value of 0.3 eV which they obtained from this analysis is in good agreement with our finding.

We have assumed that the mobility ratios μ_L/μ_Γ and μ_X/μ_Γ, which appear in Eq. (5), can be regarded as pressure independent in our analysis. However, it is to be noted that above 10 kbar the Γ_1 band is essentially depleted of electrons; therefore, above this pressure, the assumed pressure independence of μ_L/μ_Γ and μ_X/μ_Γ simply implies constancy of the mobilities μ_L and μ_X with pressure. This assumption for μ_L/μ_Γ (or μ_L) is supported by our experiments from the data on Te-doped GaSb; the resistivity is seen to rise only very slowly between 10 and 25 kbar. From the calculated curves of Fig. 2 we see that this rise can be accounted for almost entirely by the transfer of carriers into the low-mobility X_1 band, which begins in this pressure range. We believe the assumption of pressure independence of μ_X/μ_Γ above the crossover pressure is equally valid, as indicated by the saturation to an almost constant value of resistivity in Te-doped GaSb at the highest pressures. Also, our value for μ_X/μ_Γ appears a reasonable one in comparison with what has been reported for μ_X/μ_Γ for GaAs.[11,12] Finally, the absence of a maximum in the resistivity at or near the pressure at which the bands cross implies that pressure-dependent interband scattering, which would tend to decrease the mobility in this range, is not dominant in this material.[18]

ACKNOWLEDGMENTS

We wish to express our thanks to R. Maines for assistance in the high-pressure runs and to D. McLeod for sample preparation. We are indebted to A. J. Strauss of M. I. T. Lincoln Laboratories for providing the S- and Se-doped GaSb used in this work.

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Higher Absorption Edges in 6*H* SiC

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The absorption of 6*H* SiC was measured for photon energies up to 4.9 eV, where the absorption coefficient is 4.6×10^4 cm^{-1}. Samples as thin as 1.8 μ were prepared by grinding and polishing. Indirect absorption edges were found at 3.0, 3.7, and 4.1 eV. A fourth absorption edge at 4.6 eV could not be positively identified as direct or indirect.

I. INTRODUCTION

PREVIOUS absorption measurements[1] in 6*H* SiC revealed exciton and phonon structure in the indirect interband edge near 3 eV. One earlier report[2] showed measurements to 4.4 eV, but indicated no additional absorption thresholds at the higher energies. Recent reflectance measurements showed some weak structure at 4.6 eV which may be evidence of a direct transition.[3] The object of the present investigation was to look for additional structure in the absorption edge, and especially to try to locate the first direct edge. This is a matter of considerable importance for the calculation of the 6*H* SiC band structure, using an empirical method,[4] in which the value of the smallest direct gap is an important parameter to be fitted.

We were able to prepare samples of 6*H* SiC as thin as 1.8 μ, by grinding and polishing, and we made absorption measurements to nearly 4.9 eV. The typical crystal habit of hexagonal SiC restricted our measurements to one polarization direction ($E\perp c$), but this is the direction for which the reflectance measurements were made. The results show three successive indirect edges at approximately 3.0, 3.7, and 4.1 eV, and a fourth absorption edge at 4.6 eV, which also appears to be indirect. However, as explained below, it becomes increasingly difficult to distinguish between direct and indirect edges as one goes to higher energies. An indirect edge at 4.6 eV is incapable of explaining the reported structure in the reflectivity. We conclude that the character of the 4.6-eV edge has not yet been established.

II. ABSORPTION EDGES

The analysis of absorption edges in 6*H* SiC presents some new problems because of the unusual polytype structure,[5] and because of the wide energy range over which the transitions are thought to be indirect. At the

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

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[5] A. R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (John Wiley & Sons, Inc., New York, 1966).

higher thresholds it is necessary to take into account a strong background absorption, in order to determine the structure of the additional absorption.

A. Band Structure

No band-structure calculations have been published for 6*H* SiC. Because the unit cell is large (12 atoms) the Brillouin zone is small, with a high density of bands. Compared with cubic SiC, for example, 6*H* SiC has 6 times the band density, hence 36 times the number of potential absorption thresholds, both direct and indirect. However, the 6*H* structure may be compared with the simpler wurtzite or zinc-blende structures by using a large zone.[6] Because the energy discontinuities within the 6*H* SiC large zone are small, the strongest absorption thresholds are likely to be those obtained by disregarding the discontinuities entirely. In other words, the *observable* thresholds may be no more numerous than those expected for the simpler wurtzite structure, the many additional thresholds apparent in the Brillouin zone picture being either weak, unresolved, or forbidden.

