

appear predominantly to resemble the line shapes calculated in this paper; these correspond to transitions between Landau levels. At low temperatures, where exciton transitions should be favored, there is as yet insufficient data for a proper comparison.

## ACKNOWLEDGMENTS

We would like to thank Dr. L. M. Roth for reviewing this manuscript and for suggested changes. We would also like to thank H. S. Bennett, Y. Shapira, Dr. J. Furdyna, and K. J. Button for helpful discussions.

## Ultraviolet Optical Properties of Diamond\*

W. C. WALKER† AND J. OSANTOWSKI

*Physics Department, University of California, Santa Barbara, California*

(Received 7 October 1963; revised manuscript received 26 November 1963)

The absolute reflection spectrum of type IIa diamond was measured at room temperature from 4 to 30 eV and analyzed by dispersion techniques to obtain the optical parameters. Structure observed in the dielectric constant near 7, 12, 16, 20, and 24 eV was attributed to interband transitions at critical points in the joint density-of-states function. The new high-energy structure near 16, 20, and 24 eV was assigned to transitions near the *L* point of the Brillouin zone. Experimental interband transition energies are compared to band theory calculations.

## INTRODUCTION

CONSIDERABLE progress has been made recently in our understanding of the detailed physics of tetrahedrally coordinated solids through the comparison of band structure calculations<sup>1</sup> and experimental ultraviolet optical properties.<sup>2</sup> These studies have shown in some detail the similarity in band structure of Ge, Si, and the group III-V compound semiconductors. To a lesser extent this similarity has been shown to extend to certain of the group II-VI compounds. Diamond, the simplest of all tetrahedrally coordinate solids because of its extremely small core composed only the completed 1*S* shell has, however, not received the attention necessary to place it on the same basis as the others of its class in spite of the fact that extensive band calculations were carried out several years ago by Herman<sup>3</sup> using the orthogonalized plane-wave method. Herman's calculations were subsequently shown to be nearly self-consistent by Kleinman and Phillips.<sup>4</sup>

With the exception of a single recent paper by Philipp and Taft,<sup>5</sup> no experimental verification of these calculations has been made for energies greater than that corresponding to the lowest lying transition. In view of the fundamental role of diamond in solid-state

physics and the recent interest in its semiconducting form, such verification is desirable.

The present paper reports measurements of the absolute reflection spectrum of a polished, type IIa diamond for the region 4 to 30 eV. Dispersion relation analysis of the reflectivity was used to obtain the complex dielectric constant as well as the optical constants *n* and *k*. The improved purity of the diamond specimen employed and increased resolution for energies above 12 eV have lead to significant new high-energy results.

## MEASUREMENTS AND ANALYSIS

The absolute reflection spectrum, between 4 and 30 eV of a polished specimen of type IIa diamond<sup>6</sup> was measured at room temperature and at a fixed angle of incidence of 20°. The absolute accuracy of the reflectivity was determined mainly by the experimental scatter which amounted at most to 5% in the region between 12 and 20 eV. Both below and above this region the absolute accuracy of the data was about 3% and the relative accuracy somewhat better. Averaging of several independent measurements allowed structure amounting to 1 or 2% to be determined.

A Jarrell-Ash one-half meter Seya monochromator was used with a bandpass ranging from 3 to 6 Å giving an energy resolution between 0.005 and 0.1 eV depending on the spectral region involved. In the important region between 12 and 20 eV the maximum spacing between source emission lines was 0.7 eV and was more

\* Work supported by the National Aeronautics and Space Administration.

† Currently at Goddard Space Flight Center under a NASA Post-Doctoral Fellowship (on leave from the Physics Department, University of California, Santa Barbara, California).

<sup>1</sup> J. C. Phillips, *Phys. Rev.* **125**, 1931 (1962).

<sup>2</sup> H. Ehrenreich, H. R. Philipp, and J. C. Phillips, *Phys. Rev. Letters* **8**, 59 (1962).

<sup>3</sup> F. Herman, *Phys. Rev.* **93**, 1214 (1954).

<sup>4</sup> L. Kleinman and J. C. Phillips, *Phys. Rev.* **116**, 880 (1959); *ibid.* **125**, 819 (1962).

