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Optical Properties of Diamond in the Vacuum Ultraviolet

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The optical constants of diamond have been determined in the range 5.5 to 23 eV by applying the Kramers-Kronig relation to normal incidence reflectance data. There are two salient features in the curve for optical absorption. First, the absorption rises rapidly near 7 eV, indicating the onset of strong direct transitions. Second, a relatively sharp peak occurs near 12.5 eV. These data are discussed in terms of the energy band picture for diamond and related materials which have a similar band structure.

INTRODUCTION

THE band structure of diamond is fairly well understood from a theoretical point of view.[1,2] However, experimental data testing these calculations have been limited to transmission measurements on selected samples in the region of the threshold for intrinsic optical absorption.[3] Difficulties arise in preparing thin crystals for measurement at energies much above this threshold.[4]

In the present paper, information relating to optical transitions in diamond is obtained by applying the Kramers-Kronig relation to normal incidence reflectance data in the range 5.5 to 23 eV. This technique, while not accurately applicable to regions of low absorption, appears quite convenient for diamond since absorption coefficients rapidly rise to values considerably above 10^5cm^{-1} near 7 eV. This absorption edge indicates the onset of strong direct transitions. At higher energy the absorption spectrum shows a relatively sharp peak near 12.5 eV. In its gross features, the curve is reminiscent of that for silicon.[5] The similarity of band structure for these two materials, as demonstrated by calculations,[1,6] allows one to base the analysis of the present results on the rather complete interpretation given to reflectance peaks in silicon.[7]

REFLECTANCE MEASUREMENTS

The procedures employed in these measurements have been described in a previous paper.[8] Reflectance data for diamond samples at 300°K are shown in Fig. 1. The uncertainty in the data is estimated from repeated measurements on different samples to be less than 10% at any measured energy.[9] For additional accuracy, the curve was exactly matched to index of refraction data near 5.5 eV.[10] Reflectance values obtained from both natural and mechanically polished faces were not significantly different.

The data of Fig. 1 are similar to the curve of Nelson

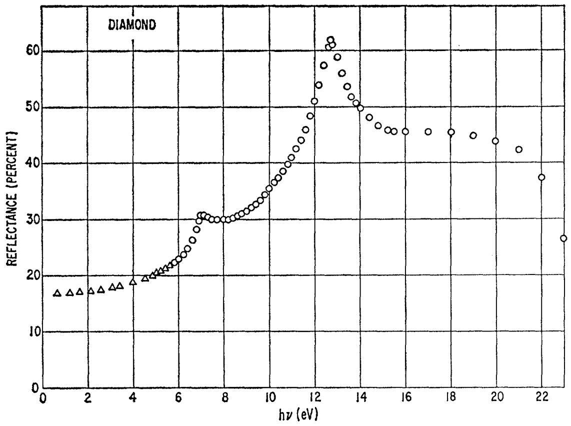

FIG. 1. Spectral dependence of the reflectance of diamond. Below 5.5 eV, the values are calculated from measurements of index of refraction (see reference 10).

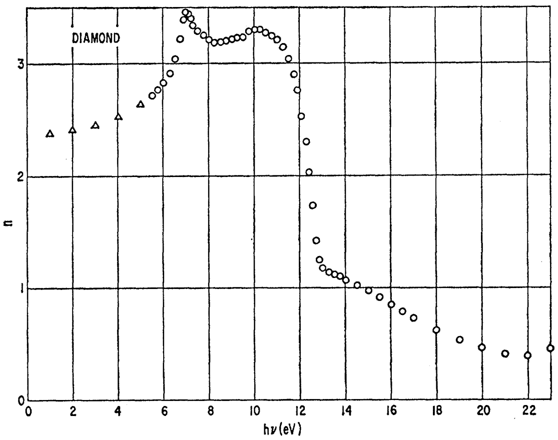

FIG. 2. Spectral dependence of the real part of the index of refraction of diamond. Below 5.5 eV, the values are taken from the literature (see reference 10).

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[1] L. Kleinman and J. C. Phillips, Phys. Rev. **116**, 880 (1959); F. Herman, *ibid.* **93**, 1214 (1954).

