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Infrared Properties of Hexagonal Silicon Carbide

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Infrared transmission and reflectivity measurements from 1 to 25 μ (microns) have been made on several samples of green alpha (hexagonal) SiC. The residual ray bands have been observed for the ordinary and extraordinary rays. The resonance frequencies are 2.380×10^{13} sec^{-1} (12.60 μ) and 2.356×10^{13} sec^{-1} (12.73 μ), respectively. From the reflectivity the high-frequency dielectric constant is found to be 6.7. A careful analysis shows that the residual ray bands can be fitted within experimental error by the classical dispersion theory with the correct choice of the dispersion parameters. From the parameters the value 10.0 is obtained for the low-frequency dielectric constant. The effective charge is 0.94*e*. Complete description of the residual ray band for the extraordinary ray required, in addition to the main resonance, a weak resonance at 2.647×10^{13} sec^{-1} (11.33 μ). A study on the effects of several different surface treatments shows the reflectivities reported here are an intrinsic property of the crystal. The room-temperature absorption coefficient as a function of wavelength in the range 1 to 10 μ has been determined from transmission measurements. A number of weak lattice bands are observed between 5 and 10 μ.

I. INTRODUCTION

ALTHOUGH the earliest infrared measurement of silicon carbide dates back to 1908, information regarding the infrared optical properties is meager, particularly when compared to the large amount of work done in recent years on silicon and germanium. The present measurements were made on hexagonal silicon carbide in the wavelength range from 1 μ (micron) to 25 μ. This region includes impurity effects (1–5 μ), a number of weak lattice bands (5–10 μ), and the fundamental lattice absorption band at 12.60 μ.

The early reflection measurements of Coblentz[1] and of Schaefer and Thomas[2] showed the strong reflectivity band (reststrahlen band) at approximately 12 μ. The crystals used, presumably of the hexagonal form, were too thick for accurate transmission measurements. However, the latter authors found that their material was transparent from 1 to $\sim$6 μ. The specimen was opaque beyond 6 μ except for a narrow transparent window at $\sim$6.9 μ. They concluded that the absorption in the 6-μ region is due to the first harmonic of the 12-μ fundamental lattice band. The absorption beyond 6.9 μ is due to the onset of the fundamental. More recently, the transmission of hexagonal SiC has been studied by Ramdas,[3] who showed that there are several additional absorption bands. Some of these bands are between 6.9 μ and the fundamental absorption band. However, the samples used by Ramdas were also thick ($d\gtrsim 0.1$ mm) so that the transmission throughout the 5–10 μ region was quite low and the absorption bands difficult to observe. Moreover, there is no evidence to indicate that any of the bands are an intrinsic property of the lattice and not related to the presence of impurities. Choyke and Patrick,[4] who have studied the visible and ultraviolet regions, report that the intrinsic absorption edge for hexagonal SiC, corresponding to the excitation of electrons from the valence to the conduction band, falls at 2.86 ev (0.433 μ). Philipp[5] has shown that the cubic (β) and hexagonal (α) forms have different absorption edges. An unpublished reflectivity measurement of α SiC by Picus is quoted in the review article of Burstein and Egli.[6] This measurement showed the familiar 12-μ reflectivity band with an additional smaller band near 12.5 μ. Mathieu and Poulet[7] studied the radiation scattered at 90° with respect to the incident beam for both polarized and unpolarized radiation. They find lattice vibrations at the wave numbers 335, 764, 789, 797, 966, and 969 cm^{-1}.