<sup>5</sup> H. R. Philipp and E. A. Taft, *Phys. Rev.* **127**, 159 (1962).

<sup>6</sup> The type-IIa diamond, a rectangular parallelepiped measuring 1.09×2.98×4.96 mm and weighing 0.28 carat was graciously supplied by Dr. F. A. Raal of the Diamond Research Laboratory, Crown Mines, Johannesburg, South Africa.

typically of the order of 0.2 eV or less. Reflectivities were determined at approximately 130 points.

A dc discharge in hydrogen at a pressure of a few tenths Torr, operated at 1000 V and 350 mA provided a usable continuum extending through the near ultraviolet to 7 eV and a many-lined molecular spectrum from 8 to 12 eV. A Weissler<sup>7</sup> spark source in argon operated at a repetition rate of 60 pulses/sec and at 8 kV provided a sufficiently constant and dense spectrum between 12 and 30 eV to enable the measurements to be performed. Emission lines of multi-ionized oxygen, nitrogen and argon constituted the bulk of the usable radiation in this region. The intensity of the spark source varied between 1 and 5% depending on the emission line used and for many points it was necessary to rely on averages of incident intensities, bracketing a reflection spectrum, to achieve the desired accuracy.

Reflection measurements were made with a vacuum reflectometer which utilized a fixed photomultiplier and a rotatable, fluorescent sensitized light pipe to monitor the incident and reflected beams. Care was taken to keep the optical path of the incident and reflected light identical and to eliminate scattered radiation. The phosphor-light pipe combination discriminates strongly against scattered light and is an excellent detector for reflection and transmission studies.

A dispersion relation analysis was performed on the final reflection spectrum using the Western Data Processing Center's IBM-7094 and a modified version of a program originally written by Nodvik and Greenstreet. To increase the accuracy of the data below 5.5 eV for this analysis, the reflection data were matched to values calculated from published indices of refraction near 3.1 and 5.5 eV.<sup>8</sup> Beyond 27.7 eV the reflection data were extrapolated to 100 eV at 0.2-eV intervals by matching the measured values to a decaying power-law function. The numerical integration for the phase angle of the reflected amplitude was cut off at 100 eV and an extrapolated reflectivity of the order of 0.1%.

## RESULTS

Reflectivity data averaged from several separate measurements are shown in Fig. 1. Peaks are observed at 7.4, 12.6, and 16.5 eV and inflection points leading to shoulders are seen at 19.2 and 22.5 eV. Comparison to the only other spectrum measured over this region, that of Philipp and Taft,<sup>5</sup> shows agreement below 12 eV. At higher energies the present results display more structure. The lack of agreement above 12 eV may be explained by the higher purity of the specimen used in the present work (type IIa rather than type I) and the increased resolution resulting from the more dense emission spectrum employed. Typical type I diamonds are

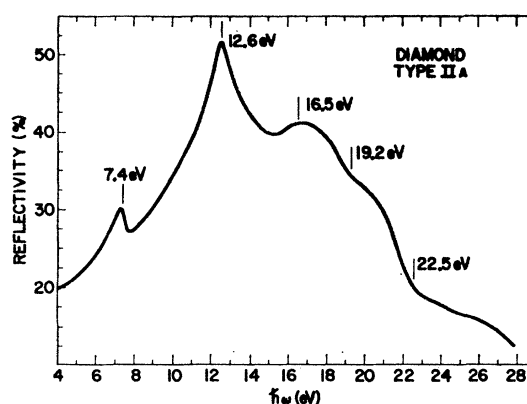


FIG. 1. Reflection spectrum of diamond.

known to have a high concentration ( $10^{20}$  atoms/cm<sup>3</sup>) of dissolved nitrogen.<sup>9</sup> Absorption of this substitutional atomic nitrogen, particularly in the ionization continuum beginning at 14.5 eV,<sup>10</sup> could perhaps account for some of the difference. The maximum reflectivity value of 52% at 12.6 eV is below the 61% value at 12.5 eV observed by Philipp and Taft. Reflectivity values below 5.6 eV were calculated from published values of  $n$ . This procedure was necessary since the measured reflection curve showed a sudden jump at 5.6 eV due to reflections from the rear surface of the crystal. This indicates that the onset of the indirect transition  $\Gamma_{25}' \rightarrow \Delta_1$  occurs at 5.6 eV in agreement with previous results.<sup>5</sup>

