operator $\vec{r} \mid m > < m \mid \vec{r}$ transforms in the same way as the polarizability tensor (like products of coordinates), these two operators are similar from a group theoretical point of view. Selection rules for Raman scattering from electronic impurity levels are discussed in more detail in Chapter III.

F. Critical Points

The topic of lattice critical points is intimately related to the interpretation of two-phonon optical spectra. This relationship will be established in a following section. In this section the properties of critical points and their connection with the energy density of states are discussed.

For a crystal containing N primitive cells, there are exactly N unique k-vectors in the Brillouin zone. These k-vectors are, by definition, uniformly distributed throughout the Brillouin zone. Assuming that the lattice dispersion relations are known, the energy density of states is given by

$$D(\mathbf{v}) \propto \int_{S} \frac{dS}{|\nabla \omega(\vec{k})|},$$
 (5)

where S is the surface in k-space such that $\omega=v$. There are certain points, known as "critical points," in the dispersion curves where $|\vec{\nabla}_{\omega}(\vec{k})|$ will either vanish or change sign discontinuously. Van Hove⁹ first investigated "analytic" critical points and showed that they produce discontinuities in slope in the density of states, with accompanying characteristic shapes. Phillips¹⁰ later extended this work to include non-analytic or "fluted" critical points, and explicitly treated lattice dispersion curve critical points.

Consider a general point $\omega_0(k_0)$ on a non-degenerate branch of the dispersion curves. In the immediate vicinity of this point, the energy may be written to second order as

$$\omega(\vec{k}) = \omega_{0} + \vec{\nabla}\omega \Big|_{\vec{k}_{0}} \cdot \vec{\xi} + \frac{1}{2} \vec{\xi}\vec{\xi} \cdot \vec{\nabla}\vec{\nabla}\omega \Big|_{\vec{k}_{0}} + \dots \qquad (6)$$

where $\vec{\xi} = \vec{k} - \vec{k}_0$. A critical point is simply that \vec{k} where the second term of (6) vanishes. The third term, representing a

second-degree polynomial of the components of \vec{k} , determines the nature of the critical point. For critical points where degeneracy exists, an expansion such as (6) cannot be performed, since the energies are solutions of a secular equation. Thus a distinction is made between analytic critical points, associated with non-degenerate branches, and non-analytic or "fluted" critical points associated with degenerate branches.

Certain points in the Brillouin zone are required by symmetry to be critical points. The set of solutions |j>, j=1, ..., n at an n-fold degenerate point k will transform according to some Fa. a representation in the "group of the wavevector" at \vec{k}_{a} .¹¹ These groups for zincblende are listed in Figure 1. The operator $\vec{\nabla}_{\!_{\mathbf{b}}}\omega$ transforms like a vector, and will generate a representation $\boldsymbol{\Gamma}_{\boldsymbol{\beta}}$ of the group of \vec{k}_{c} which, when reduced, will contain representations labeled by components of vectors. Phillips has shown that \vec{k}_{μ} is a critical point if $\langle i | \vec{\nabla}_{\mu} \omega | j \rangle = 0$, for i, j=l, ..., n. Equivalently, \vec{k}_{o} will be a critical point if the reduction of $\Gamma_{\alpha} \times \Gamma_{\beta} \times \Gamma_{\alpha}$ does not contain the totally symmetric representation. For general points in the zone, the group of the wavevector will consist of only the identity element. The product $\Gamma_{\alpha} \propto \Gamma_{\beta} \propto \Gamma_{\alpha}$ must then contain the totally symmetric representation, so general points are not symmetry-required critical points. General critical points are called "accidental."

This procedure allows a systematic test of all high-symmetry points in the Brillouin zone to determine if they are required by symmetry to be critical points. Parmenter⁷ has conducted such an analysis for zinc-blende and has found points T, X, L, and W to be symmetry required critical points. There may be other accidental critical points not required by symmetry, as determined by the detailed lattice dynamics.

The shapes generated in the density of states by various critical points depend on the behavior of the dispersion relations in the immediate neighborhood of the critical point. Phillips¹⁰ has presented a classification scheme which allows a check of the topological consistency of any supposed set of critical points. This scheme is based on "sector numbers," obtained by constructing a small sphere in k-space about the critical point $\vec{k}_{o}(\omega_{o})$ in question. The surface of the sphere is divided into sectors where $\omega > \omega_{o}$ (positive sector) or $\omega < \omega_{o}$ (negative sector). The number of separate, unconnected sectors of each type is counted. The totals are then denoted by (P,N). For example, a sphere surrounding a simple maximum point will have $\omega < \omega_{o}$ everywhere on its surface. The corresponding sector number is (0,1). Similarly, a minimum will have sector number (1,0). The only other sector numbers possible for analytic critical points are (2,1) and (1,2)

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denoting two types of saddle points. For degenerate critical points, it is also possible to have sector numbers (4,1) and (1,4) denoting "fluted" critical points. No other sector numbers are possible in three dimensions for singlyor doubly-degenerate critical points (as is the case in this study). The topological properties of a critical point and its characteristic contribution to the density of states are completely determined by the sector numbers of the point. The shapes associated with each type of point are indicated in Figure 2. Because (5) contains contributions from the entire zone, the shapes of Figure 2 will generally appear additively along with other structure in the density of states. For example, two critical points of different type at the same energy can together produce a shape in the density of states formed from a sum of two different shapes in Figure 2. Such a situation can present difficulties in the interpretation of experimentally obtained densities of states, as discussed in a later section.

Critical point sector numbers may also be defined in two dimensions. Consider a plane in the Brillouin zone which contains a critical point. A small circle, contained in the plane, is drawn around the critical point. The circumference of the circle is divided into positive and negative segments, analogous to the three-dimensional case.





The resulting two-dimensional sector numbers will obviously depend on the orientation of the plane with respect to the three-dimensional critical point. These two-dimensional critical points have no relation with the density of states. Their utility is in determining the topological consistency of critical point assignments.

In attempting to determine the type, number, and location of critical points in the Brillouin zone, a tentative assignment is made consistent with experimental data and the requirements of symmetry. This tentative set may then be tested for topological consistency using a procedure due to Phillips. To appreciate how topological constraints arise, consider a periodic function in one dimension or a closed curve in a plane. In both cases, the number of maxima equals the number of minima. Analogous constraints on the numbers and types of critical points occurring in a closed or periodic three-dimensional manifold (such as $\omega=\omega(\vec{k})$) were first obtained by Morse (see Reference 10). Phillips associates an index j and weight q with each sector number as listed in Table 4. In three dimensions, the Morse relations are

$$N_{o} \geq 1$$

$$N_{1}-N_{o} \geq 2$$

$$N_{2}-N_{1}+N_{o} \geq 1$$

$$N_{3}-N_{2}+N_{1}-N_{o} = 0$$
(7)



Critical point	Index j	Weight q
Three-Dimensional:		
(1,0) (1,2) (2,1) (0,1) (4,1) (1,4)	0 1 2 3 2 1	1 1 1 3 3
Two-Dimensional:		
(1,0) (2,2) (0,1) (4,4)	0 1 2 1	1 1 3

Table 4. Critical point topological index and weight

where $N_{\rm j}$ is the sum of the number of times a point of index j appears times its weight q. These relations apply to each branch separately. The two-dimensional Morse relations are

$$n_{0} \geq 1$$

$$n_{1}-n_{0} \geq 1$$

$$n_{2}-n_{1}+n_{0} = 0$$
(8)

where n_j is the sum of the number of times a two-dimensional critical point of index j occurs in some specified plane times its weight q. These relations also apply to each branch of the dispersion curves. The set of symmetryrequired critical points does not necessarily satisfy either (7) or (8). However, Phillips was able to determine that all critical points not in this symmetry set must have q=1. In applying the two-dimensional Morse relations, one must consider enough zones so that the chosen plane is periodic. In zinc-blende, one must include the point R(110) and its equivalences in the analysis of the $k_z=0$ plane.

A set of critical points which is consistent with all Morse relations, symmetry requirements, and experimental data may not be the true set. It is possible to add "kinks" to the dispersion curves, without disturbing any previous critical point sector numbers. These kinks, due to longrange forces, may or may not produce observable effects depending on the nature and finesse of the experiment. The Morse relations also do not give any information concerning the location of critical points in the interior of the zone (aside from whether the interior critical point is contained in a symmetry line or plane). The exact wavevector of an interior point must come from experiment or calculation.

G. Two-Phonon Scattering

To this point, the discussion has been limited to scattering events involving one phonon. It is also possible for several phonons to participate in infrared or Raman processes. Two-phonon scattering is referred to as "secondorder" scattering. Third or higher order scattering has an

intensity much weaker than second-order, and is seldom observed. Events where one phonon is destroyed and a second created are also expected to be weak in SiC due to temperature dependence of this process (discussed later). For these reasons, only Stokes processes involving the creation of two phonons will be discussed. Two-phonon Raman studies have been performed on many semiconductors, including GaP,¹² Si,^{13,14,15} ZnS,¹⁶ Ge,^{15,17} and diamond.¹⁵

Two-phonon states may be constructed from pairs of one-phonon states. If both members of the pair are from the same branch, the two-phonon state is called an "overtone"; if from different branches, a "combination" state results. As in the first-order case, the net wavevector of the twophonon state must be nearly zero in order that wavevector conservation be satisfied. This fact simplifies the task of constructing two-phonon states, since only zone-center, zero wavevector combinations and overtones need be considered. The pair of phonons must have equal magnitude, but opposite wavevectors. The lattice dynamical equations are secondorder in the time derivative. Time-reversal symmetry guarantees that for any point $\omega(\vec{k})$ on the dispersion curves, a second point will exist at $\omega(-\vec{k})$. Thus any dispersion curve point in the zone may be used to construct a twophonon zone-center overtone mode having twice the energy of the original point. More generally, any pair of points

in the zone from different branches may be combined, provided they have the same wavevector, to form a combination state having an energy equal to the sum of the energies of each point. Given a set of dispersion curves, one can add together the energies of all possible pairs of curves to form combinations, and double the energy of each curve to form overtones. In zinc-blende, which has 6 branches, this process results in 6 overtone branches and 15 combination branches. The two-phonon k=0 density of states associated with these constructed dispersion curves will contain, in the case of overtones, all the critical point shapes of the one-phonon density of states but at double the frequency. In addition, other critical points will appear in the two-phonon density of states due to critical points in the combination branches.