The published band-structure calculations are for cubic SiC (zinc blende).[7] The valence-band maxima are assumed to be at the zone center in all SiC polytypes. The lowest 6*H* SiC conduction-band minima, responsible for the 3.0-eV absorption edge, are probably at the large zone boundary; analysis of the luminescence shows that they are *off* the symmetry axis,[8] but their exact positions are not known.

B. Indirect Transitions

The theory of indirect, phonon-assisted transitions has been developed in great detail to explain the absorption edges of Ge and Si, including exciton and phonon structure.[9,10] This theory has been applied to the first[1] absorption edge of 6*H* SiC. However, if the theory is used over an extended range, the energy denominators and densities of states must be considered as variables. For 6*H* SiC we do not have sufficient information to take such variable factors into account. We therefore employ the theory in an unsophisticated way by using the simple formula

$$\alpha=\sum \alpha_i=\sum A_i(h\nu-E_{gi})^2\,, \qquad (1)$$

where α is the absorption constant in cm^{-1}, the A_i are regarded as constants, and the E_{gi} are energy thresholds. The fine structure due to excitons and phonons is disregarded (it is, in fact, unobserved at the higher thresholds), and the A_i and E_{gi} are the constants which best fit the experimental results. Thus, an A is fitted at each threshold and then considered to remain constant over the whole range of our measurements.

If an absorption edge is indirect, it is customary to plot $\alpha^{1/2}$ *versus* $(h\nu-E_g)$ to obtain a linear section. In such a plot, the sum of two indirect transitions with different thresholds does not give two linear sections, since one must sum over α, not over $\alpha^{1/2}$. However, one can see that the first linear region is followed, after a transition region, by an *almost* linear second region for a considerable energy interval. In any case, the contribution of the second portion may be found by extrapolating the first linear part and subtracting in the appropriate way. The extrapolation and subtraction procedure may be continued for additional absorption components, but only with a growing uncertainty in the validity of the extrapolations, which are based on the assumed constancy of the A parameters.

C. Direct Transitions

At 4.6 eV the reflectance measurements appear to show a small bump superimposed on a smoothly increasing background. In this region the absorption constant is still relatively small, so the reflectivity is controlled by the real part of the dielectric constant.[11] The Kramers-Kronig dispersion relations show that the real part peaks when the imaginary part has a large positive derivative.[12] For an allowed direct transition, the absorption constant increases as $(h\nu-E_g)^{1/2}$, which has a singular derivative at the absorption edge, and is therefore capable of leading to structure in the reflectivity. No such singularity exists for indirect

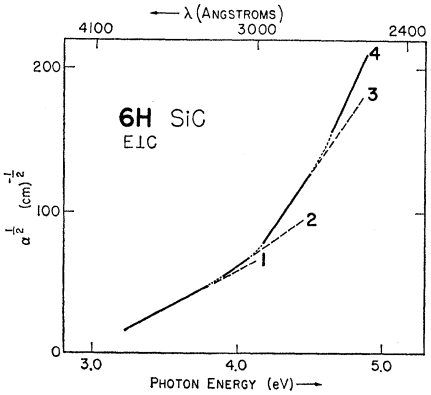

FIG. 1. Plot of $\alpha^{1/2}$ versus $h\nu$ over the whole range of measurements, with data from many samples. Measured values fall on straight-line segments (solid), or in transitional regions (dotted). The four straight-line segments are extrapolated (dashed), and numbered to facilitate the discussion.

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[6] W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Phys. Rev. **139**, A1262 (1965), Sec. XV.

[7] F. Bassani and M. Yoshimine, Phys. Rev. **130**, 20 (1963); F. Herman, R. L. Kortum, and C. D. Kuglin, Int. J. Quantum Chem. **1S**, 533 (1967).

[8] Reference 1, Sec. IV C.

[9] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957); **111**, 1245 (1958).

[10] T. P. McLean, in *Progress in Semiconductors* (Heywood and Co., Ltd., London, 1960), Vol. 5, p. 55.

[11] B. O. Seraphin and N. Bottka, Phys. Rev. **145**, 628 (1966).

[12] F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 299.

edges, or unallowed direct transitions. We do not consider exciton absorption, because the exciton structure at higher thresholds is suppressed by lifetime broadening.[13]

In absorption, both direct and indirect thresholds are observable and, in principle, are easily distinguished by their energy dependence. However, in practice, the problem is to isolate the incremental absorption from the background due to the earlier gaps.