[2] L. Kleinman and J. C. Phillips, Phys. Rev. **117**, 460 (1960).

[3] C. D. Clark, J. Phys. Chem. Solids **8**, 481 (1959).

[4] J. F. H. Custers and F. A. Raal, Nature **179**, 268 (1957); E.W. J. Mitchell, J. Phys. Chem. Solids **8**, 444 (1959); W. Kaiser and W. L. Bond, Phys. Rev. **115**, 857 (1959).

[5] H. R. Philipp and E. A. Taft, Phys. Rev. **120**, 37 (1960).

[6] L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

[7] H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962).

[8] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959). The line spectra from low pressure argon and argon-neon lamps were employed to obtain data above 13 eV.

[9] A small peak may be present in the reflectance curve for diamond near 7.7 eV. It occurs at a position of rapid change in the hydrogen-arc spectral intensity where errors in measurement are largest. This peak is not included in Fig. 1 since its magnitude is within the estimated uncertainty of the data.

[10] F. Peter, Z. Physik **15**, 358 (1923).

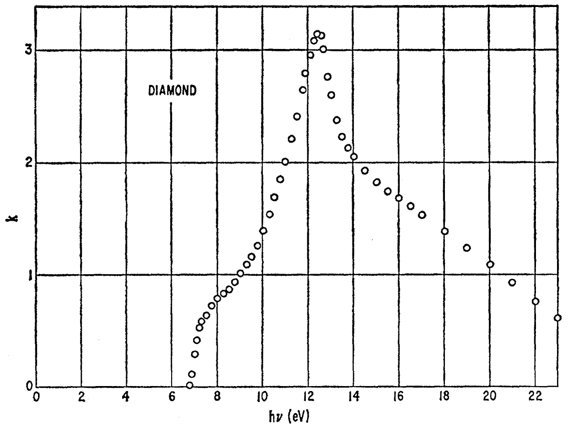

FIG. 3. Spectral dependence of the extinction coefficient (the imaginary part of the index of refraction) of diamond.

and Crocker[11] in the range 9 to 14 eV. At lower energy, however, there is considerable disagreement.[12]

RESULTS AND DISCUSSION

Values for n and k derived from the reflectance data of Fig. 1 are shown in Figs. 2 and 3.[13] Values of absorption constant, $\alpha = 4\pi k/\lambda$, are shown in Fig. 4. There are two salient features in this curve. First, the absorption rises rapidly near 7 eV and second, there is a relatively sharp peak near 12.5 eV.

In previous measurements the intrinsic absorption spectrum of diamond has been examined only in the region of the threshold near 5.4 eV. Here the results obtained in a detailed study of optical transmission at several temperatures are interpreted as indirect transitions into conducting and exciton states of the crystal.[3] Only limited transmission data are available above this energy in the literature. Custers and Raal[4] indicate the absorption constant is 10^3cm^{-1} near 5.59 eV, a value consistent with transmission measurements made at this laboratory on a polished diamond sample 1.3 mils in thickness. These data explored the energy range 5.5 to 5.7 eV. No break was observed in this curve which might indicate the onset of direct transitions.

The minimum direct gap in diamond is associated with transitions $\Gamma_{25'} \rightarrow \Gamma_{15}$ located at $k=0$. The band separation at this point is calculated to be just above 6 eV.[1,2] This region of energy is not presently accessible in transmission studies. Moreover, small values of k (and hence absorption constant) are not accurately calculable from reflectance measurements unless these data are obtained with great precision.[14] The curve of Fig. 4 does show, however, that optical absorption below 7 eV is relatively weak. It is reasonable to assume that direct transitions at Γ are strong, a situation analogous to that in silicon.[5,7] Accordingly, the onset of strong optical absorption near 7 eV ,and the corresponding peak in reflectance near 7.1 eV is associated with direct transitions at Γ.