Values for the index of refraction  $n$  and the extinction coefficient  $k$  obtained from a dispersion analysis of the data of Fig. 1 are shown in Figs. 2 and 3, respectively. Both  $n$  and  $k$  differ somewhat from those obtained by Philipp and Taft, as would be expected from the differences in the high-energy reflection data. The most significant differences are the smaller values for  $k$  below 12 eV and the large peak in  $n$  at 12.6 eV in the present work. Both of these differences may be attributed to the increased purity of the type-IIa specimen used in the present study over the type-I specimen studied by Philipp and Taft. It is well known, for instance, that type I diamonds display a broadened and enhanced absorption between 5 and 6 eV. Even though the substitutional nitrogen impurity of type I diamonds may amount to  $4 \times 10^{20}$  atoms/cc, the additional absorption due to the impurity is insufficient to account directly for the differences noted except in the immediate vicinity of the first absorption edge. It seems more likely that the present differences are due rather to the distortion of the lattice produced by this high concentration of impurities. In this regard Kaiser and Bond<sup>9</sup> report a relative change in lattice constant of up to  $10^{-4}$  between type-I and type-II specimens.

<sup>7</sup> N. Wainfan, W. C. Walker, and G. L. Weissler, *J. Appl. Phys.* **24**, 1318 (1953).

<sup>8</sup> *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1960), 42nd ed.

<sup>9</sup> W. Kaiser and W. L. Bond, *Phys. Rev.* **115**, 857 (1959).

<sup>10</sup> A. W. Ehler and G. L. Weissler, *J. Opt. Soc. Am.* **45**, 1035 (1955).

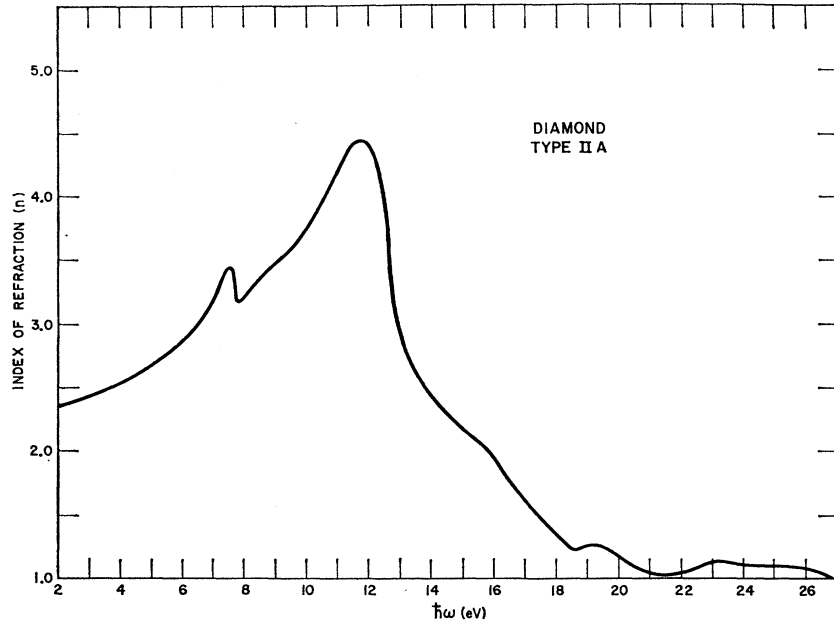


FIG. 2. Spectral dependence of the index of refraction ( $n$ ) of diamond.