III. EXPERIMENTAL PROCEDURES

A. Sample Preparation

Relatively pure hexagonal platelets of SiC were vapor grown in a carbon-tube furnace.[14] About 20 single polytype *6H* crystals were identified by their Laue-transmission patterns. Crystals ranging in thickness from 3.6 to 200 μ were mounted on apertures. The 3.6-μ sample was a small portion (about 0.3 mm^2) extending from the edge of a larger crystal, and its thickness was measured by observing its transmission-interference fringes in a spectral region of low absorption.[15]

Samples thinner than 3.6 μ were needed for absorption measurements above 4.6 eV, and were obtained by grinding and polishing *6H* crystals bonded to Suprasil II[16] with Type 650 O-I Glass Resin.[17] The thinnest sample obtained in this way was 1.8 μ, the thickness being determined by comparing its absorption with that of a sample of known thickness in a spectral region in which good absorption measurements could be made on both. A comparison of results on polished and unpolished samples showed that their absorption edges were in good agreement in the energy range over which such comparisons were possible.

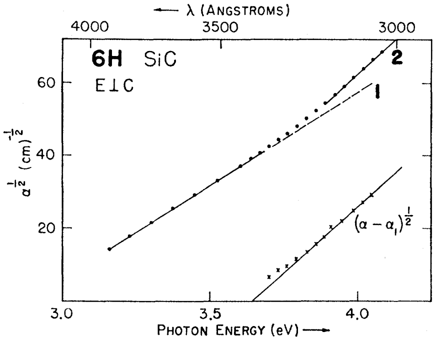

Fig. 2. Portion of data to illustrate the extrapolation and subtraction procedure. At the higher energies, the total absorption α is the sum of two parts α_1 and α_2. Values of α_1 are obtained from the dashed extrapolated line (1), and are subtracted to give $\alpha-\alpha_1=\alpha_2$. The square root of α_2 is then plotted (bottom right) to obtain values of A_2 and E_{g2}.

Table I. Parameters used in fitting Fig. 1, and estimated values of E_g when some allowance is made for exciton structure.

A (10^3 cm^{-1} eV^{-2})	Fitted E_g (eV)	Estimated E_g (eV)
2.8	2.90	3.0
4.5	3.65	3.7
28.0	4.05	4.1
50.0	4.50	4.6

B. Measurements of Transmitted Light

The relative transmission of the samples was measured by a standard comparison method. We used a Perkin-Elmer 83 monochromator with an ultrapure silica prism. The light source was a regulated xenon arc, and scattered light was reduced by the use of Corning filters, and, above 3.8 eV, by various combinations of liquid uv filters.[18] At the higher energies it becomes increasingly hard to find good filter combinations. Some combinations are good only in a small spectral range.

Samples of the proper thickness were chosen to give a convenient range of optical densities for each spectral region. The samples were at room temperature for all measurements.

Accurate measurements are more difficult at the higher photon energies because of the decreasing xenon-arc intensity, increasing scattered light, small sample aperture (for the unpolished specimens), and the large fractional absorption in even the thinnest sample. Although the spectral resolution was good at low energies and adequate to about 4.6 eV, it became somewhat unsatisfactory above 4.6 eV, being about 0.05 eV.

IV. EXPERIMENTAL RESULTS

The results from all samples are combined and plotted in Fig. 1 as $\alpha^{1/2}$ *versus* photon energy. The plot shows four linear segments (solid lines), connected by transition regions (dotted). The linear parts are extrapolated (broken lines) and numbered. Experimental points fall within the width of the lines in the first three segments, but there is more uncertainty in the fourth. The data can be fitted by Eq. (1), using the values of A_i and E_i shown in Table I. The absorption coefficient at 4.9 eV is about 4.6×10^4 cm^{-1}.

The first straight-line segment extrapolates to zero absorption at about 2.9 eV, but an interpretation of the omitted nonlinear exciton region[1] shows that the energy gap is about 3.0 eV. It is not possible to make a similar interpretation for the other segments because of the large background absorption due to earlier gaps. Hence, the fitted values of E_g listed in Table I are expected to

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[13] T. P. McLean and E. G. S. Paige, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and The Physical Society, London, 1962), p. 450.

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

[15] W. J. Choyke and Lyle Patrick, J. Opt. Soc. Am. **58**, 377 (1968).

[16] From Amersil Quartz Division of Englehard Industries, Inc.,

[17] Obtained from Owens-Illinois Technical Center.

[18] M. Kasha, J. Opt. Soc. Am. 38, 929 (1948).