Crystallographically SiC presents a complicated picture because of the large number of hexagonal and rhombohedral modifications,[8] and because of a tendency to show one-dimensional disorder in the axial direction.[9] Ramsdell and Kohn[10] list one cubic form with space group T_d^2, four hexagonal forms with space group C_{6V}^4, and nine rhombohedral forms with space group C_{3V}^5 or C_{3V}^1. (For definitions and descriptions of space groups see Bragg.[11]) A good description and correlation of the various structures has been given by Ramsdell[12] and also Wyckoff.[13] Following Wyckoff we show in Fig. 1 three hexagonal layers labeled 0, 1, and 2; these layers are identical except for being displaced from one another. All the forms of SiC correspond to some regularly repeating arrangement of these layers of carbon atoms one upon another at the uniform spacing of 2.52 A. The complete structure is then obtained by placing a silicon atom above every carbon at the Si-C

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[1] W. Coblentz, Carnegie Institution Report, 1908 (unpublished).
[2] C. Schaefer and M. Thomas, Z. Physik **12**, 339 (1923).
[3] A. K. Ramdas, Proc. Indian Acad. Sci. **37A**, 571 (1953).
[4] W. Choyke and L. Patrick, Phys. Rev. **105**, 1721 (1957).
[5] H. Philipp (private communication).
[6] E. Burstein and P. Egli, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 1455.
[7] J. P. Mathieu and H. Poulet, Compt. rend. **244**, 2794 (1957).
[8] N. Thibault, Am. Mineral. **29**, 327 (1944).
[9] H. Jagodzinski, Acta Cryst. **7**, 300 (1954).
[10] L. Ramsdell and J. Kohn, Acta Cryst. **5**, 215 (1952).
[11] W. L. Bragg, *The Crystalline State* (G. Bell and Sons, Ltd., London, 1953), Vol. I.
[12] L. Ramsdell, Am. Mineral. **32**, 64 (1947).
[13] R. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951).

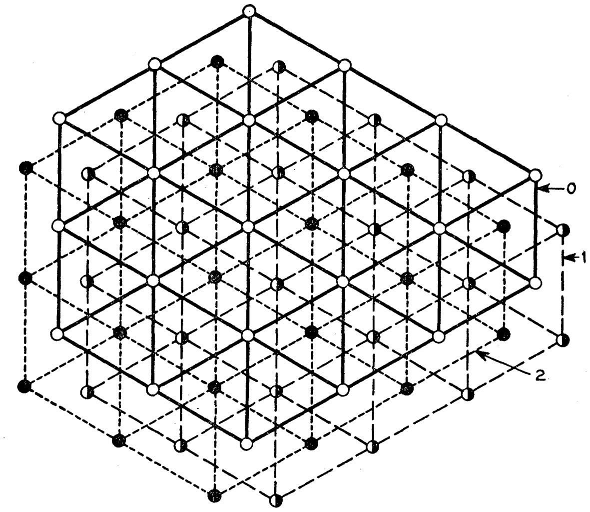

FIG. 1. Three hexagonal layers of carbon atoms from which any of the forms of SiC may be constructed. A silicon atom is above each carbon atom at a distance of 1.89 A.

distance of 1.89 A. In the resulting structure each atom of one kind has four nearest neighbors of the other kind at the regular tetrahedral positions. No distortion or dilation of the tetrahedra from one modification to another can be proved from the present x-ray measurements.

We list below the important structural data as given by Wyckoff and also Lundquist's[14] more recent and accurate values for the α-II form.

Type	Structure	Space group	Molecules	Sequence	a(A)	c(A)
β	Cub.ZnS	T_d^2	1	012	3.073	7.528
α-II	Hex.	C_{6V}^4	6	012021	3.073	15.08
α-II[14]	...	...	...	...	3.0800	15.098

The number of molecules listed refers to the true unit cell, which for the rhombohedral forms including the β form, is one third the number of hexagonal layers. In the hexagonal forms the number of molecules is equal to the number of layers. The sequence refers to the arrangement of layers in the axial direction. The a and c are the hexagonal cell dimensions. The unit cube of the β form containing four molecules has an edge[14] of 4.356 A.

There has been considerable speculation about the origin of the various modifications of SiC. Ramsdell[12] shows that the rhombohedral forms are derived from the α-II form by inserting a stacking fault at an appropriate regular interval. Frank[15] has suggested that screw dislocations stabilize the repetition periods of the stacking faults during growth. Growth spirals have been observed by Verma[16] on [0001] faces. Jagodzinski[17] reports that one-dimensional disorder in the axial direction is very common in SiC. He suggests that the stacking faults are due to edge dislocations lying in the [0001] planes. Then he proposes that a regular sequence of stacking faults superposed on a relatively small disorder is what one would expect thermodynamically from consideration of the vibration entropy which favors an ordered structure and the configuration entropy which favors a disordered structure.