The symmetries and selection rules of two-phonon states in zinc-blende have been investigated by Birman.¹⁸ Each member of a two-phonon pair of wavevector \vec{k} will belong to a representation of the group of the wavevector at \vec{k} , say Γ_{α} and Γ_{β} . The two-phonon state, having zero wavevector, must belong to zone-center representations. For combinations, the direct product $\Gamma_{\alpha} \times \Gamma_{\beta}$ is formed and reduced into zone-center representations. For overtone states, which will have $\alpha=\beta$ the symmetrized Kronecker square is formed and reduced into zone-center representations. Since general

points in the zone have wavevector groups consisting of only the identity element, overtone and combination states made from general points will contain in their reduction all zone-center representations. In addition, the symmetrized Kronecker square always contains the unit representation, so that all overtone states will have parts belonging to the totally symmetric zone-center representation.

Once the zone-center representations of the twophonon states are known, the selection rules follow the same procedure as in the one-phonon case. If the matrix element $\langle 0|\tilde{P}|V_{f}\rangle$ vanishes, (where v_{f} is now a two-phonon state) then the transition is not Raman active. In other words, the matrix element vanishes unless \tilde{P} and $|v_r\rangle$ have parts belonging to the same zone-center representation. In zinc-blende, the polarizability tensor has zone-center representation Γ_1 , Γ_{12} , and Γ_{15} . Only these representations are of relevance in the reduction of zinc-blende two-phonon states. The representations which occur (among these three) in the reduction of two-phonon states from several highsymmetry Brillouin zone points in zinc-blende have been determined by Nilsen¹⁶ and are listed in Table 5. Only actual dispersion curve representations are included.

Since all two-phonon combination states from general points in the zone and all overtone states contain Γ_1 , they will be symmetry-allowed in the Raman process. The two-phonon spectrum is therefore a continuous function of

Representation	Reduction	Representation	Reduction
[x ₅] ₂	^r 1 ^{+2r} 12 ^{+r} 15	[L ₃] ₂	^r 1 ^{+r} 12
[x ₁] ₂	^r 1 ^{+r} 12	[L ₁] ₂	Γ ₁ +Γ ₁₅
[x ₃] ₂	^r 1 ^{+r} 12	L ₃ xL ₁	^r 12 ^{+r} 15
X ₅ xX ₁	^r 15	L ₃ xL ₃	r ₁ +r ₁₂ +2r ₁₅
x ₅ xx ₃	^r 15	L ₁ xL ₁	^r 1 ^{+r} 15
x ₅ xx ₅	r ₁ +2r ₁₂ +r ₁₅	$[w_i]_2$	^r 1 ^{+r} 12
x ₃ xx ¹	^r 15	W _i xW _i	r ₁ +r ₁₂
[r ₁₅] ₂	^r 1 ^{+r} 12 ^{+r} 15	W _i xW _j	r ₁₂ ,i≠j

Table 5. Zone-center two-phonon representations for 3C SiC

frequency rather than a line spectrum. The two-phonon Raman cross section may contain contributions from all symmetryallowed two-phonon pairs throughout the zone consistent with overall energy and wavevector conservation. The secondorder spectrum can be roughly considered as being modulated by the two-phonon density of states. There will certainly be other energy dependence in the cross section. However, the important point is that the structure in the two-phonon density of states due to critical points will appear in the two-phonon Raman spectrum. This is the essential link between critical points and second-order Raman spectra. The connection has been traced from dispersion curve critical points to their manifestations in secondorder spectra. Experimentally, the inverse problem must be solved. That is, given measured spectra, one attempts to determine the positions and types of critical points in the Brillouin zone. This inverse problem is the more difficult and permits only a partial solution at best. Even with neutron scattering data (not available for SiC) a critical point assignment can never be made with absolute certainty. The inherent difficulties in applying the preceding theory to experimental analysis will be discussed in depth.

H. Experimental

It is quite difficult to grow large, single polytype crystals of 3C SiC. Fortunately, Raman scattering requires samples only slightly larger than the focused incident beam diameter. Using samples of dimensions of ~1 mm or smaller presents problems in X-ray orientation, surface preparation, and general handling. The two samples used in this study have dimensions on the order of 5-10 mm.

The crystal axes of both samples were determined using X-ray Laue back-reflection. Growth faces of 3C SiC tend to be [111] planes. In order to obtain a [100] face, a special goniometer was constructed which allows transferring the sample from the X-ray apparatus to a diamond

saw while preserving the sample orientation. The larger of the two samples, sample A, was cut in this manner. The sample orientation obtained in this manner is accurate to within 1°, as judged from subsequent X-ray checks.

The arrangement of optical components is shown in Figure 14, Appendix A. The backscattered light is collected over a finite solid angle determined by the lens diameter and the distance between the lens and the sample. This arrangement has two important experimental consequences. First, the theoretical selection rules discussed previously are based on definite, well-defined wavevectors for both the incident and scattered light. The lens in effect integrates all final wavevectors in its solid angle. However, refraction at the crystal surface tends to limit the effective size of this solid angle, so that experimental selection rules are better than might be supposed. Other limits on selection rule measurements include the polarization purity of the incident beam, the accuracy of the sample orientation, and the quality of the analyser polaroid. The overall validity of experimental selection rules may be gauged by comparing the intensity of first-order spectral lines in allowed and forbidden geometries. This ratio is 50:1 or better for all spectra presented here.

A second consequence of the experimental geometry is the need for a mirror-like sample surface. The

spectrometer is not an ideal instrument, in that intense light of any wavelength can appear as a continuous background in a spectrum (due to imperfections and multiple reflections in the spectrometer). Intense monochromatic light entering the spectrometer can produce false structure in the spectrum, referred to as "grating ghosts." A rough sample surface can Rayleigh scatter a portion of the incident laser beam into the spectrometer. A perfectly smooth sample, properly aligned, will reflect the incident beam directly back to the beam mirror, preventing its collection by the lens. This geometry at the same time guarantees the proper alignment of the sample. The [100] face of sample A was polished after sawing, using successively finer abrasive compounds, and finishing with quarter-micron diamond grit. Spectra from surfaces prepared in this manner show no grating ghosts and very low background levels. The question of surface damage is addressed later.

After ultrasonic cleaning in ACS acetone, the samples were mounted in an optical "cold finger" liquid nitrogen dewar using thermally conductive grease. The cold finger is made of OHFC copper to enhance its thermal conductivity. The temperatures quoted in this study are approximate, since there is some unavoidable sample heating due to the incident laser beam.

Spectra are recorded using a spectrometer equipped with a stepper-motor wavelength drive, cooled phototube, and photon counting electronics. This equipment is detailed in Appendix A. The procedure is to count and record the photon flux for a set period of time, move the spectrometer a set wavelength increment, and begin another count. The spectral plots presented here represent a set of discrete points joined by straight line segments. Because the spectrometer is calibrated in wavelength, the wavenumber shift must be calculated for each point using

$$\omega = 10^8 \left(\frac{1}{\lambda_i} - \frac{1}{\lambda_s} \right) \tag{9}$$

where λ_1 and λ_s are the incident and scattered wavelengths in Angstroms, and ω is the spectral energy in cm⁻¹. For true Raman processes, spectral features will have a constant ω regardless of the wavelength of the incident light. Non-Raman processes, such as flourescence, emit constant wavelength light, and will appear at different wavenumber positions in the Raman spectrum as the laser wavelength is changed. This fact allows Raman and non-Raman spectral features to be identified. Several laser lines are employed in this study from both argon and krypton lasers for the above reason and other reasons to be described.

The recorded spectra will have a wavelength dependence (in addition to that of the sample) arising

from the measurement system itself. The system response as a function of wavelength, or throughput, can be measured using a standard lamp with a known spectral output. The instrument throughput can then be removed from the spectra, as is done for all spectra presented here. Spectral wavelengths are calibrated by superimposing discharge lines from a neon lamp on the two-phonon spectrum. Wavelength errors introduced by the spectrometer drive, which may be several cm^{-1} , can be corrected. Feature energies quoted here are measured from the nearest identifiable neon line, and have an estimated uncertainty of $\pm 2 cm^{-1}$. Descriptions of the throughput and wavelength calibrations are included in Appendix C.

Photon counting statistics have a Poisson distribution. That is, successive counts for fixed time intervals and constant input will have some average count \overline{N} , and the distribution will have variance \sqrt{N} . The quality of the signal may be roughly gauged as the ratio of the mean to the variance. In other words, the quality of the signal improves as \sqrt{N} . The time allowed for photon counting at each spectral point may be made as long as needed to obtain a suitable number of counts. The total recording time is then also made longer. The two-phonon spectra presented here require recording times of several hours each with a laser power of 150 mw.

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The samples are both known to have nitrogen donor impurities in an unknown concentration. The relative nitrogen concentration of the two samples is 2:1, as discussed in Chapter III. The larger, sample A, is the purer and is used to obtain most of the two-phonon spectra. Sample B is used to judge the effects of the nitrogen donors on the twophonon spectra and as a consistency check.