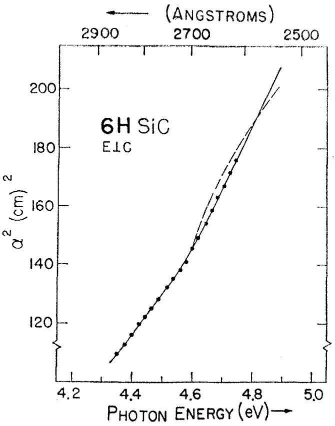

FIG. 3. Comparison of measured absorption (solid line) with the expected absorption on the assumption of a direct gap at 4.6 eV (dashed line). The strength of the direct absorption was chosen to make the total absorption agree with that observed at 4.8 eV. The data points were obtained by measurements on a thin as-grown platelet. The solid line at higher energies was obtained by measurements on ground and polished samples.

be too low. Somewhat higher values of E_g are given in the last column as estimated gaps.

An example of the extrapolation and subtraction procedure is shown in Fig. 2. The partial-absorption constant α_1 found by extrapolating the first segment is subtracted from the total α, and $(\alpha-\alpha_1)^{1/2}$ is plotted in the lower part of the figure. When $\alpha-\alpha_1$ is small, the uncertainty is large, so the exciton part due to the second gap cannot be found. Even if $\alpha-\alpha_1$ were known accurately, it is probable that lifetime broadening of the absorption edge would make it difficult to identify the exciton and phonon structure.[13] Thus, extrapolation to zero absorption provides empirical constants for fitting the data, but does not yield the energy gap with much accuracy.

The same procedure was applied to the third and fourth segments. The fourth threshold appears at about 4.6 eV, the value suggested for the first direct gap by reflectance measurements.[3] In view of the increasing theoretical and experimental uncertainties at the highest photon energies, it is important to consider whether our data can determine unequivocally whether the fourth gap is direct or indirect. This question will be considered in the next section. The other three gaps are almost[19] certainly indirect, but we are not able to identify the bands involved.

Our procedure is not sensitive enough to detect thresholds that are weak compared with the background. Such weak thresholds probably include all those which are not apparent in the large zone, but only in the Brillouin-zone picture.

V. DISCUSSION

Indirect transitions proceed through a number of intermediate states, with those favored for which the energy denominators are smallest. One or more of the energy denominators becomes very small as the region of direct transitions is approached, and it is clear from the reflectivity that the direct transitions begin soon after, if not at 4.6 eV. Thus, the parameter A_1, which we regard as constant, may actually change by a factor of 5 or more[20] between 3.0 and 4.1 eV, where the third threshold appears. The much larger value of A_3 partly reflects the decreasing energy denominators, and to some extent corrects for the growing inadequacy of the constants A_1 and A_2.

It is apparent that the occurrence of straight-line segments in the composite data is to some extent accidental, and we should not have too much confidence in the validity of our extrapolation procedure, especially as the direct transition region is approached. Thus, the incremental absorption at the fourth threshold is the least certain. Unfortunately, the total absorption is also the most uncertain here because of the experimental difficulties discussed in Sec. III B.

In Fig. 3 we show the high-energy portion of our absorption data, with points indicating values obtained from the 3.6-μ sample. Beyond the last point the data were obtained from measurements on ground and polished samples. The dashed line is obtained by adding, to the absorption indicated in Fig. 1 by the extrapolated third segment, a portion with the energy dependence $(h\nu-E_g)^{1/2}$, i.e., the expected absorption for a direct gap. We have taken $E_g=4.6$ eV and have adjusted this portion to coincide with the experimental curve at 4.8 eV also. The question is whether this dashed curve is clearly inappropriate, in view of the extrapolation and experimental uncertainties, including our rather poor resolution in this region. We think it is not possible to give a definite answer.

Although structure in the reflectance can only be explained by a direct threshold, we should point out that the structure shown in Ref. 3 is very weak, certainly not much more than the experimental uncertainty; furthermore, the condition of the crystal surface is critical in reflectance measurements, and can introduce spurious structure.[21] We conclude, finally, that we cannot yet be sure whether the absorption threshold near 4.6 eV is direct or indirect.

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[19] Transitions at some of the direct gaps introduced by the polytype structure are *forbidden*, with an energy dependence $(h\nu-E_g)^{3/2}$. Such transitions might occur before the first *allowed* direct transition, and their energy dependence would make it difficult to distinguish them from allowed indirect transitions. However, since the polytype "superlattice" potential is weak, such transitions would be both weak and forbidden, and therefore probably unobservable.

[20] The second-order matrix element has a denominator ΔE, hence the transition probability is proportional to $(\Delta E)^{-2}$.

[21] There have been uncertainties in the identification of the lowest direct gap in diamond because of the lack of reproducibility in reflectance measurements. See R. A. Roberts and W. C. Walker, Phys. Rev. **161**, 730 (1967).