II. EXPERIMENTAL RESULTS

A. Reflectivity Studies

The α-II SiC is produced in great quantity commercially. The specimens are transparent or green pyramidal crystals about 3 mm high and often larger than 25 mm^2 in basal area. X-ray measurements show the base of the pyramids to be an [0001] face. Crystals can be found where this face, as grown, is a good optical surface. The green color is characteristic of n-type material with a resistivity greater than ~1 ohm cm.[18] The crystals were supplied by the Exolon Corporation.

The solid curve in Fig. 2 gives the reflectivity, measured at near normal incidence, of a grown [0001] surface of α-II SiC. The dashed curve in Fig. 2 shows the reflectivity from the same sample when the grown surface has been ground and polished. The grinding and polishing is done by using diamond abrasives on copper plates. The two curves are the same at short and long wavelengths but differ considerably within the reflectivity band. The polished surface shows a shoulder at ~12.5 μ which is the same wavelength as the secondary peak in Picus' curve.[6] If the polished surface is oxidized for 2 hours at 1000°C, the specimen will have the reflectivity given by the third curve in Fig. 2. The small 9.3-μ reflection band is indicative of the presence of a silicon oxide layer on the sample surface.[19] The drop in reflection between 10 and 12 μ is due to absorption by this layer. If the oxide layer is removed by an HF wash, the reflectivity returns to that of the grown surface (solid curve). This sequence of

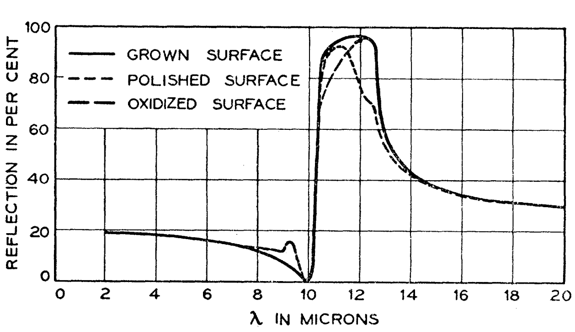

FIG. 2. The ordinary ray reflectivity as a function of wavelength for α-II SiC with three different surface conditions.

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[14] D. Lundquist, Acta Chem Scand. **2**, 177 (1948).

[15] F. Frank, Phil. Mag. **42**, 1014 (1951).

[16] A. Verma, Phil. Mag. **42**, 1005 (1951).

[17] H. Jagodzinski, Acta Cryst. **7**, 300 (1954).

[18] G. Busch, Helv. Phys. Acta **19**, 167 (1946).

[19] Schaefer, Matossi, and Wirtz, Z. Physik **89**, 210 (1934); F. Matossi and H. Krueger, Z. Physik **99**, 1 (1936).

surface treatments indicates that the reflectivity of the polished surface is not characteristic of the SiC bulk properties but rather is related to the damaged layer on the surface. From data to be presented we will find that this contention is supported by the fact that only in the spectral region where the absorption is very large do the two surfaces (grown and polished) differ in their reflectivity. We shall therefore assume that the solid curve is the reflectivity determined by the bulk properties of the material and not influenced by surface effects.

Several specimens of α-II SiC were prepared with the optic axis lying in the polished surface. The surfaces were oxidized and washed as described previously. The reflectivity of the sample when the electric vector is polarized perpendicular to the optic axis (ordinary ray) is the same as shown by the solid curve in Fig. 2. The measured reflectivity of the extraordinary ray is given by the points in Fig. 3. In this case, the reflectivity band is shifted approximately 0.1 μ to longer wavelengths and has a pronounced dip at 11.3 μ. The dip decreases continuously as the direction of polarization is rotated from parallel to perpendicular to the optic axis.