I. Results

A brief study of the Poulet intensity matrices of Table 3 indicates the possibility of arranging the experimental geometry such that polarizability components Γ_{12} and Γ_{15} may be isolated. The main results, all of sample A, are shown in Figures 3 through 5. The geometry, allowed polarizability components, and allowed first-order scattering are indicated in each spectra. Since the polarizability tensor in zinc-blende has only three parts, three spectra are sufficient to isolate the various components. The fourth geometry, in Figure 6, provides a consistency check. Experimentally, the Γ_1 spectrum is found to be much stronger than either the Γ_{12} or Γ_{15} . For reasons of clarity, the relative scales of these four spectra have been multiplied by 1:5:5:1 for Figures 3, 4, 5, and 6, respectively. These four spectra were recorded using a 4579Å (2.7 eV) argonion laser line and an instrument



 $\overline{X}(ZZ)X$ spectrum of sample A, $T=77^{\circ}K$, 4579Å laser line. Figure 3.













resolution of 7 cm⁻¹. A number of critical points are observed, many of which have been identified and noted in Figures 3, 4, and 5. The first-order TO (797 cm⁻¹) and LO (975 cm⁻¹) phonon peaks appear weakly in geometries where they are forbidden, such as Figure 3, due to the approximate nature of experimental selection rules. This is to be contrasted with Figure 4, where the LO phonon is allowed and dominates the two-phonon scattering.

The addition of impurities to a crystal has the effect of disturbing the strict translational symmetry of the lattice. Wavevector conservation, which originates directly from crystal periodicity, may be somewhat relaxed by the presence of impurities. A consequence for light scattering is that previously forbidden lattice modes may become optically active.¹⁹ Impurity-induced scattering generates a continuous spectrum since modes from the entire zone may contribute to the scattering. Sample B, having roughly double the nitrogen concentration of sample A, is used to judge the effects of the nitrogen donors on the two-phonon spectra. The sample B spectrum appears in Figure 7. The geometry, chosen to include all polarizability components, is identical to the geometry of Figure 6. The scale of Figure 7 has been adjusted to facilitate a comparison of these two spectra, and they appear to be nearly identical. Although not shown, no features appear



 $\overline{X}(Z^2)X$ spectrum of sample B, T^277^0K , 4765^{A} laser line. Figure 7.

below 400 cm⁻¹ and no features appear which can be interpreted as impurity-induced first-order scattering. The strength of the peak at 1630 cm⁻¹ does appear to scale with nitrogen concentration. This feature cannot be a first-order impurity-induced feature, as its energy is well above any first-order modes. Electronic impurity level energies are also too low to account for this feature (see Chapter III). It may be an impurity-enhanced twophonon feature, but remains unresolved. The remaining portions of these two spectra are identical (with the exception of a small feature immediately preceding the TO phonon, to be discussed later). For present purposes, sample A may be regarded as pure.

When the energy of the incident light approaches the band-gap energy in a semiconductor, it is possible for some Raman processes to be resonance-enhanced (for example, see Reference 12). Both samples A and B exhibit broad luminescence in the energy range of the indirect gap (2.4 eV) which obscures the two-phonon Raman spectrum precluding indirect gap resonance studies. The wavelength dependence of the two-phonon spectrum can be gauged using a 6471Å (1.9 eV) krypton-ion laser line, well below the indirect gap energy. This spectrum appears in Figure 8, and is to be compared with Figure 6, which has the same geometry.







The peak at 768 cm⁻¹, immediately preceding the TO phonon, appears considerably stronger in Figure 8 than in Figure 6. This peak is very close in energy to a 6H polytype phonon³ of 769 cm⁻¹. Since the penetration depth of the 6471Å laser line is greater than the 4579Å line, the spectrum represents a deeper probe of the bulk. Trace amounts of 6H polytype in the bulk could account for the wavelength dependence of this line. However, no other 6H phonons appear. Also, the laser line energy is rather far from the gap energy to assume a resonant process. This feature remains unresolved. The remaining structures of these two spectra agree quite well, which establishes them as due to Raman processes.

However, the spectrum of Figure 8 (taken at room temperature), appears relatively stronger at low energies than the spectrum of Figure 6 (taken at 77° K). This difference can be explained by the scattering temperature dependence. The thermal average over initial states for two-phonon scattering yields a temperature-dependent intensity factor²⁰ of

I(T)
$$\propto$$
 (n(ω_1)+1)(n(ω_2)+1)

for Stokes scattering, where $n(\omega_1)$ and $n(\omega_2)$ are Bose population factors for each phonon of the pair. For an overtone mode of energy 2 ω , the thermal factor is $(n(\omega)+1)$.²
The thermal factors for two temperatures and a given feature can be compared by forming the ratio $I(T_1)/I(T_2)$. Using $T_1 = 300^\circ$ K and $T_2 = 77^\circ$ K, these ratios for several overtones in the 3C SiC spectrum are shown in Table 6. (Experimental ratios from Figures 6 and 8 have been normalized to the theory for 2TA(X).)

	I(300° K)/I(77° K)		
Overtone	Theory	Experiment	
2TA(L)	1.8	2.0	
2TA(X)	1.4	1.4	
2LA(L)	1.1	1.0	

Table 6. Thermal intensity ratios of two-phonon Raman spectra in 3C SiC

These ratios cannot be taken too seriously, since matrix elements, background luminescence, crystal absorption, and other factors will have temperature dependence also. The important point is that the thermal intensity factors account for the major portion of the relative intensity differences between Figure 6 and Figure 8. The phonon energies in SiC are such that quite high temperatures would be required to significantly change the thermal factors for the structure beyond 1400 cm⁻¹. Broadband



luminescence in these samples, which increases with temperature, precludes high temperature two-phonon studies.

Difference processes, where one phonon is created and another destroyed, have thermal intensity factor

$$I(T) \propto n(\omega_1)(n(\omega_2)+1)$$

where ω_1 and ω_2 are the destroyed and created phonon energies, respectively. For Stokes processes, $\omega_2 > \omega_1$. The difference in thermal intensities of difference processes versus overtone processes is used in some materials to determine the nature of a two-phonon spectral feature (for example, see Reference 16). Assuming room temperature, a feature energy of 600 $\rm cm^{-1}$, and difference pair energies of 300 cm^{-1} and 900 cm^{-1} , one obtains I(overtone = 1.7 while I(difference) = .3. Using the same energies but T = 77K, one obtains I(overtone) = 1 and I(difference) $\sim 1^{-3}$. The example energies, typical for SiC, were actually chosen to favor I(difference). Higher feature energies generally give an even greater difference in the intensity factors. Assuming that matrix elements for difference processes are roughly comparable to combination processes, the conclusion is that no difference processes will be observed in the spectra of Figures 3 through 6 (all at T = 77K).



Preceding discussions explain the choice of the 4579Å laser line for the main spectra of Figures 3 through 6. Because sample A is quite transparent to the 6471Å line, the experimental selection rules are obscured by multiple internal reflections from flaws in the crystal and from the crystal faces. Since the luminescence near the band-gap may be avoided with either line, and since identical spectra result, the natural choice is the 4579Å line.

To investigate the effects of surface damage which could result from surface polishing, a spectrum was recorded from a [111] growth face of sample A. This spectrum appears in Figure 9. While the geometry of this spectrum is different than that of Figure 6, the allowed polarizability components are identical. There are no dramatic differences between the two spectra, indicating that surface preparation has not introduced new structure.

J. Analysis

The analysis of second-order spectra has several purposes. Among these are an accounting for the optical second-order spectra structure, extraction of phonon energies at several high-symmetry points in the Brillouin zone, and a determination of the general topology of dispersion curves in the Brillouin zone. A complete analysis requires neutron scattering results, second-order infrared

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and Raman spectra, and possibly lattice dynamical calculations. Neutron scattering and Raman scattering are complementary in several respects. Neutron scattering can give detailed energy and wavevector information from general points in the zone. Energies derived from Raman spectra are generally more accurate but are restricted to critical points. Raman results are also more difficult to interpret, since the spectra contain contributions from all parts of the zone at once. Optical spectra can give information, through selection rules and spectral shapes, on the symmetry properties of critical point phonons. Any analysis of second-order spectra without neutron data must necessarily be somewhat incomplete. Since there is no neutron data for 3C SiC, the approach here is to supplement the optical spectra with a reasonable lattice dynamical calculation.

Direct application of critical point and selection rule theory, presented earlier, to the analysis of experimental spectra involves some practical limitations. The spectral shape of an overtone critical point from a nondegenerate branch is determined by the nature of the dispersion curve critical point, since adding a branch to itself is equivalent to a simple doubling and preserves the nature of the critical point. Consider next a combination arising from two non-degenerate branches, which will

make a contribution to the two-phonon density of states given by

$$D_{2}(v) \propto \int_{S} \frac{dS}{\left| \overrightarrow{\nabla} (\omega_{1} + \omega_{2}) \right|}$$
(10)

where ω_1 and ω_2 are the branch energies and S is such that $\nu = \omega_1 + \omega_2$. This relation, a natural extension of (5), shows that the shape appearing in the second-order spectrum will depend in detail on the relative curvatures of the two critical points. A lattice dynamical calculation can give the nature of critical points in the dispersion curves, where only the signs of curvature in the immediate neighborhood of the critical point are required. Determination of (10) places a much greater demand on lattice dynamical calculations, since the relative values of the curvature near the two points are required. Dispersion curve calculations are generally not reliable enough to permit an evaluation of (10). The situation is further complicated when one or both members of the two-phonon pair are from a degenerate critical point, where non-analytic or "fluted" behavior is possible. A second complicating factor is that observed critical point shapes are often obscured by other scattering, sometimes to such an extent that even the discontinuity in slope does not appear distinctly. Determining the energy of such points from the measured spectra is of necessity somewhat subjective.

The limitations of experimental selection rules have been discussed previously. Selection rules indicate what components of the polarizability for a particular two-phonon critical point are symmetry-allowed, but not necessarily which of these components will be observed. Since the Γ_1 spectrum is much stronger than the Γ_{12} or Γ_{15} spectrum, strong $\boldsymbol{\Gamma}_1$ features may appear weakly in geometries where they are not allowed due to the approximate nature of experimental selection rules. As with critical points, selection rules of weak features are often obscured by other scattering. Since one does not strictly know what the intensity ratios should be between various polarization components of a given feature, experimental selection rules must be considered as approximate only. Their utility is mainly in approximately testing the consistency of supposed feature symmetries.

