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Kramers-Kronig Analysis of Reflectance Data for Diamond

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The use of the Kramers-Kronig relation in the analysis of reflectance data is discussed briefly. The recent results of Walker and Osantowski for diamond are reanalyzed and found to be in some error. New data are presented which appear more consistent with the expected optical behavior of diamond.

I. INTRODUCTION

FROM a theoretical viewpoint, diamond is a very special crystal. Since the carbon atom core contains only the completed $1S$ shell, the uncertainty in the core potential which affects the accuracy of band calculation should be appreciably less for this material than for the heavier semiconductors. Diamond has, perhaps, the simplest and most basic covalent band structure. It seems appropriate, therefore, to present a set of experimental parameters as accurate and consistent as possible to serve as a guide for further theoretical studies.[1]

In a recent paper, Walker and Osantowski[2] discuss the optical properties of diamond. They present curves for the optical and dielectric constants, obtained by Kramers-Kronig analysis of reflectance data. These curves disagree substantially in the energy range 5.5 to 12 eV with the previous results of the present authors[3] who utilized the same analysis technique. They attribute this discrepancy and other differences at higher energy to the improved purity of their diamond specimen[4] and the increased resolution of their monochromator.

This paper presents evidence indicating that the results of Walker and Osantowski[2] are not entirely correct. The analysis they present yields large negative values of the absorption coefficient in the region where diamond is transparent.[5,6] This nonphysical situation affects the computed values of the optical constants at higher energy and causes the disagreement with the previous work.[3] Moreover, to satisfy the required behavior at low energies ($k=0$), it is necessary to invoke an unrealistic extrapolation of their reflectance curve. Hence, it appears that their experimental reflectance values are too low, at least for energies greater than about 16 eV.

The use of the Kramers-Kronig integral, with particular emphasis on extrapolation procedures, is discussed briefly in Sec. II. It is applied to the data of Walker and Osantowski in Sec. III. A new reflectance curve is presented and analyzed in Sec. IV. The results give closely $k=0$ for all energies where diamond is transparent, and at high energies are more consistent with the expected optical behavior near the plasma frequency $h\omega_p=31$ eV.

II. KRAMERS-KRONIG ANALYSIS AND EXTRAPOLATION PROCEDURES

The use of the Kramers-Kronig relation in the analysis of reflectance data has been discussed in previous papers.[7,8] This integral may be used in the form

$$\theta(\omega_0)=\frac{1}{2\pi}\int_0^\infty \frac{d\ln R}{d\omega}\ln\left|\frac{\omega+\omega_0}{\omega-\omega_0}\right|d\omega \qquad (1)$$

to compute $\theta(\omega_0)$, which is related to the optical constants at frequency ω_0 by

$$\tan\theta=-2k/(n^2+k^2-1). \qquad (2)$$

The phase θ lies in the third or fourth quadrant depending on whether the quantity n^2+k^2 is less or greater than unity. Values outside the range $0\geqq\theta\geqq-\pi$ have no meaning, since the extinction coefficient must be positive; i.e., the absorption coefficient $\propto=4\pi k/\lambda$ *cannot* assume negative values.

The Kramers-Kronig relation is an integral over all frequencies. Since experimental data are usually limited in range, it is necessary to extrapolate the reflectance curve to remote regions of the spectrum in order to evaluate $\theta(\omega_0)$ accurately. For very high energies where optical effects are associated with excitation of core electrons, the behavior of R can be deduced from the asymptotic expression for the dielectric constant to be[9]

$$R(\omega)=c\omega^{-4}. \qquad (3)$$

At low energies, where crystals like diamond are transparent, the reflectance is usually known to a high degree of accuracy from measurements of the index of refrac-

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[1] F. Herman, Phys. Rev. **93**, 1214 (1954); L. Kleinman and J. C. Phillips, *ibid.* **125**, 819 (1962); **116**, 880 (1959).

[2] W. C. Walker and J. Osantowski, Phys. Rev. **134**, A153 (1964).

[3] H. R. Philipp and E. A. Taft, Phys. Rev. **127**, 159 (1962).

[4] The absorption of substitutional nitrogen impurities in diamond may be estimated using the absorption cross section for atomic nitrogen given by A. W. Ehler and G. L. Weissler, J. Opt. Soc. Am. **45**, 1035 (1955). It is much too small to account for the observed differences even for concentrations of $\sim10^{20}$ cm^{-3}.

