

higher spin-quartet states relative to the lowest spin quartet. This excited state is probably the lower quartet E^o of Fig. 3, though this symmetry assignment has not been confirmed experimentally. Figure 15 gives a proposed energy-level diagram for the R center in KCl, using the results noted above.

ACKNOWLEDGMENTS

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Optical Properties of Graphite*

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The complex dielectric constant $\epsilon(\omega) = \epsilon_1 + i\epsilon_2$ and associated functions are derived by application of the Kramers-Kronig relation to reflectance data for graphite obtained in the energy range to 26 eV. It is possible to divide the optical properties into two spectral regions. In the range 0 to 9 eV, intra- and interband transitions involve mainly the π bands. At higher energies, a broad absorption peak near 15 eV is associated with interband transitions involving the 3 σ electrons per atom. This viewpoint is strongly supported by evaluation of the sum rules for n_{eff} . Plasma resonances which produce peaks in the energy-loss function $-\text{Im}\epsilon^{-1}$ at 7 and 25 eV are identified and described physically. At low energies, structure in the reflectance curve near 0.8 eV is attributed to the onset of transitions between the E_2 and E_3 bands at the point K . This yields a value for γ_1 of ≈ 0.4 eV.

I. INTRODUCTION

IN recent years the study of graphite has received much attention in the literature. This crystal exhibits unique electronic properties of interest to the theoretical, as well as the experimental physicist. It is possible to observe a number of phenomena, for example; the de Haas-Van Alphen effect, magneto-reflection and resistance effects, cyclotron resonance, diamagnetic susceptibility, and so forth, which yield direct information about the Fermi surface. Theoretical work has progressed at a similar pace, and today the electronic structure of graphite for energies near the Fermi energy is well understood.^{1,2}

Optical studies yield additional information, principally about excited electronic states of the crystal. In particular, they concern effects which can be described most conveniently in terms of the frequency-dependent dielectric constant. Experimentally, the complex dielectric constant can be evaluated over an extended energy range by the well-known Kramers-Kronig analysis of reflectance data,³ a procedure which has been employed in a number of such studies to date.⁴

The main feature of the reflectance spectrum of graphite is a sharp minimum in the curve which occurs at about 8 eV. Near this energy the crystal becomes relatively transparent, and it is possible to separate, quite unambiguously, the dielectric constants associated with strong absorption processes at higher and at lower energies. For the purposes of further analysis, it is convenient to divide the optical properties of graphite into two spectral regions. In the energy range 0 to 9 eV, intra- and interband optical transitions involve mainly the π bands which arise from the one electron per atom, atomic $2p_z$ orbitals, extending above and below the carbon-layer planes which make up the graphite crystal. It is these electrons which play the principal role in the electrical conductivity. At higher energies, a broad peak of optical absorption near 15 eV is associated with interband transitions involving the 3 σ electrons per atom, which form the coplanar bonds joining one carbon to its three neighbors within the layer. This viewpoint is supported by evaluation of the sum rule for the effective number of electrons which has been used in previous work^{4,5} to indicate the distribution of oscillator strengths for transitions from the valence bands. For graphite, this integral saturates near one electron per atom just above 8 eV and again near four electrons per atom at the plasma frequency $\hbar\omega_p \approx 25$ eV where the total oscillator strength for transitions involving the combined π and σ bands is essentially exhausted.

Two peaks are observed in the energy-loss function,

* This work was reported in part at the Philadelphia Meeting of the American Physical Society [H. R. Philipp, *Bull. Am. Phys. Soc.* **9**, 211 (1964)].

¹ For a review of this work see R. R. Haering and S. Mrozowski, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 273.

² M. S. Dresselhaus and J. G. Mavroides, *IBM J. Res. Develop.* **8**, 262 (1964); *Carbon* **1**, 263 (1964).

³ H. R. Philipp and E. A. Taft, *Phys. Rev.* **113**, 1002 (1959).

⁴ See, for example, H. Ehrenreich, H. R. Philipp, and B. Segall, *Phys. Rev.* **132**, 1918 (1963).

⁵ H. R. Philipp and H. Ehrenreich, *Phys. Rev.* **129**, 1550 (1963).