A number of critical points appearing in the spectra of Figures 3 through 5 have been identified and are listed in Table 7. These assignments have also been indicated in Figures 3 through 5. The considerations leading to these assignments are detailed later. Features having an indistinct energy or selection rule, as discussed above, have been so noted. Energies of such features have uncertainties perhaps as high as $\pm 5 \text{ cm}^{-1}$. The labels of Figures 3 through 5 have been placed in the figure where the associated

	Energy	(cm ⁻¹)	Polarization		
Branch	Observed Previous ^a		Observed Allowed		
2TA(L ₃)	534	532	Γ _l	^r ı, ^r ı2	
2 ta(x ₅)	748	746	Γ _l	^r 1, ^r 12, ^r 15	
$LA(L_1) + TA(L_3)$	883	876	^b	Γ ₁₂ ,Γ ₁₅	
$2TA(\Sigma_1 \text{ or } \Sigma_2)$	945		^b	^r 1, ^r 12, ^r 15	
$TA(X_5)+LA(X_1 \text{ or } X_3)$	1010	1013	^b	г ₁₅	
$TA(L_3)+TO(L_3)$	1035	1032	^b	Γ ₁ ,Γ ₁₂ ,Γ ₁₅	
$TO(X_{5}) + TA(X_{5})$	1133	1134	г	^r 1, ^r 12, ^r 15	
$TA(X_5) + LO(X_1 \text{ or } X_3)$	1201	1202	^Г 15	^г 15	
2LA(L ₁)	1212	1220	r _l	Γ ₁ ,Γ ₁₅	
2LA(X ₁ or X ₃)	1275 [°]	1280	Γ _l	Γ ₁ ,Γ ₁₂	
$TO(X_5)+LA(X_1 \text{ or } X_3)$	1400	1401	^г 15	^г 15	
$LO(X_1)+LA(X_3)$ or		1469	^Г 15	-	
$LO(X_3)+LA(X_1)$	1460			^r 15	
$2TO(\Sigma_1 \text{ or } \Sigma_2)$	1473		rl	^r 1, ^r 12, ^r 15	
2то(х ₅)	1523	1522	Γ _l	^r 1, ^r 12, ^r 15	
2TO(L ₃)	1530	1532	Γ _l	Γ ₁ ,Γ ₁₂	
$TO(X_5)+LO(X_1 \text{ or } X_3)$	1588	1590	г ₁₅	г ₁₅	
2TO(r ₁₅)	1593	1592	Γ _l	Γ ₁ ,Γ ₁₂ ,Γ ₁₅	
$TO(L_3)+LO(L_1)$	1610 [°]	1604	г ₁₂	^r 12, ^r 15	
2LO(F ₁₅)	1952 [°]	1950	Γl	Γ ₁ ,Γ ₁₂ ,Γ ₁₅	

Table 7. Energies and feature assignments from the twophonon Raman spectrum of 3C SiC

^aThese energies derived from previous experimental measurements. ^bExperimental selection rules could not be obtained--see text. ^cIndistinct feature--see text.



critical point energy appears most distinctly, and do not imply a particular selection rule. The energies of the second column are from these previous measurements. The symmetry species of Table 7 follow Reference 16, as determined from a reduction of the atomic displacement representation into species of the point in question. Some ambiguities in species assignment remain as indicated in the first column of Table 7.

Lacking neutron data, the nature of dispersion curve critical points must be obtained by calculation. Several dispersion curve calculations have been performed for 3C SiC.^{21, 22, 23, 24} These models have variable parameters which are adjusted to fit the available experimental energies at $\Gamma,$ X, L, and along $\Lambda.$ However, these calculations are not reliable enough to extract energies for other points in the Brillouin zone. The calculation of Reference 24 includes a determination of the two-phonon density of states. The spectrum of Figure 6, which contains all components of the polarizability, is compared with this calculation in Figure 10. The agreement below 1300 cm⁻¹ is fairly good, while above 1300 cm^{-1} , where the structure is due to the optic branches, the agreement is poor. Model calculations in general have the most difficulty accounting for the optic branches. The important point is that even extensive density of states calculations are not







sufficiently detailed to permit a critical point analysis. A more complete analysis can be performed using the dispersion curves directly.

A comparison of published dispersion curves for the calculations noted shows that they share certain qualitatively similar aspects. Of concern here is the behavior of the dispersion curves in the immediate vicinity of critical points. The topology near critical points in a few cases does appear to depend on which calculation is used. Some of the calculations show extra "kinks" which may or may not be realistic. In an attempt to determine a set of critical points and their sector numbers, the calculation of Reference 21 was duplicated. Details of this calculation, including dispersion curves, are presented in Appendix D. This model is referred to as a second-neighbor ionic or SNI model. In this study, sector numbers were obtained by inspection of a small grid of solutions surrounding each critical point. Sector numbers so obtained are peculiar to the SNI model and can serve as only a rough guide. The final set is determined by considering published dispersion curves from more sophisticated models and observed spectral shapes and energies. This process is not as arbitrary as it might at first appear, since the observed spectral shapes, observed energies, and sector numbers are all tightly interwoven by the Morse relations, (7) and (8). For example, the



ordering of the energies of critical points in a given branch will have a profound effect on the topology of that branch, and hence also on the topology of the critical The results of this two- and three-dimensional points. critical point analysis are shown in Table 8. The planes [100] and [110] are used for the two-dimensional analysis. The number appearing next to each group label is the multiplicity of that point in its associated manifold (plane or volume). The branches are labeled (in order of increasing energy) as TA, LA, etc., even though the phonons have these simple polarizations only in certain directions. As pointed out by Phillips, such a set does not necessarily represent the true set. It is always possible to add pairs of kinks (and their symmetry equivalences) to a branch without spoiling the topological consistency. However, the assignments here are consistent with the observed energies and spectral shapes, and satisfy the two- and three-dimensional Morse relations.

As an example of the analysis process, including sector numbers, consider the shoulder appearing at 534 cm^{-1} (Figure 3). Table 1 shows this energy to be very close to twice the TA(L) energy, and no other combinations or overtones can be formed from Table 1 that agree as well as 2TA(L). Most assignments are performed by considering the energy first. Figures 3 through 5 show this shoulder

Branch	Γ(1)	X(2)	R(1)	W(4)	Σ(4)			
Two-Dimensi	ional; (100)	Plane:						
TA1 TA2 LA TO1 TO2 LO	(1,0) (1,0) (1,0) (0,1) (0,1) (0,1)	(2,2) (2,2) (0,1) (1,0) (1,0) (2,2)	(4,4) (1,0) (0,1) (4,4) (1,0) (0,1)	(0,1) (0,1) (2,2) (2,2) (2,2) (1,0)	(2,2) (1,0) (2,2)			
Branch	Γ(1)	X(1)	L(2)	Σ(2)				
Two-Dimensi	lonal; (110)	Plane:						
TAL TA2 LA TOL TO2 LO	(1,0) (1,0) (1,0) (0,1) (0,1) (0,1)	(0,1) (2,2) (0,1) (2,2) (1,0) (2,2)	(2,2) (2,2) (2,2) (2,2) (2,2) (2,2) (2,2)	(0,1) (1,0) (1,0)				
Branch	Γ(1)	X(3)	L(4)	W(6)	Σ(12)			
Three-Dimer	nsional:							
TA1 TA2 LA TO1 TO2 LO	(1,0) (1,0) (1,0) (0,1) (0,1) (0,1)	(4,1) (1,2) (0,1) (1,4) (1,0) (2.1)	(1,2) (1,2) (1,2) (2,1) (2,1) (2,1)	(0,1) (0,1) (2,1) (1,2) (1,2) (1,0)	(2,1) (1,0) (1,2)			

Table 8. Critical point analysis of 3C SiC^a

^aNumbers in parentheses following critical point labels indicate point multiplicity. R is the point (110). Branches are listed in order of increasing energy. Point W has mixed phonon polarization. appears only in the Γ_1 geometry. Table 7 shows that 2TA(L) is allowed in Γ_1 and Γ_{12} geometries, consistent with the observed polarization. Table 8 shows both members of the degenerate TA branch at L have sector numbers (1,2). For an overtone, the two-phonon density of states will have the same shape as the one-phonon density of states. Figure 2 shows the shape of a (1,2) point to be identical to the shape in Figure 3. The energy, polarization, and critical point shape all agree with the assignment of this feature as 2TA(L). While this spectral feature is exemplary, the assignment procedure is well illustrated.

K. Discussion

Figures 3 through 5 show the Γ_1 or totally symmetric component as the dominant component. This is generally the case for homopolar or slightly ionic materials. By comparison, second-order spectra of alkali halides may have other components comparable in strength to the symmetric component.²⁵

The second neighbor ionic (SNI) calculation, used in part to determine critical point sector numbers, was chosen due to its computational simplicity and qualitatively typical results. This calculation consists of first and second neighbor forces and a long range Coulomb interaction. The ionic charge, which appears as a parameter, is adjusted



to 1.05 to obtain the best fit with experimental phonon energies. It agrees well with the Szigeti effective charge of .94. The suitability of a rigid-ion model for a IV-IV covalent compound may be debated. However, the SNI calculation qualitatively explains a number of observed spectral features. None of the calculations can be assessed without extensive neutron data, so that calculated energies at points not experimentally measured cannot be taken as strictly reliable. A portion of the spectral structure is likely due to critical point W, but assignments are not possible without a more accurate knowledge of branch energies at W.

The energies of Table 7 agree quite well with previous measurements. Phonon energies derived from luminescence spectra actually are energies of phonons having the same wavevector as the conduction band minimum. The conduction band minimum in 3C SiC is believed to be at X (see Reference 4). Second-order Raman spectra measure phonon energies at X directly. Assuming an uncertainty in both sets of measurements of $\pm 2 \text{ cm}^{-1}$, and using the SNI branch curvatures near X, it can be inferred that the wavevector at the conduction band minimum is within 5% of X point. This experimental limit lends support to the assignment of the conduction band minimum to X point.

