Optical Study of the Electronic Structure of Diamond*

R. A. ROBERTS[†] AND W. C. WALKER

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

(Received 3 April 1967)

In order to resolve some of the experimental discrepancies existing between various published optical studies of diamond, absolute near-normal incidence-reflectance measurements have been taken on a polished type-I and both cleaved and polished type-IIa diamond crystals. These measurements covered the range from 5.5 to 11.5 eV at liquid-nitrogen temperature and from 5.5 to 31 eV at room temperature. The Kramers-Kronig analysis used in this research to determine the phase angle differs from that used in previous work inasmuch as no extrapolation of data outside the measured high-energy limit was required. The dielectric response function $\hat{\epsilon}$ was obtained over a broad energy range (5.5–31 eV). Structure in its imaginary part ϵ_2 occurring at 7.3, 7.8, 12.2, and 23 eV was observed and assigned to direct interband transitions on the basis of recent band calculations. Room-temperature data agreed with the latest previous measurement on type-I diamond over the common energy range (5.5-25 eV). The temperature insensitivity of the first peak suggests that the direct band edge is near 7.3 eV. The previously unobserved temperature-dependent 7.8-eV peak is probably caused by changes in the complex structure of the energy bands near the Γ point, although an exciton interpretation is not excluded. Evidence that the small 23-eV peak may be due to surface contamination is also presented.

INTRODUCTION

R EFLECTANCE measurements combined with the Kramers-Kronig dispersion relationship can be used to determine the dielectric response function $\hat{\epsilon} = \epsilon_1 + i\epsilon_2$ of solids. The imaginary part ϵ_2 is particularly useful because it can be related theoretically to electronic interband transitions through the joint density-of-states function. Because of the theoretical interest in diamond as the simplest covalent material and because of the discrepancies among the optical spectra reported in earlier published work,1-4 it was decided to reinvestigate diamond in greater detail.

Diamonds are classified^{5,6} as type I or type II according to their different infrared and ultraviolet absorption properties. The absorption edge occurs near 3000 Å for the type-I diamonds as compared to 2250 Å for type II. Nitrogen impurities are mainly responsible⁷ for the type-I characteristics. Type-II diamonds can be further subdivided into types IIa and IIb. The type-IIb diamonds show conductivity and phosphorescence effects not observed in the type IIa. Since type-IIa diamonds are considered to best represent the ideal diamond crystal, we examined only types I and IIa.

The first optical study of the intrinsic diamond spectrum was done by Philipp and Taft1 who determined the optical constants of a type-I diamond in the energy range from 5.5 to 23 eV by a Kramers-Kronig analysis

of room-temperature normal-incidence-reflectance data. Structure in ϵ_2 near 7 and 12 eV was observed and associated with interband edge transitions $\Gamma_{25'} \rightarrow \Gamma_{15}$ at the center of the Brillouin zone, or Γ point, and direct transitions $X_4 \rightarrow X_1$ at $k = (2\pi/a)(100)$, respectively.

A later study by Walker and Osantowski² of the absolute reflectance spectrum of a type-IIa specimen at room temperature from 4 to 30 eV showed structure in ϵ_2 near 7, 12, 16, 20, and 24 eV. The 7- and 12-eV peaks were given the same interpretation as that of Philipp and Taft. The new high-energy structure near 16, 20, and 24 eV was assigned to transitions near the L point, $k = (2\pi/a)(111)$, of the Brillouin zone. The structure at 16, 20, and 24 eV not seen by Philipp and Taft was attributed to the increased purity of the sample used by Walker and Osantowski.

Philipp and Taft³ remeasured diamond and obtained a new reflectance curve which differed only slightly from their previous measurement. They extended the measurements to 24.5 eV and observed structure near 24 eV. Philipp and Taft also reanalyzed the data of Walker and Osantowski and found inconsistencies in their results indicating that the experimental reflectance values were too low, at least for energies greater than 16 eV.