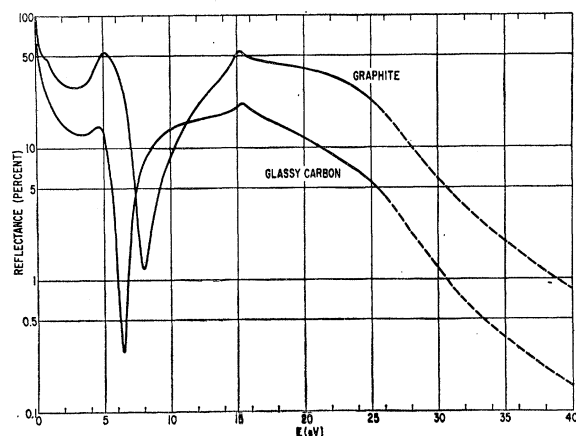


FIG. 1. The spectral dependence of the reflectance of graphite and glassy carbon. The extrapolations of the reflectance curves above 26 eV, used in the analysis of these data, are indicated by the dashed lines.

$-\text{Im}\epsilon^{-1}$. A relatively weak one near 7 eV has been attributed to the collective excitation of π electrons.⁶ It is actually a hybrid resonance which results from the cooperative behavior of both the π and σ electrons. This peak in $-\text{Im}\epsilon^{-1}$ occurs at an energy much below that calculated using the free-electron formula with one π electron per atom because of the screening effect of the positive contribution to the dielectric constant of the σ electrons. A stronger resonance near 25 eV is associated with plasma oscillations involving the combined π plus σ electrons (4 per atom). The position of this peak in graphite and other allotropic forms of carbon may be directly related to specimen density.⁷

In the present paper, the real and imaginary parts of the dielectric constant of graphite are evaluated for energies up to 26 eV. The results are discussed from the point of view outlined above. Unfortunately, reflectance data were not available for energies below 0.03 eV. Since interband transitions set in at very low energies, it is not possible to isolate in any quantitative way the free-electron behavior of graphite that was achieved in studies of the noble metals⁸ and Al.⁴

II. EXPERIMENTAL RESULTS

The reflectance spectrum of freshly cleaved graphite for unpolarized light at near-normal incidence to the carbon-layer planes is shown in Fig. 1. The techniques employed in these measurements for energies above 1 eV have been described elsewhere.⁵ In the infrared, an aluminum mirror was employed as a comparison standard.^{9,10} Data were obtained on both natural

⁶ Y. H. Ichikawa, *Phys. Rev.* **109**, 653 (1958).

⁷ L. B. Leder and J. A. Suddeth, *J. Appl. Phys.* **31**, 1422 (1960); N. R. Whetten, *Bull. Am. Phys. Soc.* **9**, 536 (1964). For diamond, Whetten finds $\hbar\omega_p \approx 30$ eV (to be published).

⁸ H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).

⁹ H. E. Bennett, M. Silver, and E. J. Ashley, *J. Opt. Soc. Am.* **53**, 1089 (1963).

¹⁰ We are indebted to D. T. F. Marple for the use of his spectrometer. See D. T. F. Marple, *Phys. Rev.* **129**, 2466 (1963).

graphite crystals and pyrolytic graphite samples annealed at 3600°C.¹¹ These latter specimens exhibit single-crystal characteristics.¹² Reflectance values were very similar to those for natural graphite. For comparison purposes, data are also given in the figure for mechanically polished glassy carbon,¹³ a material which exhibits no distinct crystal structure.¹⁴ The reflectance minimum for this material is shifted to lower energies by ≈ 1.5 eV, and reflectance values are generally lower compared to the crystalline samples. The reflectance curve for unannealed pyrolytic graphite is more like that for graphite than for glassy carbon, the minimum being shifted only ≈ 0.3 eV. These data have been omitted from Fig. 1 for reasons of clarity. The reflectance minimum becomes sharper and deeper for all samples after appreciable exposure to the atmosphere. This effect, which is limited primarily to energies between 7 and 10 eV, is presumably associated with surface contamination of some sort. It was not studied in any detail. The curves of Fig. 1 were obtained on samples exposed to air for the minimum of time necessary for mounting in the sample chamber and then, for a longer time, to the poor vacuum of the monochromator.