The absorption rises to a relatively sharp peak near 12.5 eV. In contrast to the absorption edge at 7 eV, which is associated with a maximum in the real part of the dielectric constant ϵ_1, this peak corresponds to a maximum in the imaginary part ϵ_2, the real part being zero near 12 eV and negative at higher energy. This behavior, illustrated in Fig. 5(a), is like that of an oscillator and, considering the large absorption constant associated with this peak, lends itself to interpretation as a maximum in the joint conduction-valence band density of states somewhere in the Brillouin zone.[15] However, the recent work of Marple and Ehrenreich,[16] has shown that an oscillator-like description can also be associated with a band edge, if nonparabolic band effects become appreciable near this edge. A similar absorption peak is prominent in the spectrum for Ge, Si, and 3–5 compounds. Its identification with transitions at or very near $X_4 \rightarrow X_1$ seems clearcut. This identification in Ge and Si is based on the fact that the gap at X is insensitive to changes in core potential and thus should be accurately given by band calculations.[17,18]

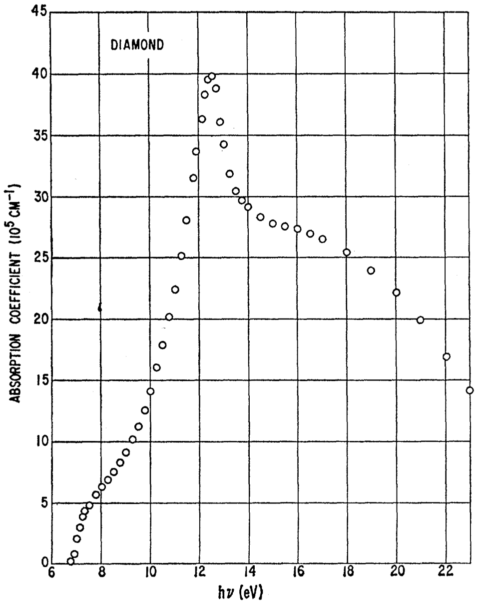

FIG. 4. Spectral dependence of the absorption coefficient ($\alpha = 4\pi k/\lambda$) of diamond.

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[11] J. R. Nelson and W. C. Crocker, Bull. Am. Phys. Soc. **5**, 431 (1960).

[12] See also S. Robin, Rev. opt. **33**, No. 8 (1954).

[13] The details relating to the calculation are given in reference 8. Beyond 23 eV, the reflectance was linearly extrapolated in a plot of $\ln R^{\frac{1}{2}}$ vs $\ln h\nu$ to 4.13% at 30 eV and to 0.149% at 50 eV. Since this extrapolation is arbitrary, the values of n and k above 20 eV are approximate.

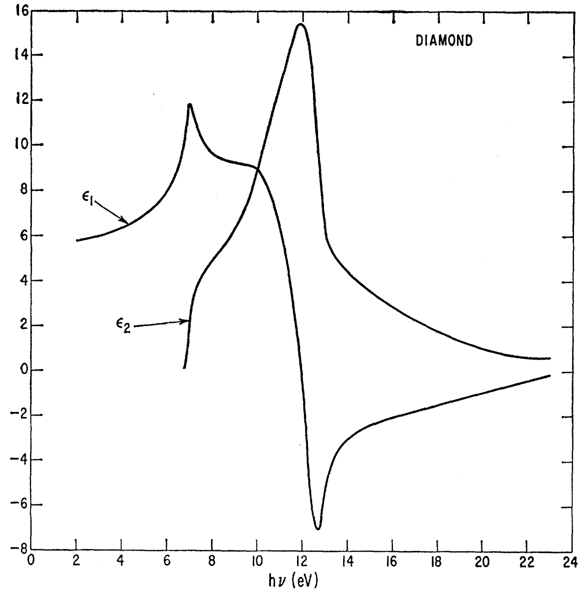
[14] For the present data, computed values of k below 0.1 are probably not reliable. At 6 eV, $k=0.1$ corresponds to an absorption coefficient of about 6×10^4cm^{-1}.

[15] M. Cardona and H. S. Sommers, Jr., Phys. Rev. **122**, 1382 (1961).