Clark, Dean, and Harris⁴ (CDH) performed extensive transmission studies on the indirect absorption edge in diamond, and also recorded the reflectance spectrum between 5 and 14 eV at room temperature and between 5 and 8 eV at 133°K. At room temperature they observed reflectance peaks at 7 and 12 eV and an additional weaker peak at 9 eV. The 9-eV peak was assumed to arise from threshold transitions at the L point. At the lower temperature they observed the 7-eV peak to be sharper, more intense, and shifted slightly to a higher energy as compared to the room-temperature results. In addition, the reflectance at low temperature was observed to drop below the room-temperature value above 7.5 eV.

^{*} Work supported by the National Aeronautics and Space Administration.

[†] Present address: Michelson Laboratories, China Lake, California.

¹ H. R. Philipp and E. A. Taft, Phys. Rev. **127**, 159 (1962). ² W. C. Walker and J. Osantowski, Phys. Rev. **134**, A153 (1964).

^{*} W. C. Walker and J. Osantowski, Phys. Rev. 134, A153 (1964).
* H. R. Philipp and E. A. Taft, Phys. Rev. 136, A1445 (1964).
* C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc. (London) A277, 312 (1964).
* R. Robertson, J. J. Fox, and A. E. Martin, Phil. Trans. Roy. Soc. London, A232, 463 (1943).
* R. Robertson, J. J. Fox, and A. E. Martin, Proc. Roy. Soc. (London) A157, 579 (1936).
* W. Kaiser and W. L. Rond. Phys. Rev. 115 857 (1950).

W. Kaiser and W. L. Bond, Phys. Rev. 115, 857 (1959).

The changes in the 7-eV peak at low temperature observed by CDH were interpreted by Phillips⁸ as due to a hybrid exciton at the Γ point. Consistent with this view he considered the drop in low-temperature reflectance as the start of an antiresonance, and suggested that the low-temperature curve would display a minimum and rejoin the room-temperature value near 8.3 eV. On this basis he placed the direct interband edge $\Gamma_{25'} \rightarrow \Gamma_{15}$ at 8.7 eV rather than near 7 eV as proposed by previous work.¹⁻³ Recent theoretical paper: have both denied⁹ and affirmed¹⁰ the existence of hyperbolic excitons. Thus, at this time the validity of the hybrid exciton model is still uncertain.

In the present study the optical constants of diamond were determined in the energy range between 5.5 and 11.5 eV at liquid-nitrogen temperature and between 5.5 and 31 eV at room temperature from a Kramers-Kronig dispersion analysis of the reflectance spectrum. The results were interpreted in terms of recent bandstructure calculations¹¹⁻¹³ not available to previous experimenters.

EXPERIMENTAL MEASUREMENTS

In this investigation a cleaved $5 \times 3 \times 1$ mm type-IIa diamond, a polished $10 \times 6 \times 1$ mm type-IIa diamond, and a polished $5 \times 5 \times 1$ mm type-I diamond, all of undetermined crystal orientation, were studied. Samples were measured both "as recieved" and after an acetonemethanol rinse followed by a mild overnight baking at 140°C in vacuum. The time taken between cleaving the crystal in air, mounting in the reflectometer and subsequent evacuation to a pressure of 10^{-6} Torr, was about $6 \min$.

The low-temperature reflectometer used to make the absolute reflectance measurements is similar in design to that described by CDH.⁴ Measurements were made at near-normal incidence (11°). A stop was placed between the slit and the sample to reduce the convergence angle and prevent the incident beam from over filling the sample surface. The geometry of the sample and rotating light pipe was such that the same area of the sodium salicylate coated light pipe was illuminated by both the incident and reflected beams. The distance between the sample and light pipe was approximately 1.5 in. Movement of the light pipe to angles other than that for specular reflection indicated negligible scattered light.

For the low-energy work (5.5-11.5 eV), at both liquid-nitrogen and room temperatures, a lithium fluoride window was used as a vacuum seal between the monochromator and reflectometer systems. This window also served to eliminate second-order effects from wavelengths below 1050 Å. A 15 liter/sec ion-titanium sublimation pumping system attached to the reflectometer maintained a chamber pressure less than 10^{-7} Torr. This separate pumping system guaranteed that the sample in the reflectometer was not exposed to oil vapor from the diffusion pump of the monochromator. Oil contamination is a possible cause of some of the discrepancies in earlier measurements. During the highenergy measurements (11.5–31 eV) both the ion pump and the window between the reflectometer and monochromator were removed.