B. Transmission Studies

Transmission studies of α-SiC have been made at room temperature by using specimens prepared with plane parallel surfaces and with thicknesses between 0.2 and 0.04 mm. The measurements cover the wavelength range from 1 to 15 μ and were made using the conventional sample in-sample out technique. The absorption coefficient was calculated from the measured transmission by using the expression[20]

$$T=\frac{(1-R)^2e^{-\alpha x}}{1-R^2e^{-2\alpha x}},$$

where x is the sample thickness, α is the absorption coefficient, and R is the reflectivity for the same wavelength at which the transmission, T, is measured. The values of R are taken from the solid curve in Fig. 2. By using samples of different thicknesses, the absorption coefficient was shown to be independent of the thickness. Figure 4 shows the absorption coefficient as a function of wavelength for three different colored regions of a green SiC specimen. From the colors we know that the regions of greatest and least absorption correspond to the greatest and least impurity concentrations, respectively.[21] By moving the specimen through the light beam, the absorption was found to be nearly constant within each region. A number of absorption bands are seen at wavelengths greater than 5.5 μ. The height of each band measured above the level of the 4–5 μ absorption is the same for all three regions of the crystal and the bands are therefore attributed to the SiC lattice. Transmission measurements for the ordinary and extraordinary rays show the bands are present in both cases.

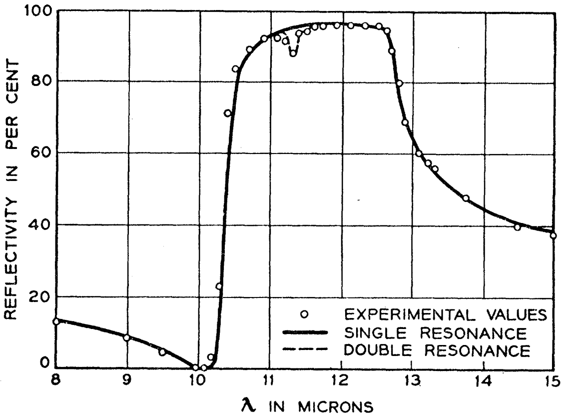

FIG. 3. Reflectivity *vs* wavelength of α-II SiC for the extraordinary ray. The points are experimental values and the curves are theoretically calculated.

III. DISCUSSION OF RESULTS

According to the classical dispersion theory of crystals,[22] the susceptibility χ and conductivity σ in the neighborhood of a resonance frequency ν_0 are given by

$$\chi=\rho\frac{1-\nu^2}{(1-\nu^2)^2+\gamma^2\nu^2}, \tag{1}$$

and

$$\frac{\sigma}{\nu}=2\pi\rho\frac{\gamma\nu}{(1-\nu^2)^2+\gamma^2\nu^2}, \tag{2}$$

where ν is the measured frequency divided by ν_0, σ is the conductivity divided by ν_0, and the dimensionless parameters γ and ρ may be called the width and strength of the resonance, respectively. In the Lorentz theory, ρ is given by

$$\rho=\frac{Ne^2}{4\pi^2m^*\nu_0^2}, \tag{3}$$

where N is the concentration of ion pairs and m^* is their reduced mass. The index of refraction, n, and extinction coefficient, k, are given by

$$n^2=\tfrac{1}{2}\{[\epsilon^2+4(\sigma/\nu)^2]^{\frac{1}{2}}+\epsilon\}, \tag{4}$$

and

$$k^2=\tfrac{1}{2}\{[\epsilon^2+4(\sigma/\nu)^2]^{\frac{1}{2}}-\epsilon\}, \tag{5}$$

where

$$\epsilon=\epsilon_0+4\pi\chi, \tag{6}$$

and ϵ_0 is the high-frequency ($\nu\gg1$) dielectric constant.

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[20] H. Y. Fan and M. Becker, *Symposium Volume of the Reading Conference*, edited by H. K. Henisch (Butterworths Scientific Publications, London, 1951).

[21] G. Busch and H. Fabhart, Helv. Phys. Acta **19**, 463 (1946).

[22] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 17.