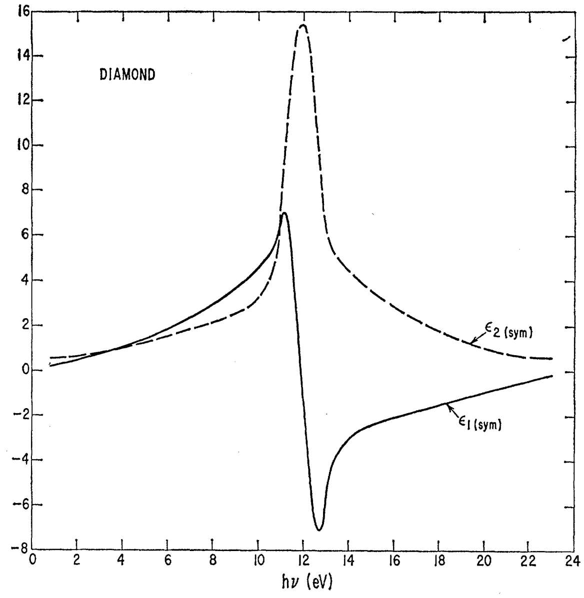
[16] D. T. F. Marple and H. Ehrenreich, Phys. Rev. Letters **7**, 87 (1962).

[17] 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.

[18] J. C. Phillips, Phys. Rev. **125**, 1931 (1962).



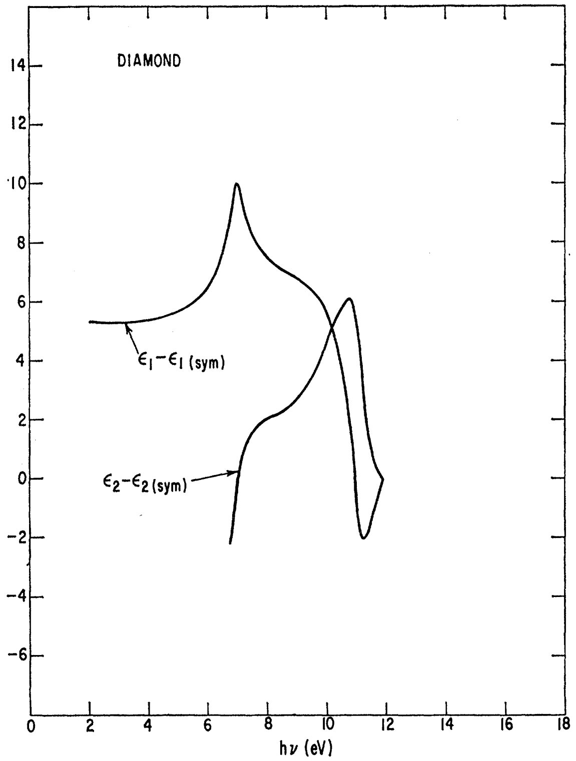
(a)



(b)

Although this argument cannot be directly extended to diamond,[18] considerations of band shape, and analogy with Si data, favor similar interpretation.

Additional information concerning optical transitions in the region 8 to 11 eV can be obtained by making use of the oscillator-like nature of the 12.5-eV absorption peak. Assuming the behavior of the dielectric constant to be that for a true oscillator, the values of ϵ_1 and ϵ_2 obtained on the high-energy side of this peak can be



(c)

FIG. 5. (a) Spectral dependence of the dielectric constant of diamond. (b) Representation of the dielectric constant associated with the 12.5-eV absorption peak, as a true oscillator. (c) Dielectric constant associated with optical absorption below 12 eV in diamond [curve 5(b) subtracted from curve 5(a)].

symmetrized with respect to the low-energy side as shown in Fig. 5(b) and then subtracted, leaving the dielectric constant associated with absorption below 12 eV. This curve is shown in Fig. 5(c) and clearly indicates an additional absorption edge in the region of 9 eV. Although the above procedure is somewhat arbitrary, it is worth speculating that the gap for the onset of transitions at L may be about 9 eV.

The energy bands of cubic boron nitride have been compared with those of diamond in a paper by Kleinman and Phillips.[2] The minimum energy gap is estimated to be about twice that for diamond. Crude reflectance data obtained here on a small boron nitride sample indicate structure in the region 9 to 10 eV and a peak near 14.5 eV. These data are quite marginal but are evidence in support of a larger gap in boron nitride compared to diamond.

ACKNOWLEDGMENT

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