A 1-m normal-incidence scanning monochromator was used with a 1200 line/mm magnesium fluoride coated grating blazed at 1500 Å which gave a first-order dispersion of 8.3 Å/mm. With $300-\mu$ slits, a bandwidth of 4 Å (corresponding to an energy resolution of 0.01 eV at 2000 Å to 0.3 eV at 400 Å) or better was obtained over the region measured. The wavelengths of the source lines were determined to a precision of ± 1 Å. For the 5.5-11.5-eV region, a dc hydrogen-glow discharge in a boron-nitride capillary similar to that described by Rustgi¹⁴ was used. For the high-energy region, argon gas, excited by a thyratron-ignitron controlled pulsed power supply, gave a useful line spectrum from Lyman α (1216 Å) to 400 Å. Bottled gas of prepurified grade was used in both cases without additional filtering.

Using the hydrogen source, reflectance data were obtained with a relative precision of 1%, whereas with the argon source there was a 5% scatter of points on any one run, although 3% structure could be observed by averaging several runs. The data between 13 and 19 eV should be considered less reliable than results at lower or higher energies because the line intensities were least stable in this region.

RESULTS

Figure 1 shows composite reflectance curves for the polished type-I and cleaved type-IIa diamond samples. The curves are the result of assembling the reflectance values below 5.5 eV as calculated from index-of-refraction data, the measured liquid-nitrogen reflectance values between 5.5 and 11 eV, and the room-temperature reflectance values between 11 and 31 eV. The lowtemperature results for the polished type-IIa sample are not shown but are essentially the same as those for the cleaved sample except that the 7-eV structure is less pronounced. No measurement of this sample was made for energies greater than 11.5 eV.

A detailed comparison of the room- and low-temperature data between 5.5 and 11 eV is shown in Fig. 2. The main interest in the low-temperature work in this region is the reflectance behavior between 7 and 8 eV where the small 7.2-eV peak remains virtually un-

⁸ J. C. Phillips, Phys. Rev. 139, A1291 (1965).
⁹ C. B. Duke and B. Segall, Phys. Rev. Letters 17, 19 (1966).
¹⁰ J. Hermanson, Phys. Rev. Letters 18, 170 (1967).
¹¹ W. Saslow, T. K. Bergstresser, and M. L. Cohen, Phys. Rev. Letters 16, 354 (1966).
¹² F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, J. Phys. Soc. Japan Suppl. 21, 7 (1966).
¹³ R. Keown, Phys. Rev. 150, 568 (1966).

¹⁴ O. P. Rustgi, J. Opt. Soc. Am. 55, 630 (1965).



FIG. 1. (a) Composite reflectance spectrum of a polished type-I diamond. (b) Composite reflectance spectrum of a cleaved type-II*a* diamond.

changed from the room-temperature result but a new peak at 7.6 eV unobserved at room temperature becomes apparent. These features were consistently observed for all samples.

Because of the high Debye temperature for diamond (2200°K), we did not expect much difference between



FIG. 2. Detailed comparison of reflectance spectra near 7 eV obtained by Clark, Dean, and Harris (CDH) and Roberts, Roessler, and Walker (RRW).

liquid-nitrogen and room-temperature reflectance measurements¹⁵ and this was verified by our results in the 5.5–11.5-eV region with the exception of the peak near 7.6 eV. With the present apparatus it was not possible to extend the low-temperature measurements beyond 11.5 eV since, with windowless operation, the impurities backstreaming into the reflectometer from the monochromator would build up on the cold sample surface and give reflectance results not intrinsic to diamond. It seems reasonable to assume that the unmeasured lowtemperature reflectance above 11 eV continues to match that at room temperature.