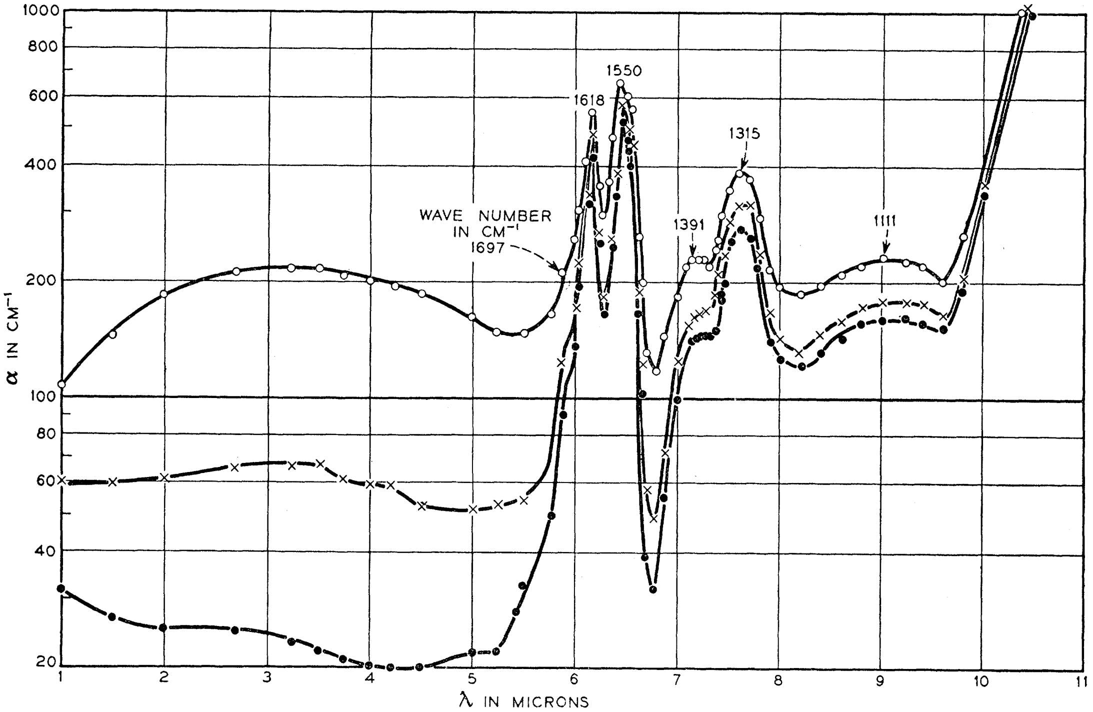

FIG. 4. Absorption coefficient as a function of wavelength of α-II SiC. The three curves are for regions of a specimen with different impurity concentration.

A knowledge of ρ, γ, ν_0, and ϵ_0 allows the optical parameters, n and k, to be calculated. The optical constants n and k as functions of frequency completely describe the optical properties of a cubic crystal such as β-SiC. For a uniaxial crystal such as α-II SiC we may hope to describe the absorption of the ordinary ray with one set of parameters ρ, γ, ν_0, and ϵ_0, and that of the extraordinary ray with a somewhat different set.

The theoretical reflectivity for normal incidence is

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}. \tag{7}$$

Figure 5 shows the experimental data for the reflectivity of the ordinary ray from α-II SiC. The solid curve is the R calculated from (7) for the parameters

$$\begin{aligned} &\rho=0.263, \\ &\gamma=0.006, \\ &\nu_0=2.380\times10^{13}\ \text{sec}^{-1}\ (12.60\,\mu), \\ &\epsilon_0=6.7. \end{aligned} \tag{8}$$

The optical constants, n and k, as functions of wavelength are given in Fig. 6. The parameters (8) were selected to obtain a best fit by trial and error with the aid of an IBM-650 computer. The agreement between theory and experiment is considerably better than has been observed for the fundamental reflection bands in alkali halides[23] or MgO.[24] In these crystals one or more subsidiary maxima are observed on the short-wavelength side of the main band.