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

[6] J. F. H. Custers and F. A. Raal, Nature **179**, 268 (1957).

[7] T. S. Robinson, Proc. Phys. Soc. (London) **B65**, 910 (1952).

[8] F. C. Jahoda, Phys. Rev. **107**, 1261 (1957); H. R. Philipp and E. A. Taft, *ibid.* **113**, 1002 (1959).

[9] H. R. Philipp and H. Ehrenreich, J. Appl. Phys. **35**, 1416 (1964); M. Cardon and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

tion obtained on bulk prism samples,[10] or can be estimated from measurements of dielectric constant. It is in the region between the highest energy datum point and energies where Eq. (3) is applicable that most careful consideration must be given to extrapolation procedures. In this range, labeled ΔE_R, the reflectance does not follow any simple rules, although its general behavior can be deduced provided the interval does not contain strong structure such as that characteristic of interband transitions.[11] To this end we must require that $\theta(\omega')$ be known for at least a single frequency ω'. For insulators, ω' can be chosen in the transparent region where $\theta=0$. Since the contribution to $\theta(\omega')$ for all energies outside the range ΔE_R can be computed using index of refraction data, experimental reflectance values, and Eq. (3), it follows that the exact contribution of ΔE_R to $\theta(\omega')$ is thus also known.

Since we have postulated that strong interband transitions are absent in the range ΔE_R, the main effects will be those associated with the plasma resonance. The plasma frequency ω_p is known for a number of crystals from characteristic electron energy loss data, or can be estimated using the free electron formula

$$\omega_p=(4\pi ne^2/m)^{1/2},$$

where n is the appropriate density of valence electrons.[12] The reflectance is expected to remain reasonably high for energies below $\hbar\omega_p$, and to decrease rapidly above the plasma frequency.[13] For crystals having deep-lying core states, it is found[9,14,15] that $d\ln R/d\ln\omega<-4$ near ω_p, and slowly increases to the asymptotic slope $d\ln R/d\ln\omega=-4$, with increasing frequency (i.e., the reflectance curve is steeper near ω_p).

An extrapolation of the above form can be made somewhat quantitative by the requirement that it gives (1) the appropriate contribution to $\theta(\omega')$ discussed earlier, and (2) for frequencies above ω_p, values of $\theta(\omega)$ which approach, but are never more negative than $-\pi$. At ω_p, $-\pi<\theta(\omega_p)<-\pi/2$, since n and k are usually small.

For insulators, of course, $\theta(\omega)$ must be zero for *all* frequencies in the transparent range. This condition subjects the extrapolation to further refinement, provided the reflectance curve at low frequencies has been very accurately determined.

III. ANALYSIS OF THE RESULTS OF WALKER AND OSANTOWSKI

The phase θ, computed from the reflectance curve of Walker and Osantowski[2] using Eq. (1), is shown in Fig. 1. Curve A uses closely the extrapolation of the above authors, and gives the n and k values they report.[2] The large positive values[16] of the phase in the region below 7 eV correspond to negative absorption coefficients of magnitude greater than $10^5\ \mathrm{cm}^{-1}$ for energies where diamond is transparent.[5,6] This situation is physically unacceptable and leads to erroneous conclusions, particularly those concerning the behavior of the optical constants for energies below 12 eV. Curves B and C use different extrapolations constructed to give $\theta=0$ at 4 and 5.5 eV, respectively. Each extrapolation assumes the asymptotic slope $d\ln R/d\ln\omega=-4$ for energies above 35 eV. They require a slope of -0.805 and $+1.08$, respectively, between 28 eV, the highest energy datum point of Ref. 2, and 35 eV. These slopes, which are necessary to give the desired values of θ at lower energy, indicate that the reflectance curve is relatively flat in the vicinity of the plasma frequency near 31 eV. Indeed, to obtain curve C requires that the curve rise in this region. This behavior appears quite inconsistent with that expected and observed for a number of materials.[14,15] We are led, therefore, to the conclusion that reflectance values reported in Ref. 2 are too low, at least for energies above 16 eV. In light of this, the observed structure near 16.5 and 20 eV should be subject to review. The fact that neither extrapolation B nor C results in $\theta=0$ for all energies in the region of transparency indicates possible errors in the reflectance