We should mention the large quantitative differences between previous reflection measurements on diamond. For example, the maximum of the 12-eV peak has been observed to be as high as $65\%^3$ and as low as $45\%^{.16}$ A likely explanation of this difference is that it is due to various degrees of contamination of the crystal surface. We found that in the region of flatness from 15 to 19 eV, the reflectance varied from a value of 55% after baking to as low as 32% for a sample left overnight in the reflectometer. It is clear that surface preparation is very critical for reflection measurements and can account for many of the previous discrepancies. Diffusion pump oil is the most likely source of this contamination during windowless operation.

The Kramers-Kronig analysis used in this work was based on a method suggested by Roessler¹⁷ and did not depend upon an extrapolation of the high-energy reflectance data as in previous work. Briefly, the method is as follows. The integral for the reflectance phase angle, which is a function of the reflectance, is divided into three parts: a contribution from below the measured range, one encompassing the measured range, and one from the region above the measured range. The two contributions to the integral for the regions outside the measured range can be written as functions of the particular frequency at which the phase angle is being evaluated times a coefficient which is nearly independent of this particular frequency. Knowledge of two frequencies at which the crystal is transparent, i.e., for which the phase angle is zero, permits evaluation of these coefficients and hence the phase angle at all frequencies below the upper measurement limit.¹⁷

Eighty-five reflectance values were used in the computer program to approximate the reflectance curve by a series of line segments. The density of points chosen was highest in the regions of reflectance structure where rapid changes required short line segments in order to represent the curve. Once the phase angle is known the other optical properties may be determined from stand-

¹⁵ J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18. ¹⁶ D. M. Reessler, Ph.D. thesis, Kings College, London, 1966

⁽unpublished).

¹⁷ D. M. Roessler, Brit. J. Appl. Phys. 16, 1119 (1965); 16, 1359 (1965); 17, 1313 (1966).

ard relations. The sign conventions used in this work are $\hat{n} = n + ik$, $\hat{\epsilon} = \epsilon_1 + i\epsilon_2$, $\epsilon_1 = n^2 - k^2$, and $\epsilon_2 = 2nk$.

The results of the Kramers-Kronig analysis for the real and imaginary parts of the complex dielectric response function for the two types of diamond are shown in Figs. 3 and 4. Also shown in these figures is the energyloss function $-\text{Im}(1/\hat{\epsilon}) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$ which correlates with electron energy-loss experiments.¹⁸

A detailed comparison of our results for the dielectric response function of a type-I diamond with that of Phillip and Taft⁶ is shown in Fig. 5. The only differences are relatively small ones in the absolute magnitude of the peaks and the temperature effects near 7 eV. Philipp and Taft made only room-temperature measurements. This is the first time that good quantitative agreement has been obtained between different observers measuring the same type of diamond.

DISCUSSION

As reported earlier,¹⁹ the significant features of our low-temperature reflectance data are the lack of tem-



FIG. 3. The real and imaginary part of the dielectric function and the energy-loss function for a polished type-I diamond.

perature dependence of the 7.2-eV peak, the appearance of a peak at 7.6 eV, and the lack of structure near 9 eV.

In contrast to the behavior reported by CDH,⁴ the present low-temperature data show only a slight sharpening of the 7-eV peak and in no instance was a drop in reflectance below that at room temperature observed. A detailed comparison of our reflectance data near 7 eV with that of CDH is shown in Fig. 2. Phillips⁸ interpreted the strong temperature dependence in the CDH data as due to a hybrid exciton at the Γ point and thus placed the direct interband edge $\Gamma_{25'} \rightarrow \Gamma_{15}$ at 8.7 eV. Our temperature-independent 7.2-eV peak leads us to conclude that the direct edge is near 7.3 eV and the



FIG. 4. The real and imaginary parts of the dielectric function and the energy-loss function for cleaved type-IIa diamond.

structure in ϵ_2 at this same energy is attributable to an M_0 edge at Γ together with other direct interband transitions in the vicinity of the Γ point. This interpretation agrees with the theoretical prediction²⁰ that the direct gap must be less than 7.5 eV.