In obtaining a theoretical fit to the data we have found that the following principles apply:

a. The initial choice of ν_0 should correspond to the steepest point on the long wavelength side of the reflection peak. Alternatively one could use Havelock's formula[25]

$$\nu_0=\nu_{\max}\left[1+\frac{n_+{}^2-n_-{}^2}{6n_-{}^2-4}\right]^{\frac{1}{2}}, \tag{9}$$

where $\nu_{\max}$ is the frequency at the reflectivity maximum, and n_+ and n_- are the limiting indexes of refraction at long and short wavelengths, respectively.

b. The initial choice of ϵ_0 should give the observed limiting reflectivity at short wavelengths according to the formula

$$R_{\nu\to\infty}=\left[\frac{\epsilon_0^{\frac{1}{2}}-1}{\epsilon_0^{\frac{1}{2}}+1}\right]^2. \tag{10}$$

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[23] M. Czerny, Z. Physik **65**, 600 (1930); R. Barnes and M. Czerny, Z. Physik **72**, 447 (1931); R. Barnes, Z. Physik **75**, 723 (1932); K. Korth, Nachr. Akad. Wiss. Gottingen Math-Phys. Kl. 576 (1932); C. Cartwright and M. Czerny; Z. Physik **85**, 269 (1933); C. Cartwright and M. Czerny, Z. Physik **90**, 457 (1934); H. Hohls, Ann. Physik **29**, 433 (1937).

[24] Burstein, Oberly, and Plyler, Proc. Indian Acad. Sci. **28**, 388 (1948).

[25] T. H. Havelock, Proc. Roy. Soc. (London) **A105**, 488 (1924).

c. The initial choice of ρ should give the correct limiting reflectivity on the long wavelength side of the band. Alternatively, it may be chosen to give the static dielectric constant according to formulas (1) and (6) in the limit $\nu \rightarrow 0$.

d. The initial choice of γ is governed by the maximum reflectivity. The approximation

$$\max R \sim 1-(\gamma/\pi\rho) \tag{11}$$

is rough but useful. From these parameters a theoretical R curve is calculated. Assuming that there is no need to readjust ϵ_0, we fix ρ, γ, ν_0 as follows:

e. Leaving ϵ_0, ν_0, and γ fixed, adjust ρ by trial and error to give the correct width to the reflection band.

f. Leaving ϵ_0, ν_0, and the new ρ fixed, adjust γ to give the correct maximum reflectivity.

g. Finally ν_0 is adjusted to shift the theoretical curve into alignment with the experimental curve. This prescription succeeds only in ideal cases such as we have here, and in many cases no fit can be found. It is therefore significant that the single-resonance classical formulas give an excellent fit to the measured reflectivity of the extraordinary ray in α-II SiC.

Our value for the long-wavelength dielectric constant is

$$\epsilon = 10.0.$$

From microwave measurements Hofman, Lely, and Volger[26] give the value 10.2 ± 0.2. From this agreement we conclude that there are no strong lattice absorption bands between 12.6 μ and the microwave region.

The solid curve in Fig. 3 is the single resonance calculation for the reflectivity of the extraordinary ray. The parameters used in this case are

$$\begin{aligned} \rho &= 0.263, \\ \gamma &= 0.007, \\ \nu_0 &= 2.356 \times 10^{13}\ \mathrm{sec}^{-1}, \\ \epsilon_0 &= 6.7, \end{aligned} \tag{12}$$

which are nearly the same as those in (8). However, as seen in Fig. 3, the single-resonance curve does not completely describe the reflectivity of the extraordinary ray. The experimental points indicate a dip at 11.3 μ which is not present in the solid curve. We have sought to characterize the dip by fitting the observed reflectivity with a two-resonance theory. The procedure is to write χ and $\sigma_0\nu$ each as the sum of two terms of the form (1), (2), and (6). The parameters

$$\begin{array}{ll} \rho_1 = 0.262, & \rho_2 = 0.006, \\ \gamma_1 = 0.007 \pm 0.0005, & \gamma_2 = 0.0055 \pm 0.0005, \\ \nu_1 = 2.356 \times 10^{13}\ \mathrm{sec}^{-1}, & \nu_2 = 2.647 \times 10^{13}\ \mathrm{sec}^{-1}, \\ \epsilon_0 = 6.7 \pm 0.1, & \epsilon_0 = 6.7 \pm 0.01, \end{array} \tag{13}$$

give a reasonable fit to the data. The double resonance differs from the single resonance in Fig. 3 only in the dashed portion of the curve. The first set of parameters is nearly the same as (12) and describes what we continue to call the fundamental resonance. The second set describes a weak resonance having a strength approximately 0.3% that of the fundamental. The double resonance used in this case brings to mind the subsidiary maxima often observed in other ionic crystals.