The dielectric constants, ϵ_1 and ϵ_2 , and the energy-

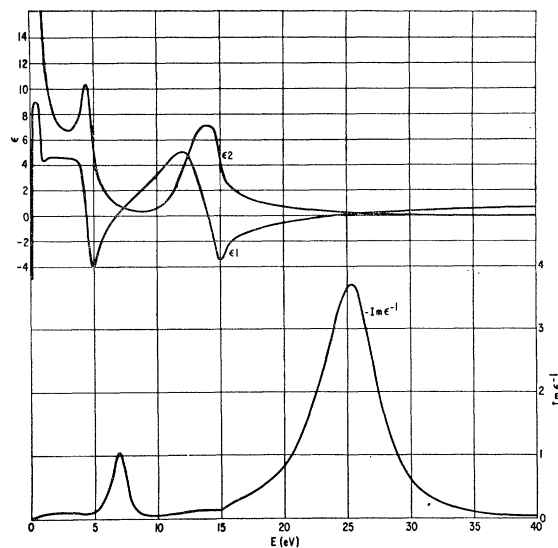


FIG. 2. The spectral dependence of the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , and the energy-loss function $-\text{Im}\epsilon^{-1}$ for graphite obtained by Kramers-Kronig analysis of the curve of Fig. 1.

¹¹ We are grateful to F. H. Horn for the natural graphite crystals, and to E. R. Stover and R. J. Diefendorf for supplying us with pyrolytic graphite samples.

¹² C. A. Klein, W. D. Straub, and R. J. Diefendorf, *Phys. Rev.* **125**, 468 (1962).

¹³ This material was obtained from Tokai Electrode Company Ltd., Japan, through International Carbon Corporation, 500 Fifth Avenue, New York 36, N. Y., and from Plessey International Ltd., England.

¹⁴ For some properties of this material see S. Yamada and H. Sata, *Nature* **193**, 261 (1962); and J. C. Lewis, B. Redfern, and F. C. Cowland, *Solid State Electron.* **6**, 251 (1963).

loss function, $-\text{Im}\epsilon^{-1}$, obtained by Kramers-Kronig analysis of the reflectance curve for graphite are shown in Fig. 2. For this analysis, the reflectance curve was extrapolated beyond 26 eV (1) to give realistic values of the phase θ at all energies above 26 eV, and (2) to agree with the expected behavior of the dielectric constants for energies near and above the plasma frequency.^{15,16} The asymptotic slope $d \ln R/d \ln \omega = -4$ was assumed for energies above 50 eV. In the range 26 to 50 eV, suitable extrapolations satisfying the above criteria could be obtained which positioned the maximum in the energy-loss function between 25 and 26.5 eV. To help resolve this ambiguity, transmission measurements were made on thin sections of crystal, $\approx 400 \text{ \AA}$ in thickness, for energies in the region 7 to 11 eV and compared with the results of Kramers-Kronig analysis. The best fit was obtained using the extrapolation indicated by the dashed lines in Fig. 1. The corresponding peak in $-\text{Im}\epsilon^{-1}$ occurs just above 25 eV, as shown in Fig. 2. This value agrees well with the results of characteristic energy-loss experiments.⁷

Previous optical work on graphite has been confined mainly to the region 1 to 6 eV. The present results agree qualitatively with these data. The absorption coefficients we calculate are generally larger and reflectance values somewhat higher than those in the literature.^{17,18}

III. DISCUSSION

The curves of Fig. 2 describe three distinct effects, namely free-electron effects at very low energies characterized by negative values of ϵ_1 ,¹⁹ interband transitions which produce structure in ϵ_1 and ϵ_2 ,²⁰ and plasma effects which are associated with peaks in the energy-loss function.²¹

It is convenient to distinguish in addition the spectral regions above and below 9 eV. Near this energy the crystal becomes relatively transparent, as evidenced by the small values of ϵ_2 , and it is possible to separate quite unambiguously the dielectric constants associated with each of these regions. Without resort to a specific theoretical model, we can write

$$\epsilon(\omega) = \epsilon^\pi(\omega) + \delta\epsilon^\sigma(\omega), \quad (1)$$