The structure at 952 cm⁻¹ (Figure 3) has been assigned as $2TA(\Sigma)$ at $\vec{k} \approx .65$ (1,1,0) (per SNI calculation). This assignment is based on the fair agreement in energy of the observed feature with calculated energies. The SNI calculation shows this point to have sector number (2,1), in agreement with the observed shape. The polarization properties of this feature could not be obtained, as they are obscured by the LO phonon in some geometries.

Phonon density of states calculations for 3C SiC show a gap between the acoustic and optical branches. For overtone modes, this gap should be replicated in the twophonon spectrum at double the energy. Some weak structure does appear in this region (~1280+1470 cm⁻¹) which may be due to combinations with critical points at W or threephonon modes. This structure remains unidentified.

The strong scattering beginning at 1474 cm⁻¹ marks the onset of overtone scattering from the TO branch. This structure has an energy well below the energy of 2TO(X) (1522 cm^{-1}) or 2TO(L)(1532 cm⁻¹), indicating that the energy minimum of the TO branch is not located at X or L. The SNI calculation exhibits such a minimum along Σ at $\vec{k} \approx .7$ (1,1,0). The feature has therefore been assigned to 2TA(Σ) with sector number (1,0), in agreement with the observed shape. Dispersion curves of other calculations do not show this minimum, to the credit of the SNI calculation.

The strong scattering beginning at $\sim 1670 \text{ cm}^{-1}$ is mainly from LO overtones. Unfortunately critical points in the optic branches are closer together in energy than the acoustic branches, making assignments more difficult. Model calculations also have the most difficulty accounting for the optic branches. If the impurity-dependent feature at 1630 cm⁻¹ (discussed previously) is disregarded, there appears to be a gap between the TO and LO branches. The SNI calculation shows only a very narrow gap between these branches, especially along Σ (see Appendix D). Assignment of structure from the optic branches must await more refined calculations or possibly neutron scattering data from only selected critical points. Knowledge of branch energies at W, for example, would be a great aid in assessing the validity of various model calculations and would allow for a more complete accounting of the observed spectra.

CHAPTER III

RAMAN SCATTERING FROM NITROGEN ELECTRONIC IMPURITY LEVELS IN 3C SiC

A. Background

An important aspect of semiconductor applications is the ability to modify host crystal electrical transport properties with the inclusion of various impurities. The thermal behavior of electrical transport properties in doped semiconductors can be accounted for by the presence of states existing just below the conduction band or just above the valence band, referred to as donor and acceptor states, respectively. This study and the following discussion are limited to donor states of substitutional impurities.

If a group V impurity atom is substituted for an atom of a IV-IV semiconductor, the extra electron does not participate in the tetrahedral bonding. Instead, it is weakly bound to the impurity by the extra unit of nuclear charge. The ionization energy of the bound electron, as measured from the minimum of the conduction band, can vary from several meV to several hundred meV, depending on the impurity and the host semiconductor. The donor electron can be thermally liberated to the conduction band, where

it can participate in electrical conduction. Because semiconductor band gaps are usually considerably larger than the donor binding energies, the electrical properties of semiconductors are dominated by impurity electrons (except at very high temperatures). In this simple picture, the carrier concentration varies roughly as $exp(-E_0/2kT)$, enabling early workers to extract the ionization energy E_0 from transport measurements.²⁶

Much of the early theoretical work on donor states and application to real materials was performed by Kohn and Luttinger,²⁷ and the method is often called the Kohn-Luttinger effective-mass theory (EMT). Qualitatively, in the effective mass picture the extra unit nuclear charge polarizes the host lattice and creates an impurity potential in the lattice. At large distances from the impurity cell, this potential is

$$U(\vec{r}) = \frac{-e^2}{\epsilon r}$$
(11)

where ε is the static dielectric constant of the host crystal. For direct gap materials, effective mass theory assumes the impurity electron as weakly bound and has an orbit large enough that (11) applies. The resulting impurity states have a hydrogen-like spectrum (measured from the conduction band minimum) given by

$$E_n = -\frac{1}{n^2} \frac{m^*}{m\epsilon^2} Ry$$
 (12)

where Ry is the hydrogenic Rydberg, ε is the host crystal static dielectric constant, and m* is the isotropic effective mass of the impurity electron. Experimentally, it is found that this simple picture can account fairly well for the excited state energy levels of weakly bound donors but is not satisfactory for ground state levels or for "deep" (tightly bound) impurities in general. This failing arises from the fact that 1S ground states, or "deep" states in general, have wavefunctions with an appreciable amplitude in the impurity cell, where the potential cannot be described by (11). Excited states, on the other hand, have a much smaller amplitude at the impurity cell so that (11) and (12) become more realistic. These simple considerations provide the motivation for a more rigorous approach (described later) which treats indirect gap materials.

Technological advances have made it possible to produce silicon and germanium with very closely controlled impurity concentrations, and most work concerning donor levels has focused on these two materials. The most direct method of studying impurity levels is with infrared absorption or Raman scattering. The energies and symmetries of the donor levels can be obtained directly using optical methods in conjunction with uniaxial stress and Zeeman

effect studies.²⁸ Raman scattering from donor levels was first observed in Si,²⁹ and subsequently in GaP,³⁰ Ge,³¹ some polytypes of SiC,³² and CdS.³³

In this chapter, the observation of Raman scattering from nitrogen donors in 3C SiC is described. Much of the experimental and theoretical discussion of Chapter II is applicable. This study is limited to dilute nitrogen concentration, so that impurity wavefunction overlap is negligible.

B. Donor Levels

The original Kohn-Luttinger treatment of impurity levels in semiconductors has undergone considerable refinement since its introduction. The simple hydrogenic picture of donor levels predicts the same energy levels for all single donor impurities. For example, the donor level energies of a IV-IV semiconductor having a group V impurity are predicted by EMT to be independent of the actual impurity. Experimental results do not indicate identical energies for different group V donors, especially for ground state energies. However, EMT does account well for the excited states of "shallow" donors. The applicability of this theory to a particular impurity can only be established by comparison with subsequent experiment. In indirect-gap materials the conduction band minimum and its symmetry



equivalences give rise to n-fold degenerate levels in the EMT, where n is the number of minima or "valleys." This degeneracy is actually lifted by "intervalley mixing,"³⁴, ³⁵ which gives rise to the experimentally observed "valley orbit splitting."³⁶

The EMT is obtained in the following manner. The host crystal wavefunctions satisfy the one-electron approximation

$$|(-h^2/2m)\nabla^2 + V_0|\Psi = E_0\Psi$$
 (13)

where V_0 is some effective potential having the symmetry properties of the host lattice. The solutions are Bloch functions, labeled with band index n and wavevector \vec{k} , $\Psi_n(\vec{k},\vec{r})$ and $E_{no}(\vec{k})$. The impurity wavefunctions satisfy

$$|(-h^2/2m)\nabla^2 + V_0 + U|\phi = E\phi \qquad (14)$$

where U is the perturbation potential due to the impurity and E is measured from the conduction band minimum. In the conventional EMT, the impurity wavefunction is expanded as

$$\phi(\vec{r}) = \sum_{j=1}^{N} \alpha_{j} F_{j}(\vec{r}) \Psi(\vec{k}_{j}, \vec{r})$$
(15)

where N is the number of equivalent minima or valleys in the conduction band at wavevector \vec{k}_j , and the α_j are numerical coefficients. $F_i(\vec{r})$ is called the envelope function, since

it modulates the Bloch function $\Psi(\vec{k}_j, \vec{r})$ and produces the impurity electron binding. The $F_j(\vec{r})$ satisfy the effective mass equation³⁷

$$|\mathbf{E}_{oj}(-i\nabla) + \mathbf{U}(\vec{r})| \mathbf{F}_{j}(\vec{r}) = \mathbf{E}\mathbf{F}_{j}(\vec{r})$$
(16)

where E_{oj} is the energy of the host crystal at the jth minimum with \vec{k} replaced by $-i\nabla$.

Several key assumptions are made in obtaining (16). Note that in (15) there is no sum over bands. The EMT assumes that the perturbation potential $U(\vec{r})$ is too weak to couple to other bands. Typically, the energy between the valence and conduction band at the minimum, that is $E_c(\vec{k}_j)-E_v(\vec{k}_j)$, is several eV, while the donor binding energy is of order .1 eV. Similarly, the potential $U(\vec{r})$ is assumed to be slowly varying so that it has no strong high frequency Fourier components. Finally, (16) is basically a onevalley equation, neglecting the fact that the N valleys are coupled. The correct many-valley equation is given by³⁶

$$\sum_{i=1}^{N} \alpha_{i} \exp[i(\vec{k}_{i} - \vec{k}_{j}) \cdot \vec{r}] | E_{oi}(-i\nabla) + U(\vec{r}) - E|F_{i}(\vec{r}) = 0. \quad (17)$$

The solutions of (16) are N-fold degenerate, while the solutions of (17) provide for the observed level splitting. The assumptions above were first investigated in a systematic,

quantitative way by Pantelides and Sah.³⁹ Their principal result is that the assumptions concerning the impurity potential are realistic provided that the impurity atom has the same core structure as the replaced host atom. Such impurities are referred to as "isocoric," and their perturbation to the host crystal potential can be well represented by (11). Any agreement of EMT with experiment for non-isocoric impurities is strictly coincidental.