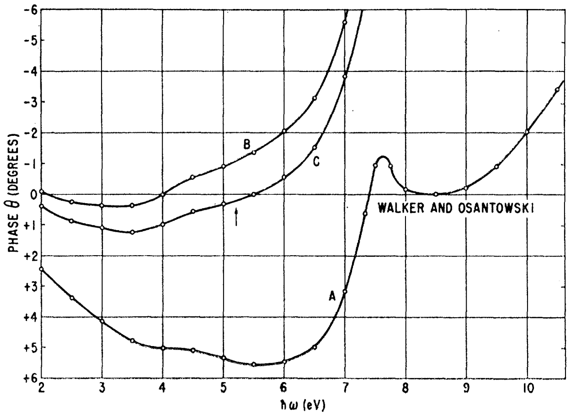

FIG. 1. The phase $\theta(\omega)$ versus $\hbar\omega$ computed from Eq. (1) and the reflectance data of Walker and Osantowski (Ref. 2). Curve A uses their extrapolation. Curves B and C use different extrapolations, described in the text, which give $\theta=0$ at 4 and 5.5 eV, respectively. The band gap of diamond near 5.2 eV is indicated by the arrow (Ref. 5).

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[10] F. Peter, Z. Physik **15**, 358 (1923). *The Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio 1962), 44th ed., quotes Peter's value for sodium light ($\lambda=5893$ Å) $n=2.4173$.

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

[12] L. Marton, Rev. Mod. Phys. 28, 172 (1956); D. Pines, *ibid.* **28**, 184 (1956).

[13] H. R. Philipp and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963), footnote 13.

[14] H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).

[15] H. Ehrenreich, H. R. Philipp, and B. Segall, Phys. Rev. **132**, 1918 (1963). W. R. Hunter, J. Opt. Soc. Am. **54**, 208 (1964).

[16] Walker and Osantowski (Ref. 2) mention that their analysis gave some negative values for k in this region. They apparently did not realize the significance of this situation and its influence on the calculated optical constants at higher energies.

values at lower energies, although the extent to which θ goes positive is certainly reduced compared to curve A.

The absorption coefficient, $\alpha = 4\pi k/\lambda$, is shown in Fig. 2 for each of the above extrapolations. The values indicated by Δ are those of Ref. 3, and show the general agreement of the two sets of data when the requirements on θ are qualitatively satisfied. This is a fairly obvious result, since the two reflectance curves[2,3] are similar below 10 eV.

IV. A REFLECTANCE CURVE FOR DIAMOND: ANALYSIS AND DISCUSSION

New reflectance data for diamond are shown in Fig. 3. This curve differs only slightly from our previous measurements presented in Ref. 3. For energies below 5.5 eV, the values were computed using the formula for the index of refraction given by Peter.[10] A smoothed reflectance curve for this region is plotted on an expanded scale in the lower half of the figure. Reflectance values shown here are considerably higher than those of Ref. 2 for energies above about 10 eV. The detail reported at 16.5 and 19.2 eV does not appear in this curve. However, we do observe structure near 24 eV. All measurements indicate a reflectance minimum just above 23 eV, and a peak (not an inflection) at about 24.5 eV. The curve of Fig. 3 has been drawn flat in this region since, for energies above 23 eV, we have some reservations concerning the accuracy of these data.

