

Lattice Absorption Bands in SiC

LYLE PATRICK AND W. J. CHOYKE
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received March 29, 1961)

Using four phonon energies, $TA=0.045$, $LA=0.067$, $TO=0.0955$, and $LO=0.1055$ ev, it is possible to explain, as summation bands, the ten absorption bands lying in the energy range 0.130 to 0.300 ev. Phonon energies close to three of the four given here have been obtained by an analysis of the indirect interband absorption in SiC.

I. INTRODUCTION

LATTICE absorption bands attributed to two-phonon and three-phonon combinations (summation or difference bands) have been reported recently in Ge,¹ Si,² GaP,³ and InSb.⁴ The process which results in a summation band is absorption of a photon with emission of two or more phonons. A difference band involves phonon absorption also, hence difference bands are weak except at high temperatures.

The strongest bands are usually two-phonon summation bands. In these, momentum conservation requires that the wave vectors of the two emitted phonons be equal and opposite (neglecting the small photon momentum). The shape of the band is determined by the density in energy of the phonon states in the two branches of the vibrational spectrum to which the emitted phonons belong. Phonon distribution functions usually have strong maxima corresponding to phonons whose wave vectors lie near the Brillouin zone (BZ) boundary. The energy of the photon absorbed in a two-phonon summation band is therefore the sum of two phonon energies, each of which represents phonon energies near the BZ boundary in a particular branch of the phonon spectrum. If the energy at the BZ boundary depends strongly on the wave-vector direction, the broadening of the phonon distribution function will broaden the summation band, and may possibly introduce some structure into it.

The optical or acoustical branches of the spectrum which are involved in the various combination bands may be identified if other measurements of the phonon spectrum exist, e.g., the neutron scattering measurements in Ge¹ and Si.⁵ In other cases plausible phonon energy values have been found which fit a large number of bands.^{3,4}

In many semiconductors the absorption which produces hole-electron pairs is, in a certain energy range, due to a process which requires phonon assistance (indirect absorption).⁶ An interpretation of such spectra

provides a method of finding phonon energies at those special places, within or on the boundary of the BZ, at which there are conduction band minima (or possibly valence band maxima). These special positions are at the BZ boundary in Ge and near the BZ boundary in Si.⁶ Because only small special groups of phonons are involved, phonon energies found in this way are not precisely those required to fit combination bands. Nevertheless, the agreement may be good enough to permit a correct assignment of the branches of the spectrum which make up the combination bands.

In SiC, recent measurements of indirect absorption^{7,8} have yielded phonon energies which we shall use to interpret the lattice combination bands of SiC. The positions of the conduction band minima have not yet been established for SiC, but it is apparent that they are at or near the BZ boundary.

A number of fairly strong absorption bands have been observed in SiC on the high-energy side of the fundamental lattice absorption.⁹⁻¹¹ These have been considered to be combination bands, but no assignment of phonon branches has been given. We have found one additional band, and some structure in two of the bands; and we can now specify the phonon branches which contribute to each band. The phonon energies (in ev), which we have used to fit ten combination bands, are $TA=0.045$, $LA=0.067$, $TO=0.0955$, and $LO=0.1055$.

II. EXPERIMENTAL PROCEDURES

We used about 20 samples, all of which were single crystals grown in our laboratories by D. R. Hamilton.¹² These were of the two most common SiC polytypes,¹³ 6H and 15R. All were (0001) platelets, ranging in thickness from 50 to 1500 μ , and the light was directed along the optic axis of the hexagonal (6H) or rhombohedral (15R) crystals.

⁷ W. J. Choyke and Lyle Patrick, *Proceedings of the International Conference on Semiconductor Physics*, Prague, 1960 (to be published).

⁸ Lyle Patrick, W. J. Choyke, and D. R. Hamilton, *Bull. Am. Phys. Soc.* **6**, 148 (1961).

⁹ W. G. Spitzer, D. Kleinman, and D. Walsh, *Phys. Rev.* **113**, 127 (1959).

¹⁰ J. A. Lely and F. A. Kroger, in *Semiconductors and Phosphors* (Interscience Publishers, Inc., New York, 1958), p. 514.

¹¹ H. G. Lipson, in *Silicon Carbide* (Pergamon Press, New York, 1960), p. 371.

¹² D. R. Hamilton, *J. Electrochem. Soc.* **105**, 735 (1958).

¹³ A. R. Verma, *Crystal Growth and Dislocations* (Butterworths Scientific Publications, Ltd., London, 1953), Chap. 7.

¹ B. N. Brockhouse and P. K. Iyengar, *Phys. Rev.* **111**, 747 (1958).

² F. A. Johnson, *Proc. Phys. Soc. (London)* **73**, 265 (1959).

³ D. A. Kleinman and W. G. Spitzer, *Phys. Rev.* **118**, 110 (1960); D. A. Kleinman, *Phys. Rev.* **118**, 118 (1960).