The many-valley equation (17), while correct, does not yield much insight into the nature and symmetries of the impurity levels. Instead, the one-valley equation (16) and group theory can be used to obtain the level symmetries (but not their energies). In the vicinity of a conduction band minimum at, say, $\vec{k}_1 = (1,0,0)$, and using (11), the onevalley equation (16) becomes

$$\left[-\frac{h^2}{2m_1}\frac{\partial^2}{\partial x^2} - \frac{h^2}{2m_t}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{\epsilon_r} - E\right] F_1(\vec{r}) = 0 \quad (18)$$

where $E_{0}(\vec{k})$ has been expanded to second order. The form of $E_{0}(-i\nabla)$ in (18), appropriate for 3C SiC, is determined by the symmetry of the zone and depends on which minimum is being considered. (The factors $1/m_{1}$ and $1/m_{t}$ are conventional effective masses along and transverse to the wave-vector of the minimum, respectively.) Equation (18) is very similar to the hydrogen equation, and the convention has


been adopted of labeling the first few levels with hydrogen-like labels. For $m_1 = m_t$ (spherical valleys) the solutions of (18) are exactly hydrogen-like (15, 25, 2P, etc.). For $m_1 \neq m_t$, the hydrogenic P level splits into a singlet and a doublet, which are labeled P_o and P_t . This labeling is somewhat misleading, since the solutions to (18) have prolate spheroidal symmetry rather than spherical symmetry. Solutions of (18) have been obtained numerically for various m_1/m_t ratios.⁴⁰

In the one-valley approximation, every term in the sum (15) has the same energy by virtue of the N-fold degeneracy of (18). The degenerate set is referred to as the 1S manifold, 2P_o manifold, etc. The wavefunctions $\phi(\vec{r})$ are solutions of (14) (where the Hamiltonian has the symmetry of the impurity site) and must belong to representations of the impurity site symmetry group. For zinc-blende this group is T_d . The conduction band minima in 3C SiC are at X point, 42 (yielding three equivalent minima), and Bloch functions at X transform under the group of the wavevector at X, D_{2d}. Solutions of (18) must belong to representations of $D_{\infty h}$. Products of functions such as $F_i(\vec{r}) \Psi(\vec{k}_i, \vec{r})$ will belong to representations of the group formed from the operations common to both $D_{\infty h}$ and D_{2d} , or D_{2d} . The Frobenius reciprocity theorem⁴¹ may then be used to determine the subduced representations in T_d . This

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analysis for 3C SiC is indicated in Table 9. Group representation labels follow Reference 8. The correspondence of the representation labels here with those of Chapter II for T_d are $A_1(\Gamma_1), E(\Gamma_{12}), T_1(\Gamma_{25}), T_2(\Gamma_{15})$.

Manifold	Г(D _{∞h})	Г(D _{2d})	r(T _d)
S	Σ_{g}^{+}	Al	A _l +E
Р	$\Sigma_{u}^{+}(P_{O})$	Al	A _l +E
	$\Pi_u(P_{\pm})$	E	^T 1 ^{+T} 2

Table 9. Donor level symmetries

The important result is that the threefold degenerate solutions of (18) have been split by taking proper account of the true symmetry of (14). The states are commonly referred to as $1S(A_1)$, 1S(E), $2P_0(A_1)$, etc. The same result can be obtained by realizing that the set of functions $F_j(\vec{r})\Psi(\vec{k}_j,\vec{r})$ will transform into one another under the operations of T_d , generating a representation which can be reduced in T_d . The coefficients α_j in (15) for each representation can be found using projection operators, giving a set $\phi(\vec{r})$ having the proper symmetry (i.e., that of (14)). The set $\phi(\vec{r})$ so determined will have only approximate energies in that they arise from the one-valley approximation (16), which neglects



inter-valley mixing. These sets for the S manifold are given by (15) with

$$\alpha_{j}(A_{1}) = \frac{1}{\sqrt{3}} (1,1,1)$$

$$\alpha_{j}(E) = \frac{1}{\sqrt{2}} (1,-1,0), \frac{1}{\sqrt{2}} (1,0,-1)$$

where j = 1,2,3 denotes the minimum along k_x , k_y , and k_z , respectively.

Group theory does not give the ordering of the levels. The assumption is made that the totally symmetric $1S(A_1)$ level is the ground state since it has a non-vanishing amplitude at the impurity center and will have a greater overlap with the binding impurity potential. Higher manifolds are not expected to exhibit significant splitting, since they have a smaller amplitude in the vicinity of the impurity cell. The ordering of the first few levels in 3C SiC, determined by luminescence spectra in conjunction with Zeeman studies,⁴² is $1S(A_1)$, 1S(E), $2P_0$, 2S, $2P_{\pm}$. The splitting of manifolds above the 1S manifold is experimentally found to be negligible, so that only the splitting of the 1S manifold need be considered.

C. Raman Scattering

Having obtained the symmetries of the donor levels, the Raman selection rules may be obtained by group theory. The scattering intensity for given initial and final states $|i\rangle$ and $|f\rangle$ is proportional to⁴³

$$\left| \sum_{m} \left(\frac{\langle \mathbf{f} | \vec{\mathbf{r}} \cdot \vec{\mathbf{e}}_{1} | \mathbf{m} \rangle \langle \mathbf{m} | \vec{\mathbf{r}} \cdot \vec{\mathbf{e}}_{s} | \mathbf{i} \rangle}{E_{1} - E_{m} - h\omega_{s}} + \frac{\langle \mathbf{f} | \vec{\mathbf{r}} \cdot \vec{\mathbf{e}}_{s} | \mathbf{m} \rangle \langle \mathbf{m} | \vec{\mathbf{r}} \cdot \vec{\mathbf{e}}_{1} | \mathbf{i} \rangle}{E_{1} - E_{m} + h\omega_{1}} \right) \right|$$
(19)

where \vec{e}_s, ω_s and \vec{e}_i, ω_i refer to the scattered and incident photons. The dyadic operator $\vec{r} \mid m > < m \mid \vec{r}$ will transform like products of coordinates⁶ in the same way as the polarizability tensor discussed in Chapter II. The photon polarization vectors will select certain components of the dyadic which will belong to representations of the crystal point group, say Γ_d . The matrix elements of (19) will vanish unless the direct product $\Gamma_f x \Gamma_d x \Gamma_i$ contains the totally symmetric representation. If $|i\rangle$ is the totally symmetric A₁ ground state, (19) will vanish unless $\Gamma_f = \Gamma_d$. Exactly as in Chapter II, a set of Raman intensity matrices may be defined corresponding to the irreducible components of the dyadic operator. Thus, the intensity matrices of Table 3 apply. By adjusting polarization vectors \vec{e}_i and \vec{e}_s and using the zinc-blende intensity matrices, the symmetry of an excited level may be experimentally determined (assuming a transition from the ground state).

By making assumptions about the energies of the intermediate states, (19) may be used to obtain estimates

of the relative Raman scattering intensities of transitions between various impurity levels.⁴⁴ Such calculations have been performed for donors in 6H SiC.³² A general result of Reference 32 is that transitions between manifolds (say 1S+2S) are of order $E_B^2/(E_c(\vec{k}_j)-E_v(\vec{k}_j))^2$ less intense than transitions within a split manifold (say $1S(A_1)+1S(E)$), where E_B is the ground state ionization energy and E_c and E_v denote conduction and valence band energies at $\vec{k}=\vec{k}_j$, the conduction band minimum. This ratio for shallow donors (such as nitrogen in 3C SiC) is typically of order 10^{-4} . Strong donor spectral lines are then expected to indicate transitions within a given split manifold.

D. Experimental

Samples A and B of Chapter II, used in this study, have nitrogen donors in an unknown concentration. The color of pure 3C SiC is pale yellow due to weak intrinsic absorption in the blue. Nitrogen doping is known to shift the color to yellow-green, due to free carrier intraband absorption which absorbs preferentially in the red.⁴⁵ Sample A visually appears pale yellow, with very little green observable. Sample B appears dark green-yellow, indicating a greater concentration of nitrogen donors than Sample A. Sample donor concentrations will be discussed further following the presentation of sample spectra.

The experimental geometry employed here, as in Chapter II, is back-scattering. The helium temperature spectra are recorded using a commercial optical dewar equipped with a temperature control system. Other experimental aspects, such as sample preparation, mounting, laser heating considerations, and experimental selection rules have been discussed in Chapter II. The spectra of this chapter are not corrected for throughput since they are over a limited spectral range. The experimental geometry and equipment are detailed in Appendix A.

E. Results

The room temperature first-order spectrum of sample A is shown in Figure 11a, recorded using a 4579Å argon-ion laser line and instrument resolution of 3.7 cm^{-1} . The indicated geometry allows components A_1 and E, but not the LO or TO. The first-order phonons appear weakly due to experimental limitations. The two small lines near 50 cm⁻¹ are laser flourescence lines, designated F. The background structure beyond 400 cm⁻¹ is recognizable as two-phonon scattering. This spectrum is repeated in Figure 11b at 77° K, showing the appearance of a new line. This spectral line was investigated using a different laser line (4765Å) in order both to avoid the small flourescence lines and establish the line as due to a Raman process.





Figure 11. $\overline{X}(ZZ)X$ spectra of sample A, 4579Å laser line.



These spectra, at 7° K, are shown in Figures 12a and 12b. with instrument resolution of 3.7 cm^{-1} . The strengths of the line in these two geometries is in the ratio 3:1. The Poulet intensity matrices of Table 3 show that this line has E symmetry, meaning it appears in geometries appropriate to an $A_1 \rightarrow E$ transition. The symmetry of this line has been investigated in a number of geometries, and is found to be purely E within the limits of experimental selection rules as discussed previously. A high-resolution search for other structure was performed, especially in the region close to the laser shoulder, without success. (The laser shoulder limits this search to energies greater than $\sim 5 \text{ cm}^{-1}$.) Sample B, which is thought to be more heavily doped with nitrogen, exhibits the same line, but with roughly twice the absolute intensity of sample A. The energy of this line, measured from a nearby laser flourescence line, is $67.5 \pm .5 \text{ cm}^{-1}$.

The strength and deconvoluted width of this line in sample A as a function of temperature is presented in Figure 13. The linewidth in sample B is roughly 10% greater than sample A at 77° K. As mentioned previously, the samples are unavoidably heated to some extent by the incident laser power. The temperatures of Figure 13 are measured by a thermocouple attached to the edge of the sample with thermal grease. The thermocouple does not measure the true









temperature of the sample at the point of the incident laser focus. To assess the effect of laser heating, the linewidth at 77° K was measured using incident laser powers of 50, 100, and 200 mw. The linewidths at 50 and 100 mw were identical to within experimental error, while the linewidth at 200 mw was roughly 5% greater. The linewidths of Figure 13 were therefore measured using 100 mw laser power to minimize sample heating errors.