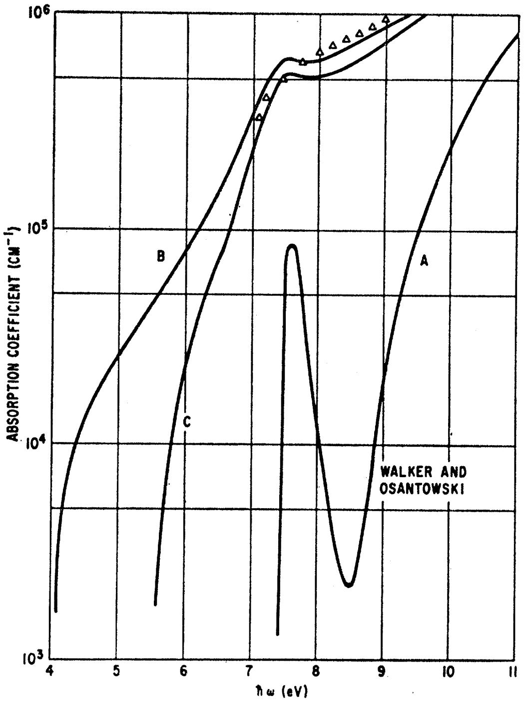

FIG. 2. The absorption coefficient, $\alpha = 4\pi k/\lambda$, versus $\hbar\omega$ obtained by Kramers-Kronig analysis of the reflectance data of Walker and Osantowski (Ref. 2). Curve A uses their extrapolation. Curves B and C use different extrapolations described in the text. In each case, the values become negative for energies below the last plotted point. Data points of Philipp and Taft (Ref. 3) are indicated by Δ.

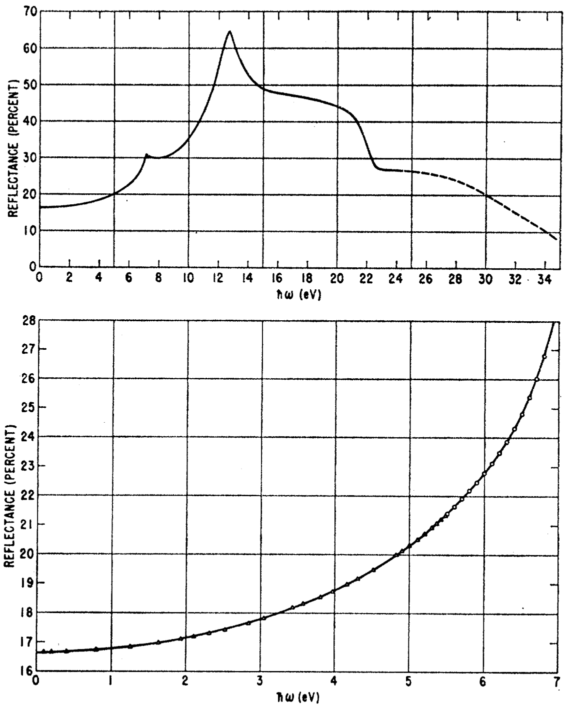

FIG. 3. The spectral dependence of the reflectance of diamond. Below 5.5 eV the values are calculated from index of refraction data (see Ref. 10). This region is shown in more detail in the lower part of the figure. The extrapolation used in the analysis of these data is indicated by the dashed line for $\hbar\omega$ above about 25 eV.

Absorption coefficients, obtained by Kramers-Kronig analyses of the above curve, are shown in Fig. 4 for energies near the band gap. Corresponding values for θ are given in the insert. The curve for α is not intended to be quantitative, especially for energies below 6.5 eV where values of k are less than 0.01. However, it does show surprising agreement with the transmission studies of Custers and Raal[6] who indicate an absorption constant of 10^3 cm^{-1} near 5.59 eV.

The dielectric constants and energy loss function $-\mathrm{Im} 1/\epsilon$ are plotted in Fig. 5. There is some evidence of structure near 16 eV which shows up only weakly in expanded plots of ϵ_1 and ϵ_2, and more convincingly as a plateau in the curve for absorption coefficient. Structure near 23 eV, presumably associated with interband transitions,[17] shows up clearly in the dielectric constants and produces a weak peak in the energy loss function. The extrapolation indicated in Fig. 3 was constructed to give a prominent peak in $-\mathrm{Im}\ 1/\epsilon$ near the

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[17] This small peak is presumably unrelated to a more prominent peak near 22 eV, observed in characteristic energy-loss experiments on amorphous carbon. The carbon peak is attributed to the collective excitation of valence electrons. For crystalline graphite, this structure occurs near 25 eV, while for diamond it is calculated to be near 31.1 eV. See L. B. Leder, and J. A. Suddeth, J. Appl. Phys. 31, 1422 (1960).