⁴ S. J. Fray, F. A. Johnson, and R. H. Jones, *Proc. Phys. Soc. (London)* **76**, 939 (1960).

⁵ B. N. Brockhouse, *Phys. Rev. Letters* **2**, 256 (1959).

⁶ G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, *Phys. Rev.* **108**, 1377 (1958); *ibid.* **111**, 1245 (1958).

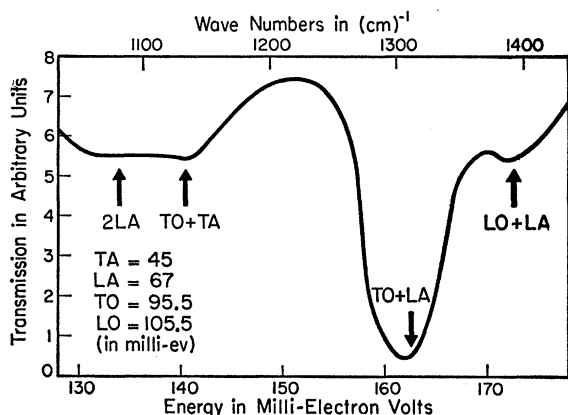


FIG. 1. Two-phonon optical-acoustical summation bands. Arrows point to the energy values calculated by using the four assigned phonon energies.

Our measurements were made at room temperature, using a double-beam Perkin-Elmer model 221 spectrometer with prism-grating interchange. The spectrometer was flushed with dry nitrogen to eliminate some spurious structure which was traced to absorption by water vapor, and which lay in the same spectral region as the narrowest SiC peaks. No attempt was made to calculate absorption coefficients, as our interpretation requires only the positions of all bands on an energy scale.

III. EXPERIMENTAL RESULTS

The combination bands fall into three groups, shown in Figs. 1-3. Different scales were used for the three figures in order to bring out the peak positions more clearly. Only the peak positions are significant for the interpretation. The strongest peaks are those of Fig. 2;

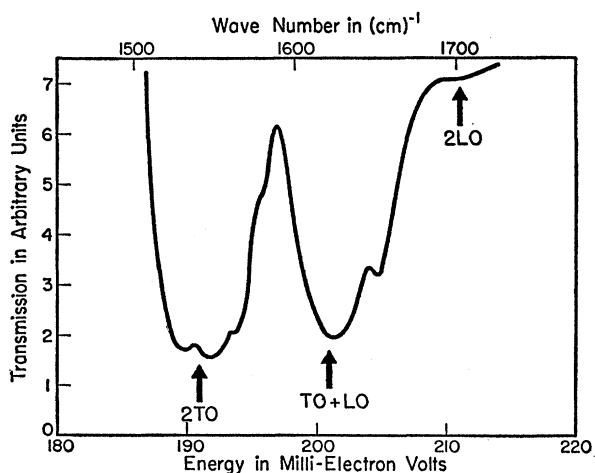


FIG. 2. Two-phonon optical-optical summation bands. Arrows point to calculated values. These are the strongest bands.

the weakest, those of Fig. 3. No peaks were found in the portions of the spectrum omitted.

The arrows indicate that a fairly good fit to ten combinations can be made by using four phonon energies. For convenience, we label the four phonons *TA*, *LA*, *TO*, and *LO*, although the phonons are strictly transverse (*T*) or longitudinal (*L*) only in special symmetry directions.

The phonon energies found in the indirect absorption were used as a guide in choosing the four values $TA=0.045$, $LA=0.067$, $TO=0.0955$, and $LO=0.1055$ ev. The order of the branches *TO* and *LO* was determined by the fact that the fundamental lattice absorption⁹ (*TO* at zero wave vector) is at 0.0984 ev. The high-energy side of the *2TO* peak lies very close to twice 0.0984 ev. Apparently the *TO* branches are quite flat. A detailed comparison of observed and calculated peaks is given in Table I.

The three-phonon combination bands shown in Fig. 3 are quite weak, and were measured only on thick crystals (~ 1 mm). Their relative strength may be judged from Figs. 3 and 4 of reference 11. The values of absorption coefficients for the strong peaks have been given⁹ by Spitzer *et al.*

Both *6H* and *15R* samples had the same bands, and even the same structure in the peaks of Fig. 2. This structure may be due to the anisotropy of SiC, or to the fact that there is more than one *TO* branch.

The order of prominence of the four phonons seems to be *TO*, *LA*, *LO*, and *TA*. *TA* appears in only one peak (at 0.1407 ev), hence is not well determined by our fit, but we have used the same energy value as that found in the indirect absorption measurements (see following section).

All ten bands are summation bands. Because of the large energy of SiC phonons, it is necessary to go to higher than room temperature to observe difference bands.