Much of the published ϵ_2 structure on a large number of materials has been explained by considering only critical points associated with points of high symmetry in the band structure. However, even though these highsymmetry critical points give rise to singularities in the joint density-of-states function they are often confined to a small region in k space involving a relatively small number of electronic states which make only a small contribution to structure in ϵ_2 .²⁰ Thus the principal structure in ϵ_2 is often due not to transition thresholds at high-symmetry critical points but to transitions extending over regions in k space where the energy bands are nearly parallel. For Si, Kane²¹ has shown that transitions from large regions of k space around the symmetry points are required to explain the structure in ϵ_2 .



FIG. 5. Comparison of present results for type-I diamond (solid line) with those of Philipp and Taft (dashed line).

¹⁸ L. Marton, L. B. Leder, and H. Mendlowitz, in Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 183. ¹⁹ R. A. Roberts, D. M. Roessler, and W. C. Walker, Phys. Rev.

Letters 17, 302 (1966).

 ²⁰ F. Herman (private communication).
 ²¹ E. O. Kane, Phys. Rev. 146, 558 (1966).





The high-symmetry points may, however, still be useful as tags to locate regions in k space where the large parallel band contributions occur. A summary of the proposed electronic structure identification for diamond based mostly on parallel band arguments is given in Table I.

In Fig. 6 the recent energy-band calculation by Saslow, Bergstresser, and Cohen¹¹ (SBC) is compared with the calculation by Herman *et al.*¹² The 7.3-eV peak in ϵ_2 for diamond can be attributed to transitions starting with the M_0 , $\Gamma_{25'} \rightarrow \Gamma_{15}$ edge and extending over

broad regions in k space near the Γ point. In particular, we note from Fig. 6 that the energy bands run quite parallel away from the Γ point in the Δ direction for a considerable distance and thus a large number of states in the conduction and valence bands are separated by about 7 eV.

The strong temperature dependence of the 7.8-eV peak in ϵ_2 (7.6 eV in reflectance) suggests two possible interpretations: (1) The band calculations, Fig. 6, indicate that several critical points exist near the center of the Brillouin zone.¹¹ Slight temperature changes in

| Γ_{ABLE} I. Summary of the important features of the electronic spectrum of diamor | ıd. |
|---|-----|
| | |

| $\hbar\omega$ (eV) | | Band | | Theoretical gaps (eV) | |
|--------------------|----------------------------|---|---|-----------------------|-------|
| ϵ_2 | $-\mathrm{Im}(1/\epsilon)$ | identification | Comments | (Herman) | (SBC) |
| 7.3 | ••• | $\Gamma_{25'} 	o \Gamma_{15}$ | Transitions along $\Gamma\Delta$ with threshold at fundamental M_0 edge | 6.8 | 7.8 |
| 7.8 | ••• | Uncertain | Perhaps due to complex energy- band structure | | |
| 12.2 | ••• | $\begin{array}{c} \Sigma_2 \to \Sigma_3 \\ X_4 \to X_1 \end{array}$ | Wide region of parallel bands near X | 11.6 | 12.9 |
| 16 | | $X_1 \rightarrow X_1$ | High-energy tail of 12.2-eV peak. Parallel bands near X | 18.4 | 24 |
| 23 | 23 | $\Gamma_{25'} \rightarrow \Gamma_1$ or extrinsic | Evidence for sensitivity to surface preparation. | 21.5 | |
| | 30 | Plasma resonance | Experimental electron energy loss $=31 \text{ eV.}^{\circ}$ | | |

» Reference 22.

734

the lattice parameters may give rise to small shifts in the separation of the threefold degenerate $\Gamma_{25'}$ valence and Γ_{15} conduction bands. Shifts in the separation of these bands near Γ along $\Gamma\Delta$ could introduce additional transitions with energies near 7.8 eV. (2) An exciton elsewhere in the Brillouin zone could produce a temperature-dependent peak. This would require a criticalpoint energy gap of about 8 eV in order to give a reasonable binding energy.¹⁵ No gaps of this order appear in either of the recent calculations.