It will be noted that the structure in the reflectivity curve near 7 eV shows up as a peak in  $n$  but is absent in  $k$ . This can be explained by the fact that the magnitudes of the  $k$  values in this region are of the order of 0.2 or less. Such small values are not accurately given by the dispersion analysis. The  $k$  values are proportional to the sine of the imaginary part  $\theta$  of the reflected amplitude. Thus as  $\theta$  approaches zero, small errors accumulated in the dispersion inversion become magnified and may even cause meaningless negative values of  $k$  to appear. This situation does not occur in the calculation of the index so that accurate values of  $n$  can be obtained

at small energies. It was found that the  $k$  values near the first absorption band were very sensitive to the extrapolation technique employed. For the reason mentioned above it was not practical to adjust the extrapolation to yield accurate  $k$  values for small energies. Instead the extrapolation was chosen in such a way that the  $n$  values agreed with published values near 2 eV and so that the calculated values of  $n$  and  $k$  were internally consistent.

The correlation of the reflection peaks with basic mechanisms is shown more directly by the real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric constant. These

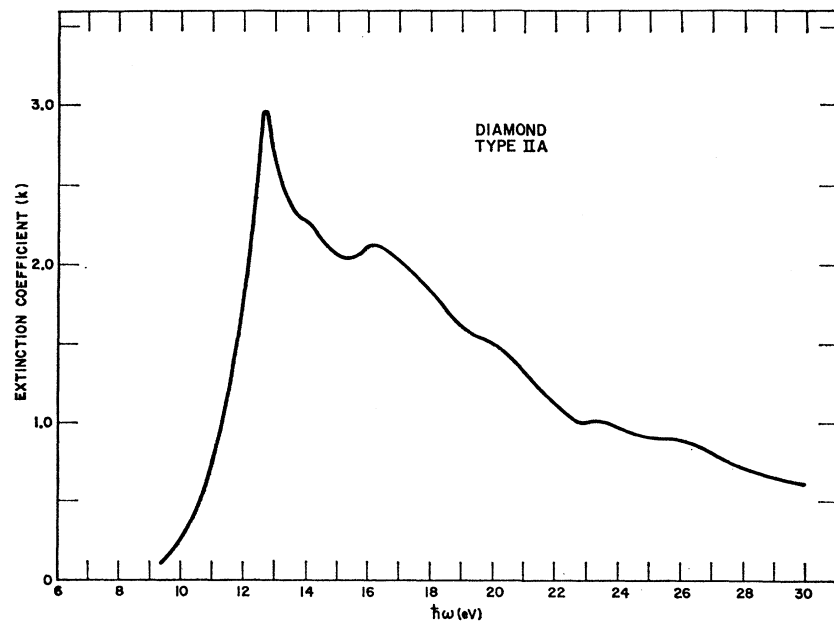


FIG. 3. Spectral dependence of the extinction coefficient ( $k$ ) of diamond.

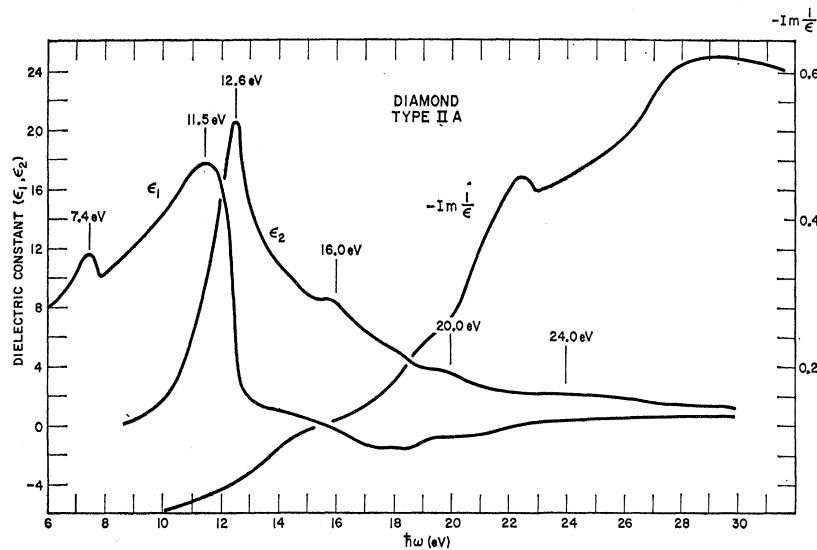


FIG. 4. Spectral dependence of the real part ( $\epsilon_1$ ) and the imaginary part ( $\epsilon_2$ ) of the dielectric constant of diamond.