F. Discussion

The observed line is attributed to a $lS(A_1)+lS(E)$ transition between nitrogen donor levels, referred to as a valley-orbit transition line. The symmetry and impurity concentration dependence of the line are the main reasons for this assignment. The intensity temperature dependence is also consistent with this assignment. Figure 13 shows the line intensity approaches a constant as the temperature is lowered, persisting to 7° K. If another impurity state existed which was significantly lower in energy than the two states involved in the observed transition, the intensity would fall at low temperature as the donor electron returns to this hypothetical ground state. Thus to within energy $kT(\sim 5 \text{ cm}^{-1} \text{ for } T=7^\circ \text{ K})$, the observed transition is from the true ground state. Preceding theoretical estimates of the inter- versus intra-manifold transition intensity

strongly favor the assignment $lS(A_1) \rightarrow lS(E)$. With increasing temperature the ground state is depopulated, accounting for the intensity decrease with increasing temperature. The linewidth is thought to be due mainly to perturbations of the impurity site by acoustic phonons.⁴⁶

The relative strength of the line in samples A and B indicates that sample B has approximately twice the nitrogen concentrations of sample A. It is found in Si⁴⁷ and Ge⁴⁸ that the width of valley-orbit lines is a sensitive function of impurity concentration when the concentration is near the metal-nonmetal transition. Since the linewidths of samples A and B vary by only 10% while their concentrations differ by a factor of two, the concentrations must be far from the metal-nonmetal transition.

If the conduction band minima in 3C SiC were not at X, but instead along Δ (as in Si), there would be six equivalent minima instead of three, so that the 1S manifold would contain six levels. Taking proper account of the true impurity site symmetry, these six levels will split into $1S(A_1)$, 1S(E), and $1S(T_2)$ levels. Assuming a specific two-band model, Colwell and Klein³² have calculated the Raman cross section for transitions between levels of the split 1S manifold. They find the cross section proportional to



$$\begin{vmatrix} \mathbf{N} \\ \mathbf{\Sigma} \\ \mathbf{j} \\ \mathbf{k} \\ \mathbf{k}$$

where N is the number of equivalent minima, \vec{e}_1 and \vec{e}_s are polarization vectors of the incident and scattered photons, w and v are representation labels, and \tilde{M}_j is defined by

$$M_{\alpha\beta,j} \propto \frac{\partial^2 E(\vec{k})}{\partial k_{\alpha} \partial k_{\beta}} \Big|_{k_j}^{\downarrow}.$$

For the minima here, \tilde{M}_j is diagonal. If the transition $lS(A_1) \rightarrow lS(T_2)$ is observed, then the conduction band minimum cannot be at X. Using the α_j^V appropriate to a sixfold minimum along Δ ,³⁹ it can be shown that (20) vanishes for the $lS(A_1) \rightarrow lS(T_2)$ transition. Because of the many EMT approximations involved in (20), its vanishing implies only that this transition is likely quite weak. This transition is allowed by group theory, since the dyadic operator in (19) has parts belonging to T_2 . Thus failure to observe this transition does not preclude the existence of a $lS(T_2)$ level. Raman scattering in this case is not an effective method of establishing the position of the conduction band minima. However, the failure to observe the $lS(A_1) \rightarrow lS(T_2)$ transition here is consistent with the assignment of the conduction band minima to X.

Recent luminescence spectra of 3C SiC⁴⁹ have revealed several inter-manifold energies, and show no observable valley-orbit splitting of manifolds above the 1S manifold. These inter-manifold energies are listed in Table 10, with level energies measured negatively from the conduction band minima.

Levels	Energy difference (cm ⁻¹)
2P _± -2P ₀	-38
2P _± -2S	- 25
2P _± -3P _o	+25
2P _± -3P _±	+45

Table 10. 3C SiC nitrogen donor level spacing

Several important 3C SiC parameters are obtained in Reference 49. The effective mass m_t is extracted from the Zeeman splitting of the $2P_{\pm}$ level giving $m_t = .24$. Since the EMT is expected to apply quite well for excited levels, the intermanifold energies above in conjunction with the EMT calculations of Reference 40 give $\varepsilon = 10$, $m_1 = .67$, and an EMT 1S manifold energy of 47.1 meV (380 cm⁻¹). Energy difference between donor-acceptor pair and free electron to bound acceptor luminescence components gives an experimental estimate of the $1S(A_1)$ binding energy of 54 meV (436 cm⁻¹). Most importantly, observation of two-electron satellites of

the $2P_{\pm}$ state directly yields the $lS(A_1)$ ground state energy of 53.6 meV (432 cm⁻¹) (see Reference 49 for details).

The transition energy observed in this study for the $lS(A_1)+lS(E)$ transition is 67.5 cm⁻¹. A rough estimate of the $lS(A_1)$ binding energy can be obtained by assuming the 1S manifold valley-orbit splitting approximately preserves the "center of mass" (as in degenerate perturbation theory). Making this assumption, and using the EMT 1S manifold energy of 380 cm⁻¹, the ground state $lS(A_1)$ energy becomes

 $380 \text{ cm}^{-1} + (2/3) \times 67.5 \text{ cm}^{-1} = 425 \text{ cm}^{-1}$.

This value is consistent with the $lS(A_1)$ energy of 436 cm⁻¹ from luminescence measurements.

CHAPTER IV

SUMMARY

A. Two-Phonon Spectra

The intensity of the second-order spectra of 3C SiC is dominated by the Γ_1 or totally symmetric component of the polarizability, in agreement with spectra of other IV-IV semiconductors. Feature energies and assignments are consistent with previously measured phonon energies at Γ , X, and L. Analysis of the spectra indicates that the minimum of the TO branch is not at X but along Σ , at an energy of 737 cm⁻¹. Critical point $TA(\Sigma)$ (which appears in the dispersion curves of all published calculations for 3C SiC to date) is found to have an energy of 476 $\rm cm^{-1}$. The observed spectra in conjunction with a model calculation are used to arrive at a set of critical point sector numbers. This set is consistent with the observed spectral shapes, energies, and selection rules, and satisfies the two- and threedimensional Morse relations for all phonon branches. The close agreement between Raman and luminescence measurements of X point phonons supports the assignment of the conduction band minimum to X point. Results from the two-phonon spectra agree quite well with previous experimental results and



may serve as additional input for more refined lattice dynamical calculations.

At present, there is insufficient information to make feature assignments to critical point W. These assignments require either neutron scattering data or reliable lattice calculations. It may be practical to perform neutron scattering on the small 3C SiC samples available at selected points in the Brillouin zone. Knowledge of phonon energies at W, for example, would greatly aid the interpretation of the second-order spectra.

The effect of impurities on second-order spectra could be better assessed if high-purity samples were available. Neutron-activation analysis in SiC is not practical because of the long decay times of activated host atoms. Transport measurements require samples large enough to be cut into well-defined shapes, which has not been possible with 3C SiC. Impurity concentration at present can only be gauged in a very qualitative fashion. The variation of 2:1 in nitrogen concentration in the samples here is found to have a small effect on the second-order spectra, and a negligible effect on the identified critical points. Purer samples have less luminescence, which might allow higher temperature second-order spectral recordings. Surface damage due to sample preparation has no effect on the second-order spectra.

B. Nitrogen Donor Spectra

The low temperature spectra of nitrogen doped 3C SiC show an additional Raman line at $67.5 \pm .5$ cm⁻¹. This line is identified as a transition between donor impurity levels. The thermal behavior, symmetry, theoretical estimates, and concentration dependence of this line strongly favor its assignment to the $lS(A_1) \rightarrow lS(E)$ valley-orbit transition. No other structure is observed, consistent with the assignment of the conduction band minimum to X point and with theoretical estimates of cross sections of other transitions. The thermal behavior indicates that the $lS(A_1)$ level is the true ground state. The observed valley-orbit 1S manifold splitting agrees with luminescence measurements and EMT. The measured 1S manifold splitting may stimulate a calculation of the isocoric donor levels in SiC:N along the lines of Reference 39.

If more heavily doped samples of known concentrations become available, the behavior of this line can be studied as a function of donor concentration, up to and through the Mott transition.^{47, 48}

Transitions to higher manifolds are expected to be very weak, but might be observable using modulation spectroscopy. The $2P_{\pm}$ levels will be split by a magnetic field. A modulated magnetic field in conjunction with a synchronous detector might produce detectable signals.

APPENDICES

APPENDIX A

- A -----

EXPERIMENTAL GEOMETRY AND EQUIPMENT

APPENDIX A

EXPERIMENTAL GEOMETRY AND EQUIPMENT

The geometry employed throughout is direct backscattering. The arrangement of optical components is shown in Figure 14. The incident beam from the laser is passed through a prism and iris to remove laser plasma flourescence lines from the main beam. The laser beam is highly linearly polarized in the plane of the drawing as it emerges from the laser. The polarization rotator permits the polarization of the incident beam to be adjusted perpendicular to the plane of the paper. The beam is focused to a small spot on the sample by the small lens. A small dielectric coated mirror diverts the incident beam onto the sample surface. Experimentally it is found that this mirror will produce a reflection of mixed polarization unless the incident polarization is in or perpendicular to the plane of incidence. Only these configurations were employed in order to maintain the polarization purity of the incident The sample is adjusted to reflect the main beam back beam. to the mirror so it is not collected by the lens. Although not shown, the dewar windows are adjusted so that window reflections are also blocked by the small mirror from entering the collection lens. The remaining scattered









light is collected by the lens, analyzed by the polaroid, and passes through the polarization scrambler. The spectrometer response is polarization dependent, necessitating the use of a polarization scrambler to remove this dependence. The lens focal length and diameter and relative positions are adjusted such that the laser spot on the sample is imaged on the spectrometer entrance slit, while at the same time the first mirror of the spectrometer is just filled by the incident light. All components are centered on the spectrometer axis. The entrance slit opening lies in the plane of Figure 14. The laboratory coordinates employed in this study are indicated.