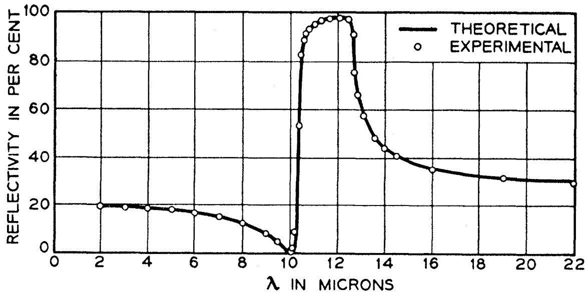

FIG. 5. The points are the experimental values of the ordinary ray reflectivity of α-II SiC. The theoretical curve is also shown.

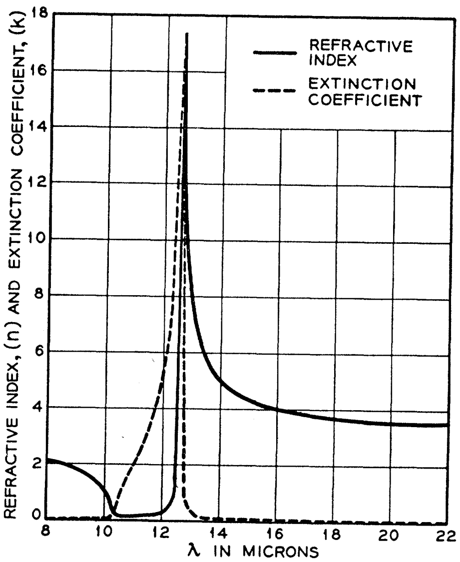

FIG. 6. The theoretically calculated optical constants for α-II SiC.

In an isotropic polar crystal the frequency ν_L for long-wavelength longitudinal vibrations is given by[27]

$$\nu_L/\nu_0 = (\epsilon'/\epsilon_0)^{\frac{1}{2}}, \tag{14}$$

where ν_0 is the infrared fundamental resonance frequency, and ϵ_0 and ϵ' are respectively the high-frequency and low-frequency dielectric constants. The only anisotropy in the optical properties of α-II SiC that we have found is the small shift ν_0 between the ordinary and extraordinary ray. One would also expect two slightly different longitudinal frequencies. Assuming

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[26] Hofman, Lely, and Volger, Physica **23**, 236 (1957).

[27] Lyddane, Sachs, and Teller, Phys. Rev. **59**, 673 (1941).

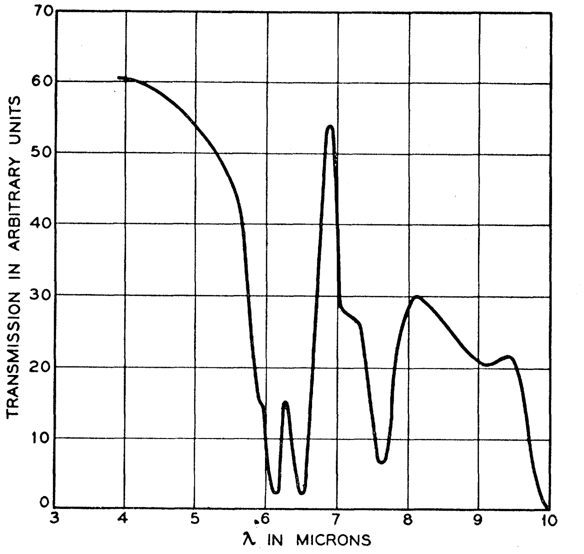

FIG. 7. The experimental transmission as a function of wavelength for β SiC. The transmission is on an arbitrary scale.