parameters derived from well-known relations connecting them to  $n$  and  $k$  are shown in Fig. 4. As is the case with  $n$  and  $k$  the values of  $\epsilon_1$  and  $\epsilon_2$  differ somewhat from those of Philipp and Taft.<sup>5</sup> It can be shown that the energy loss per unit volume of the radiation passing through the solid is proportional to  $\epsilon_2\omega$ . Thus, peaks in  $\epsilon_2$  correspond directly to the positions of interband transitions. The present results show three definite transitions at 12.6, 16.0, and 20.0 eV together with an indication of an additional one near 24 eV. The 7.4-eV reflection peak, although due to a direct interband transition, fails to show up strongly in  $\epsilon_2$  for the reason mentioned earlier in the description of the curve for  $k$ . It is clear from Fig. 4 that the reflection peak at 7.4 eV is associated with a maximum in  $\epsilon_1$ , that at 12.6 eV is due to simultaneous maxima in  $\epsilon_1$  and  $\epsilon_2$ , and the higher peaks are due almost entirely to structure in  $\epsilon_2$ .

The energy loss function  $-\text{Im } 1/\epsilon$  is shown also in Fig. 4. Although insufficient electron energy loss data for diamond exists to justify a detailed comparison, certain features of this curve are of interest. The broad peak near 30 eV, while it cannot be taken too seriously due to the sensitivity of the dispersion analysis at energies above 27 eV to the arbitrary extrapolation employed, at least indicates an electron-plasma frequency of this magnitude. This should be compared to the free-electron plasma frequency  $\omega_p \approx 31$  eV calculated on the basis of four free electrons per atom. It is also interesting that a prominent energy loss in carbon at 22 eV coincides with the 22.5-eV peak in the energy loss function.

#### DISCUSSION

In view of the special status of diamond among the covalent bonded solids it is of interest to compare the results of the preceding section with the general be-

havior of the optical properties of Si, Ge, and the III-V compounds. In a recent paper, Philipp and Ehrenreich<sup>11</sup> show that tetrahedrally bonded semiconductors have quite similar optical behavior. They point out that the spectral dependence of the dielectric constant divides naturally into a region governed by valence to conduction-band transitions and a region governed by the electron plasma oscillation. In those materials possessing  $d$  electrons a third region involving transitions originating in the  $d$  band occurs. The dielectric constant reflects these regions by displaying a strongly structured behavior with peaks and shoulders corresponding to the various interband transitions followed by a significant decrease as the interband oscillator strengths become saturated. The dielectric constant then begins to behave much like that for an ideal plasma given by  $\epsilon_1 \approx 1 - (\omega_p/\omega)^2$ , ( $\omega_p$  is the plasma frequency) until  $d$ -band transitions force it to peak once more. Figure 4 shows that a similar situation occurs in diamond. Because the plasma frequency of diamond is large (30 eV) and the  $1s$  core electrons are very strongly bound, the optical properties of diamond are governed solely by valence band transitions. Thus, the peaks in  $\epsilon_1$  at 7.4 and 11.5 eV and in  $\epsilon_2$  at 12.6, 16.0, 20.0, and 24 eV correspond to interband transitions between bands displaying critical points in the joint density of states function as described by Brust, Phillips, and Bassani.<sup>12</sup> The evidence for a 9-eV transition derived by Philipp<sup>5</sup> by considering the 12.6-eV transition as due to an ideal oscillator appears from the present work no longer valid.

By using as guides, estimates of oscillator strengths

<sup>11</sup> H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).