An important consideration in Raman spectroscopy is the fluctuation of the laser output during recording. The Coherent Radiation Model CR-5 argon ion laser used here is equipped with a light regulator which maintains a constant output to within .5%. The CR-5 laser has a polarization purity of 100:1 or better.

The remaining apparatus is listed in brief below along with some key specifications.

- Collection Lens--Cannon 85 mm f:1.5 camera lens
- Spectrometer--Spex Industries Model 1406 .85-meter Czerny-Turner double monochromator equipped with Compudrive (stepper-motor driven wavelength drive) and 1200 grooves/mm, 5000 Å blaze wavelength gratings.

- Phototube--RCA 31034A with extended red response, hand picked for low dark count (-2 counts/sec at -20° C).
- Phototube Housing--Products for Research model TE-104-RF housing, RF shielded, and thermoelectrically cooled to -20° C.
- Photon counting electronics--SSR Electronics model 1120 pre-amplifier/discriminator, model 1108 photon counter with digital outputs.
- Recorder--Kennedy model 1600 incremental digital recorder, 7 track, 200 bpi.
- Control electronics--Fabricated at MSU, coordinates spectrometer drive with photon counter, writes data digitally on the recorder in a form compatible with MSU computers.
- Software--permanently resident on MSU disk drives, provides data reduction, smoothing, correcting, and plotting.
- Power meter--Coherent Radiation model 210 multi-range power meter.
- Helium Dewar--Janis Research Model 10DT helium optical cryostat equipped with Au +.07% Fe versus Cu thermocouples, sample heater, and a temperature control system.
- Nitrogen Dewar--Fabricated at the MSU glassblowing laboratory, equipped with Au +.07% Fe versus chromel thermocouples, sample heater, and a temperature control system.
ZINC-BLENDE INTENSITY MATRICES

APPENDIX B

APPENDIX B

ZINC-BLENDE INTENSITY MATRICES

The Poulet intensity matrices⁶ for zinc-blende are presented here. These are to be used with polarization vectors expressed in and directed fully along the principal laboratory axes defined in Figure 14. For arbitrary polarization orientations, the methods of Chapter II must be used. The column labeled "orientation" indicates the direction of vectors in the crystal system which are parallel to the principal lab axes. These tables assume incident \vec{k} along -x and scattered \vec{k} along x for backscattering, incident \vec{k} along -x and scattered \vec{k} along y for right angle scattering. The intensity matrices for $\Gamma_{15}(T_2)$ can be obtained by adding together the LO and TO matrices. The $\Gamma_1(A_1)$ intensity matrix is the unit matrix in all geometries. The matrices have been normalized such that entries are integers. Table 12 is normalized by 3/2 relative to Table 11.

Table 11. Zinc-blende backscatter intensity matrices

Orientation	I(E)	I(LO)	I(TO)
100 (X)	4 0 0	0 0 0	0 3 3
010 (Y)	0 4 0	0 0 3	3 0 0
001 (Z)	0 0 4	0 3 0	3 0 0
100	4 0 0	0 0 0	0 3 3
0 <u>1</u> 1	0 1 3	0 3 0	3 0 0
011	0 3 1	0 0 3	3 0 0
110	1 0 3	0 3 0	3 0 0
001	0 4 0	3 0 0	0 0 3
110	3 0 1	0 0 0	0 3 3
111	0 2 2	4 0 0	0 1 1
112	2 1 1	0 1 0	1 2 2
110	2 1 1	0 0 1	1 2 2
īī2	1 1 2	2 0 1	1 2 0
110	1 1 2	0 2 0	2 1 1
111	2 2 0	1 0 0	0 1 4
110	1 2 1	0 1 2	3 0 0
111	2 0 2	1 0 0	0 4 1
112	1 2 1	2 0 0	0 1 3

.

Table 12. Zinc-blende right-angle intensity matrices

Orientation	I(LO)	I(TO).
100 (X)	0 0 3	0 6 3
010 (Y)	0 0 3	6 0 3
001 (Z)	3 3 0	3 3 0
100	0 3 0	0 3 6
011	3 3 0	3 3 0
011	0 0 3	6 0 3
101 010 101	3 3 0 3 0 0 0 0 3	3 3 0 3 0 6 0 6 3
111 112 110	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4 1 2 1 <u>6</u> 4 2 4 <u>-</u>
1 <u>1</u> 2	2 2 1	4 2 1
110	2 2 1	2 4 1
111	1 1 0	1 1 8
110	1 1 2	5 1 2
111	1 4 0	1 4 2
112	2 0 1	2 2 5

Note: "6" ~ 5.8; "-" ~ .2.

APPENDIX C

THROUGHPUT AND WAVELENGTH CALIBRATION

APPENDIX C

THROUGHPUT AND WAVELENGTH CALIBRATION

The spectral response of the apparatus is wavelength dependent. Over a limited spectral range, the instrument may be considered to have an approximately constant response. The second-order spectra of Chapter III extend over a broad spectral range, necessitating a correction for system response variations. Given a true spectrum $M(\lambda)$, the measured spectrum $M'(\lambda)$ is given by

 $M'(\lambda) = T(\lambda)M(\lambda)$

where $T(\lambda)$ characteristizes the instrument throughput with wavelength. $T(\lambda)$ can be determined by measuring the spectrum of a source with a known spectral intensity. Referred to as standard lamps, these sources have a true intensity $S(\lambda)$. From the measured intensity, $S'(\lambda)$, the system throughput can be determined as

$$T(\lambda) = S'(\lambda)/S(\lambda).$$

Having $T(\lambda)$, the true spectrum $M(\lambda)$ is given by

$$M(\lambda) = M'(\lambda)/T(\lambda).$$

The standard lamp used in this study, a General Electric 6.6A/T4Q/1CL-200W quartz-iodine lamp, has an output which has been characterized by the National Bureau of Standards⁵⁰ for use as a spectral standard.

In recording the standard lamp spectrum, it is essential to duplicate as nearly as possible the conditions under which the correctable spectrum $M'(\lambda)$ was recorded. The technique used in this study to simulate the actual experimental conditions is shown in Figure 15. The iris simulates the laser spot of an actual experiment and is placed in the same position as an actual sample. The MgO slide, used to provide a diffuse reflecting surface, is placed as closely as possible to the iris. The slide is prepared by coating a glass slide with smoke from a burning magnesium ribbon. The reflectance of slides prepared in this manner has a variation with wavelength of less than 1% over the entire optical spectrum.⁵¹ A light shield prevents the lamp output from entering the spectrometer directly. The effective intensity may be adjusted by varying the lamp to slide distance.

There are several important reasons for attempting to simulate a point source (as is the case in an actual experiment). First, the lens, polaroid, and scrambler must be filled, meaning as much of their area as possible should participate in the light transmission. In particular, the







scrambler cannot produce complete polarization mixing unless an appreciable part of its area intervenes. Incomplete scrambling in conjunction with the polarization dependence of the spectrometer can produce a net throughput not representative of the true throughput. Also, the entire area of the spectrometer gratings must be irradiated to obtain a true response. Only a point source can satisfy these requirements, leading to the point source simulation of Figure 15. Experimentally, it is found that the throughputs measured with the polarization analyser along y and z are very nearly identical. The measured throughput as shown in Figure 16 is used to correct all spectra presented in Chapter II.

The mechanical drive of the spectrometer can introduce wavelength variations in measured spectra. To minimize such errors, the second-order spectrum was recorded with neon discharge lines superimposed. The neon lamp is placed near the sample in the plane of Figure 14 in order that the relatively weak neon lines be observable. The calibration spectrum is shown in Figure 17. Energies quoted in Chapter II are measured from the nearest identifiable neon line. The wavelengths of some representative lines, obtained from MIT wavelength tables,⁵² are compared with their measured wavelengths in Table 13. The random peakto-peak wavelength error in the spectrometer drive is found







Figure 17. Wavelength calibration spectrum.



Measured wavelength (Å)	Mit tables (Å)
4614.82	4614.39
4656.82	4656.39
4704.84	4704.40
4750.06	4749.58
4810.54	4810.06
4863.74	4863.08
4892.72	4892.10
4957.68	4957.03
5005.70	5005.16

Table 13. Neon calibration lines

to be $\sim \pm .3$ Å. A systematic mean offset of $\sim .5$ Å is easily corrected for. Random errors can only be minimized by measuring spectral features from the nearest calibration line.



APPENDIX D

SECOND-NEIGHBOR IONIC (SNI) CALCULATION



APPENDIX D

SECOND-NEIGHBOR IONIC (SNI) CALCULATION

The SNI calculation²¹ employs a simple rigid-ion model with first and second neighbor force matrices and a long-range Coulomb part. An advantage of the SNI calculation is that force constants may be simply related to experimental lattice energies at Γ , X, and L. For x, y, and z directed along the C₂ axes in zinc-blende, the most general forms of the force matrices allowed by the symmetry of the lattice are

$$\tilde{F}_{0} \equiv \begin{vmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{vmatrix} (\text{first neighbor}), \quad \tilde{F}_{1} = \begin{vmatrix} \mu & \nu & \delta \\ \nu & \mu & \delta \\ \delta & \delta & \lambda \end{vmatrix} (\text{second neighbor})$$

where i = 1 or 2 for Si or C second neighbor interactions. The SNI calculation assumes $\delta = 0$, and $\mu = \nu$. The last parameter of the calculation is an effective ionic charge Z. The parameters which result in the best fit for 3C SiC are given in Table 14. The calculation is straightforward, and further details may be found in Reference 21. The dispersion curves are shown in Figure 18 along the (100), (110), and (111) directions. Sector numbers were determined by solving the secular matrix in a grid around each critical

Parameter	Value (nt/m)
α	91.35
β	54.81
μ _l	16.26
λl	-26.57
μ ₂	4.25
λ2	3.30

Table 14. SNI parameters for 3C SiC

Note: Z = 1.049.

point. The species assignments indicated in Figure 18 follow Reference 18. The SNI calculation has enough freedom to duplicate exactly experimental phonon energies at Γ , X, and TO(L). The remaining calculated L energies agree with experiment to within 10%.









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