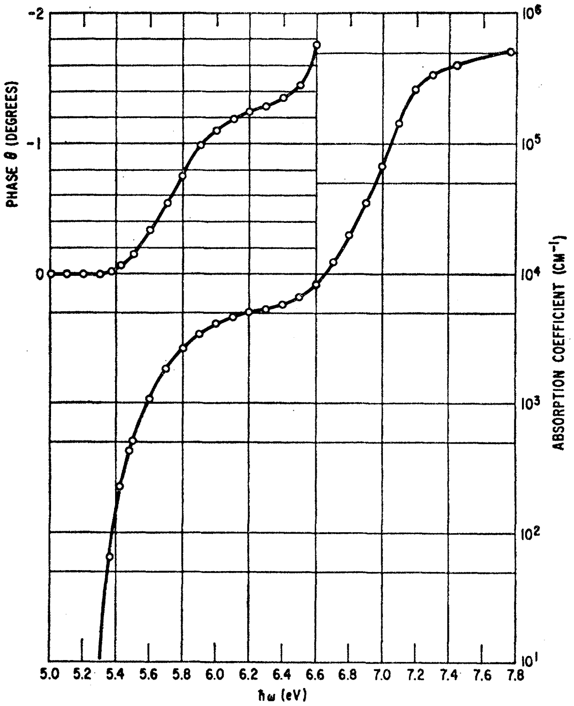

FIG. 4. The absorption coefficient $\alpha = 4\pi k/\lambda$ versus $\hbar\omega$ obtained by Kramers-Kronig analyses of the reflectance curve of Fig. 3. Corresponding values of the phase θ are given on a linear scale in the insert.

calculated plasma energy for diamond, $\hbar\omega_p = 31$ eV. The magnitude of this peak, $-\text{Im}\ 1/\epsilon \cong 2.4$, is about that expected. It should be larger than for Si,[14] but certainly not as sharp as for Al[15] where damping of plasma oscillations is small. Structure near 20 eV reported in Ref. 2 does not appear in these curves.

The assignments given to peaks in the curves of Fig. 5 near 7.3 eV ($\Gamma_{25'} \rightarrow \Gamma_{15}$) and 12.5 eV ($X_4 \rightarrow X_1$, $\Sigma_4 \rightarrow \Sigma_1$) seem clearcut.[2,3] However, band calculations for diamond[1] still leave unresolved the interpretation of structure at higher energies. Phillips has outlined possible choices for this structure.[18] His comments are included in the discussion of Ref. 2 and will not be repeated here. It is hoped that the recent experimental papers on diamond will stimulate additional theoretical progress.

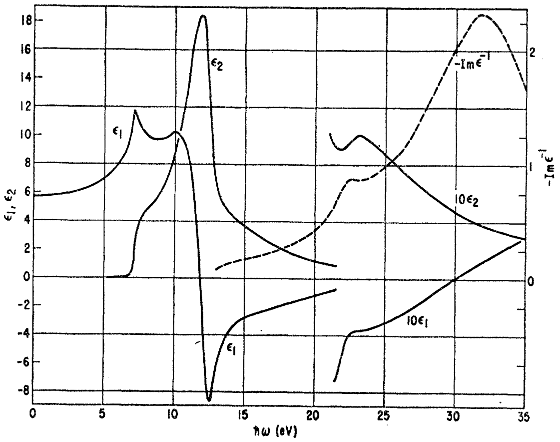

FIG. 5. The spectral dependence of the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2, and the energy loss function, $-\text{Im}\epsilon^{-1}$ for diamond.

Note added in proof. C. D. Clark, P. J. Dean, and P. V. Harris [Proc. Roy. Soc. (London) **A277**, 312 (1964)] have recently published precise values for the absorption coefficient of diamond for energies to 6 eV. In addition, they measured the reflectance. The values they give for R near 12.5 eV are considerably lower than those we report. Their data show some detail near 9 eV, and a rather striking enhancement of the peak near 7 eV when the sample is cooled. On the basis of these data, J. C. Phillips (to be published) offers a revised interpretation of the optical properties of diamond. He associates the temperature-dependent peak near 7 eV with an exciton resonance and places the direct threshold $\Gamma_{25'} \rightarrow \Gamma_{15}$ at about 8.7 eV.

P. J. Dean and D. M. Roessler [see P. J. Dean and J. C. Male, Phys. Chem. Solids **25**, 311 (1964), Ref. 33] indicate $\hbar\omega_p \cong 23$ eV from the results of reflectance studies on diamond. We attribute structure near 23 eV to interband effects and postulate $\hbar\omega_p \cong 31$ eV. N. R. Whetten (to be published) observes a characteristic energy loss peak near 30 eV for diamond which supports our point of view.

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[18] We are grateful to Professor J. C. Phillips for sending this information to us.