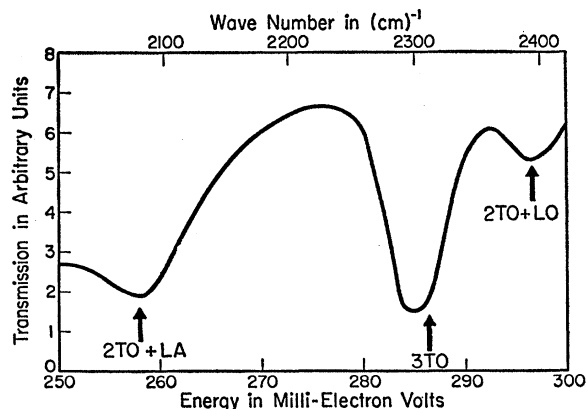


FIG. 3. Three-phonon summation bands. These bands are relatively weak.

IV. DISCUSSION

The phonon spectrum of a lattice containing two atoms per unit cell has six branches. In certain symmetry directions there may be degeneracy of the transverse modes, so that the distinct phonon energies at the BZ boundary reduce to the four commonly labeled *TA*, *LA*, *TO*, and *LO*. If, for other directions of the wave vector, the separation of the transverse branches is small, and the energy dependence of BZ boundary values is small, then four phonon energies may be enough to fit combination bands, and it is convenient to use the labels *TA*, *LA*, *TO*, and *LO*.

The number of atoms in the *6H* SiC unit cell is 12. Hence, there are 36 phonon branches, and it may seem strange that we can fit the 10 two-phonon and three-phonon summation bands using only four phonon energies. However, we were unable to find any differences in energy between the peaks of the *6H* and the *15R* combination bands; and a less detailed measurement⁹ of cubic SiC shows the same energy values for the peaks which could be measured. We therefore conclude that a change from cubic to the more complicated structures of *6H* and *15R* polytypes does not introduce any additional strong singularities into the phonon spectrum. It is thus possible to use the four phonon energies which we would naturally use to fit the combination bands of cubic SiC. In contrast, the SiC polytypes

TABLE I. Comparison of observed and assigned summation band energies.

Observed peaks (cm ⁻¹) (10 ⁻³ ev)		Assignment, using <i>TA</i> = 45, <i>LA</i> = 67, <i>TO</i> = 95.5, <i>LO</i> = 105.5 (10 ⁻³ ev) Branches	
?	?	134	2 <i>LA</i>
1135	140.7	140.5	<i>TO</i> + <i>TA</i>
1308	162.1	162.5	<i>TO</i> + <i>LA</i>
1390	172.3	172.5	<i>LO</i> + <i>LA</i>
1548	191.9	191	2 <i>TO</i>
1622	201.1	201	<i>TO</i> + <i>LO</i>
1700	210.7	211	2 <i>LO</i>
2080	257.8	258	2 <i>TO</i> + <i>LA</i>
2300	285.1	286.5	3 <i>TO</i>
2390	296.3	296.5	2 <i>TO</i> + <i>LO</i>

TABLE II. Comparison of "interband" and "lattice band" phonon energies.

	"Interband" phonons (in 10 ⁻³ ev)		"Lattice band" phonons (in 10 ⁻³ ev)
	<i>6H</i>	<i>15R</i>	
<i>TA</i>	43	45	45
<i>LA</i>	69	72	67
<i>TO</i>	94	94	95.5

can easily be distinguished by their interband absorption edges.^{7,8}

We now compare phonon energies derived from indirect absorption (the "interband" phonons), with the phonon energies we have used to fit the summation bands (the "lattice band" phonons). The orientation, in both cases, is with the electric vector perpendicular to the crystal axis. These energies (in milli-electron volts) are shown in Table II for the phonons we have labeled *TA*, *LA*, and *TO*. The indirect absorption measurements have not given us a value for *LO*. In view of the uncertainty of 0.002 ev in "interband" phonon values, there is good agreement for *TA* and *TO*.

For *LA*, the difference is thought to be significant and is not unexpected. The fact that the BZ boundary phonon energy in a special direction may be quite different from the maximum in the phonon distribution is well illustrated in Si. Johnson's "lattice band" energies² for *TA* and *TO* in Si are in good agreement with Brockhouse's BZ boundary phonon energies⁵ for the [100] direction, the direction for "interband" phonons. For *LA*, however, Johnson finds 0.041, as against Brockhouse's 0.049 ev. In Si, *LA* and *LO* are degenerate in the [100] direction, which makes *LA* particularly high in this direction at the BZ boundary.

The good agreement between "interband" and "lattice band" phonons can now be used as evidence that the condition band minima in *6H* and *15R* SiC lie at or near the BZ boundary.

ACKNOWLEDGMENTS

We wish to thank D. R. Hamilton for the SiC samples, and Ivar Kesse for the use of the spectrometer.