that (14) may be used for uniaxial crystals, we calculate for longitudinal waves propagating along the optic axis $\nu_L = 2.91 \times 10^{13}$ sec^{-1}. The frequency ν_L for longitudinal waves propagating perpendicular to the optic axis should be slightly different. If we use (14) with the infrared frequency for the extraordinary ray, we obtain 2.88×10^{-13} sec^{-1}, which is perhaps a lower limit for ν_L. These are rather close to two of the frequencies reported by Mathieu and Poulet,[7] 2.91×10^{13} sec^{-1} and 2.90×10^{13} sec^{-1}. The weak resonance ν_2 in (13) is apparently not a longitudinal vibration. Indeed, the excitation of longitudinal vibrations by light is forbidden except through the depolarizing field arising from the boundaries of the sample or inhomogeneities inside the sample.

There is no doubt that silicon carbide must be considered an ionic crystal. The fundamental absorption band is comparable in strength to those found in the alkali halides. Szigeti's formula,[28] which gives the dielectric constant at long wavelengths in terms of the optical refractive index $\epsilon_0^{\frac{1}{2}}$ and the effective charge e^*, may be written

$$\epsilon = \epsilon_0 + 4\pi\rho, \tag{15}$$

with

$$\rho = \frac{Ne^{*2}}{4\pi^2 m^* \nu_0^2}\left[\frac{\epsilon_0+2}{3}\right]^2, \tag{16}$$

where N is the concentration of ion pairs and m^* their reduced mass. It may be noted that this ρ is the same as that appearing in (3) except for the factor $[(\epsilon_0+2)/3]^2$ arising from Szigeti's definition of effective charge. Our measurements and analysis enable us to determine ϵ_0, ν_0, and ρ quite accurately. By using the values

$$N = 4.84 \times 10^{22} \text{ cm}^{-3},$$
$$m^* = 1.396 \times 10^{-23} \text{ g},$$
$$\rho = 0.263,$$
$$\epsilon_0 = 6.7,$$
$$\nu_0 = 2.38 \times 10^{13} \text{ sec}^{-1},$$

we find an effective charge

$$e^*/e = 0.94.$$

By using the reflectivity curve of Picus,[6] Burstein and Egli estimated e^*/e to be ~ 1.3.

The transmission of a polycrystalline cubic SiC specimen[29] has been measured between 4 and 10 μ and is shown in Fig. 7. All of the absorption bands seen in the α-II form (see Fig. 4) are also seen in the cubic material. It has been determined[30] that the transverse optical fundamental is the same for cubic SiC and the ordinary ray in α-II SiC. The value of ν_L for the cubic form is 2.91×10^{13} sec^{-1} ($\lambda = 10.3$ μ) and this should be the highest frequency of the fundamental vibrations. Therefore, the lattice absorption bands at higher frequencies ($\lambda = 5$–10 μ) are interpreted as combination bands. While these bands are an order of magnitude greater in absorption than any of the combination bands in germanium or silicon,[31] they are at least two orders of magnitude smaller than the fundamental resonance in Fig. 6.

The impurity sensitive absorption in the range 1 μ to 5 μ is very much in disagreement with existing theories for both free-carrier absorption[32] and impurity photoionization.[33] Kobayasi[34] (1956) has proposed that β-SiC has a degenerate single-valley conduction band. If this is the case, the 1–5 μ absorption may be due to interband transitions in the conduction band. More recently Kobayasi[34] (1958) has published a calculation predicting a nondegenerate many-valley conduction band similar to that of silicon and in agreement with the hypothesis of Choyke and Patrick.[4] Therefore, we do not as yet have a good understanding of the absorption in this region.

Note.—Since completing the above work, an unpublished report by J. Lely and F. Kröger was brought to the attention of the authors. This report was presented in 1956 at the International Symposium on Semiconductors and Phosphors, Garmisch-Partenkirchen and contains infrared studies of SiC similar to some of the work presented here.

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[28] B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).

[29] This specimen was kindly supplied by Dr. G. Slack of the General Electric Laboratories, Schenectady, New York.

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