The reflectance peak observed by CDH and Roessler¹⁶ near 9 eV did not appear in the present work even though this region was carefully examined. This result is in agreement with the earlier measurements of Philipp and Taft^{1,3} and Walker and Osantowski.²

The 12.2-eV peak in ϵ_2 probably arises from direct transitions from the large number of states in the parallel bands extending from the (X_4-X_1) critical point to the $(\Sigma_2-\Sigma_3)$ point and beyond as shown in Fig 6. These bands are parallel over almost this entire region with an energy separation near 12 eV. Qualitatively, because of this wide region of parallel bands, one would expect a large contribution to ϵ_2 and in fact the experimentally determined 12-eV peak dominates the range studied. Transitions originating along $L\Lambda$ at an energy tail of this peak.

No definite sharp structure was observed near 16 eV either in reflectance or in ϵ_2 . It is to be noted, however, that the shape of ϵ_2 in the high-energy tail of the 12-eV peak indicates that a number of transitions are taking place. An examination of Herman's energy-band structure, Fig. 6, near X shows that the separation $X_1 \rightarrow X_1$ is near 16 eV and that the bands running out from this point in the Σ direction are parallel for a considerable distance; transitions between these states could account for the slow decay in ϵ_2 near 16 eV.

There is evidence for structure near 23 eV, as a small but definite maximum observed in both R and ϵ_2 . This energy corresponds fairly well with the energy difference $\Gamma_{25'} \rightarrow \Gamma_1$ (about 22 eV) calculated by Herman. Other less likely possibilities are $L_1 \rightarrow L_1$ or $L_1 \rightarrow L_3$ which occur near 23 and 24 eV, respectively. These transitions are not allowed, but there may be sufficient states close to these points to explain the peak. From the SBC calculation, we again find the $L_1 \rightarrow L_1$ is separated by 23 eV but $L_1 \rightarrow L_3$ is more nearly 25 eV. Another possibility exists, however, namely, $X_1 \rightarrow X_1$, which is near 24 eV.

The free-electron plasma resonance for diamond is near 31 eV. Figure 4 shows a peak in the energy-loss

function $-\text{Im}(1/\hat{\epsilon})$ near 30 eV in good agreement with this resonance. Whetten²² has carried out electron energy-loss measurements for diamond and found a dominant peak near 31 eV, again in agreement with the present results. It is interesting to note that whereas Philipp and Taft³ chose an extrapolation which would give a prominent peak in $-\text{Im}(1/\hat{\epsilon})$ near 31 eV, in the method used in this work the 30-eV peak comes directly out of the analysis. It should also be noted that Whetten obtained the energy-loss peak at different energies depending upon the surface treatment. When his system had been baked overnight with no special cleaning of the diamond surface, the dominant energy loss occurred near 23 eV with the 31-eV loss being less prominent. But when hydrogen was admitted to the system and the diamond heated to 700°C for 20 min, the dominant loss was at 31 eV with the 23-eV peak much reduced. It may well be that the small peak in ϵ_2 at 23 eV is due to a small amount of surface contamination.

SUMMARY

Structure in ϵ_2 was observed at 7.3, 7.8, 12.2, and 23 eV and assigned according to recent energy-band calculations. Table I summarizes these assignments. The temperature insensitive 7.3-eV peak suggests that the direct band edge is near this energy and casts doubt on the hybrid exciton interpretation. The previously unobserved temperature-dependent peak at 7.8 eV has been tentatively assigned to transitions induced by changes in the complex energy bands near the Γ point. There is evidence that the 23-eV peak is not intrinsic to diamond but due to surface contamination. The excellent agreement with the latest previous room-temperature measurement on a type-I diamond is significant since different samples and methods of analysis were used.

ACKNOWLEDGMENTS

We wish to acknowledge the support of this work by the National Aeronautics and Space Administration. We are especially grateful to Dr. F. A. Raal of the Diamond Research Laboratory, Crown Mines, Johannesburg, South Africa for supplying all the diamond samples used in this research. We also wish to thank M. L. Cohen and F. Herman for theoretical discussions, and F. Herman for permission to use Fig. 6. In addition, we wish to thank D. M. Roessler for assistance during the measurements and H. R. Philipp for sending an enlarged graph of his results.

²² N. R. Whetten, Appl. Phys. Letters 8, 135 (1966).