<sup>12</sup> D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 92 (1962).

for various transitions, the "insensitivity"<sup>1,13</sup> of certain transitions to shifts in the core energy and certain crystal selection rules it is possible to make a tentative identification of the above transitions. Thus, in agreement with Philipp and Taft,<sup>5</sup> we can assign the 7.4-eV transition to  $\Gamma_{25}' \rightarrow \Gamma_{15}$  at the center of the Brillouin zone and that at 12.6 eV to the two transitions  $X_4 \rightarrow X_1$  at  $k = (2\pi/a)(100)$  and  $\Sigma_4 \rightarrow \Sigma_1$  at  $k = (2\pi/a)(0.61, 0.61, 0)$ . This assignment can be made with some confidence on the basis of the results of Ref. 12 which show that for a broad range of band structures obtained by varying chemical shifts or crystal potential parameters certain features of the band structure retain the same shape. The pairing of  $X_4 \rightarrow X_1$  and  $\Sigma_4 \rightarrow \Sigma_1$  was shown to be one such feature. An interpretation of the remaining structure may be made by considerations based on oscillator strengths and selection rules. Kleinman and Phillips<sup>4</sup> have shown that the largest part of the oscillator strength comes from the smooth part of the wave function outside the core. This is particularly true in diamond because of the small extent of the core. The oscillator strength for those portions of the wave function outside the core are large between levels which are degenerate in the nearly free-electron approximation. This criterion leads to the consideration of transitions between the states  $\Gamma_{25}'$ ,  $\Gamma_{15}'$ , and  $\Gamma_2'$  at the center of the Brillouin zone,  $L_3'$ ,  $L_1$ ,  $L_3$ , and  $L_2'$  at the  $L$  point and  $X_4$  and  $X_1$  at the  $X$  point. In addition, since the group of the  $k$  vector at  $L$  contains the inversion operator we need consider transitions only between states of opposite parity. Using these criteria, the broad, strong peak at 16.3 eV may be assigned to  $L_3' \rightarrow L_1$ . The hint of structure in the curve for  $k$  near 14 eV is probably due to  $L_3' \rightarrow L_3$ . Assignment of the 20.0 and 24.0 eV transitions is more tentative but they may be at or near  $L_3' \rightarrow L_2'$ . Although this transition cannot occur precisely at  $L$  because of the parity selection rule, transitions near this point may proceed with relatively large oscillator strengths.

The experimental energy gaps and their assigned transitions are summarized in Table I and compared with the theoretical values for these transitions tabu-

TABLE I. Comparison of experimental and band theory interband transitions of diamond.

Transition	Experimental gap $E_{\text{exp}}$ (eV)	Theoretical gap $E_{\text{th}}$ (eV)	$\Delta E$ (eV)
$\Gamma_{25}' \rightarrow \Gamma_{15}$	7.4	6.1	1.3
$X_4 \rightarrow X_1$	12.6	13.8	1.2
$L_3' \rightarrow L_1$	16.3	13.6	2.7
	unresolved, near		
$L_3' \rightarrow L_3$	14.0	13.6	$\sim 0.5$
$L_3' \rightarrow L_2'$	24.0	25.6	1.6

lated by Kleinman and Phillips<sup>4</sup> from calculations based on Herman's crystal potential. These calculated values are essentially the same as those originally obtained by Herman<sup>3</sup> and are felt to be the most accurate yet available. It is clear that the insensitive gaps, as expected, agree better with theoretical results than does the sensitive gap  $L_3' \rightarrow L_1$ . Even for this transition, however, the agreement is remarkably good. Assuming that the insensitive level  $L_3'$  is correctly given by the calculated value, the present assignment would require a shift of the  $L_1$  level upward by 2.7 eV thus separating the nearly coincident  $L_3$  and  $L_1$  levels. The consistency of the agreement between the experimental and theoretical values for the several transitions identified indicates that the absolute accuracy of the band calculation is within 2 eV. It would be extremely interesting to see if a re-evaluation of the band structure of diamond using improved techniques would better the agreement with the sensitive  $L_3' \rightarrow L_1$  transition.

The location of each of these transitions could be improved by low-temperature reflection and fluorescence measurements which may partially resolve the spin-orbit splitting of the  $L_3$  and  $L_3'$  levels as well as separate the  $L_3' \rightarrow L_3$  transition from the 12.6-eV peak.

#### ACKNOWLEDGMENTS

The authors are grateful to Dr. J. C. Phillips of the University of Chicago for supplying much of the information concerning the detailed assignment of the various interband transitions and to Dr. J. Nodvik of the University of Southern California for his help with the original dispersion analysis program.

<sup>13</sup> F. Herman and S. Skillman, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences Publishing House, Prague, 1961), p. 20.