where the labels π and σ denote absorption processes in

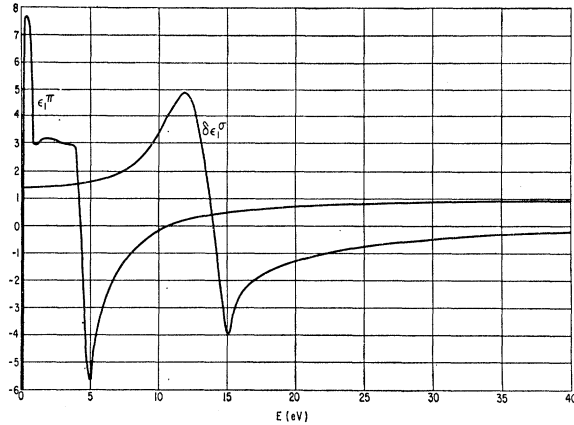


Fig. 3. The decomposition of the experimental ϵ_1 for graphite into π and σ components, ϵ_1^π and $\delta\epsilon_1^\sigma$.

the energy region below and above ≈ 9 eV, respectively. For the present purposes, this separation may be made quantitative by assuming $\delta\epsilon_2^\sigma = 0$ for $\hbar\omega < 9$ eV and $\epsilon_2^\pi \rightarrow 0$ for energies above 9 eV.²² The Kramers-Kronig relation

$$\delta\epsilon_1^\sigma(\omega_0) = -\frac{2}{\pi} \int_0^\infty \frac{\omega \delta\epsilon_2^\sigma(\omega)}{\omega^2 - \omega_0^2} d\omega \quad (2)$$

can then be used to calculate $\delta\epsilon_1^\sigma(\omega)$. The results are shown in Fig. 3 where we also plot $\epsilon_1^\pi = \epsilon_1 - \delta\epsilon_1^\sigma$, obtained by subtracting $\delta\epsilon_1^\sigma$ from the experimental values. The separation of ϵ_2^π and $\delta\epsilon_2^\sigma$ is already obvious in Fig. 2.

The gross division of the optical spectra of graphite into regions involving principally transitions from occupied π and σ bands, respectively, is speculative. Prior experimental evidence concerning this point is based mainly on the soft x-ray emission spectroscopy of Chalklin.²³ In this work a single broad band is observed some 15 to 20 eV in width, which shows some fine structure. The calculations of Coulson and Taylor²⁴ estimate the width of the π bands to be about 5 eV. On this basis the emission curve can be separated into π and σ components which overlap at least partly.²⁴ Other theoretical work does not make this issue clear. Lomer²⁵ estimates that the occupied σ bands lie about 1 eV below the Fermi level, while Corbato²⁶ indicates that optical effects involving σ electrons do not set in until much higher energies ≈ 6 eV, although the σ bands cross over parts of the π bands.

¹⁵ H. R. Philipp and H. Ehrenreich, J. Appl. Phys. **35**, 1416 (1964).

¹⁶ H. R. Philipp and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963); H. R. Philipp and E. A. Taft, *ibid.* **136**, A 1445 (1964).

¹⁷ S. Ergun and J. T. McCartney, *Proceedings of the Fifth Conference on Carbon* (Pergamon Press, Inc., New York, 1963), Vol. 2, p. 167; S. P. F. Humphreys-Owen and L. A. Gilbert, *Industrial Carbon and Graphite* (Society of Chemical Industry, London, 1958), p. 37.

¹⁸ J. R. Nelson, Bull. Am. Phys. Soc. **7**, 332 (1962).

¹⁹ See, for example, L. G. Schulz, Phil. Mag. Suppl. **6**, 102 (1957).

²⁰ See, for example, H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962).

²¹ See, for example, P. Nozieres and D. Pines, Phys. Rev. **113**, 1254 (1959).

²² Above 9 eV, the form of ϵ_2^π is assumed to be similar to that of ϵ_2 in Fig. 2 for energies above ~ 25 eV. This extrapolation is used in Fig. 4 to compute the dashed curve and in Fig. 5 to compute $-\text{Im}(\epsilon^\pi)^{-1}$. The values of ϵ_2^π in this region are negligible compared to $\delta\epsilon_2^\sigma$.

²³ F. C. Chalklin, Proc. Roy. Soc. (London) **A194**, 42 (1948).

²⁴ C. A. Coulson and R. Taylor, Proc. Phys. Soc. (London) **A65**, 815 (1952).

²⁵ W. M. Lomer, Proc. Roy. Soc. (London) **A227**, 330 (1955).

²⁶ F. J. Corbato, *Proceedings of the Third Conference on Carbon* (Pergamon Press, Ltd., London, 1959), p. 173.

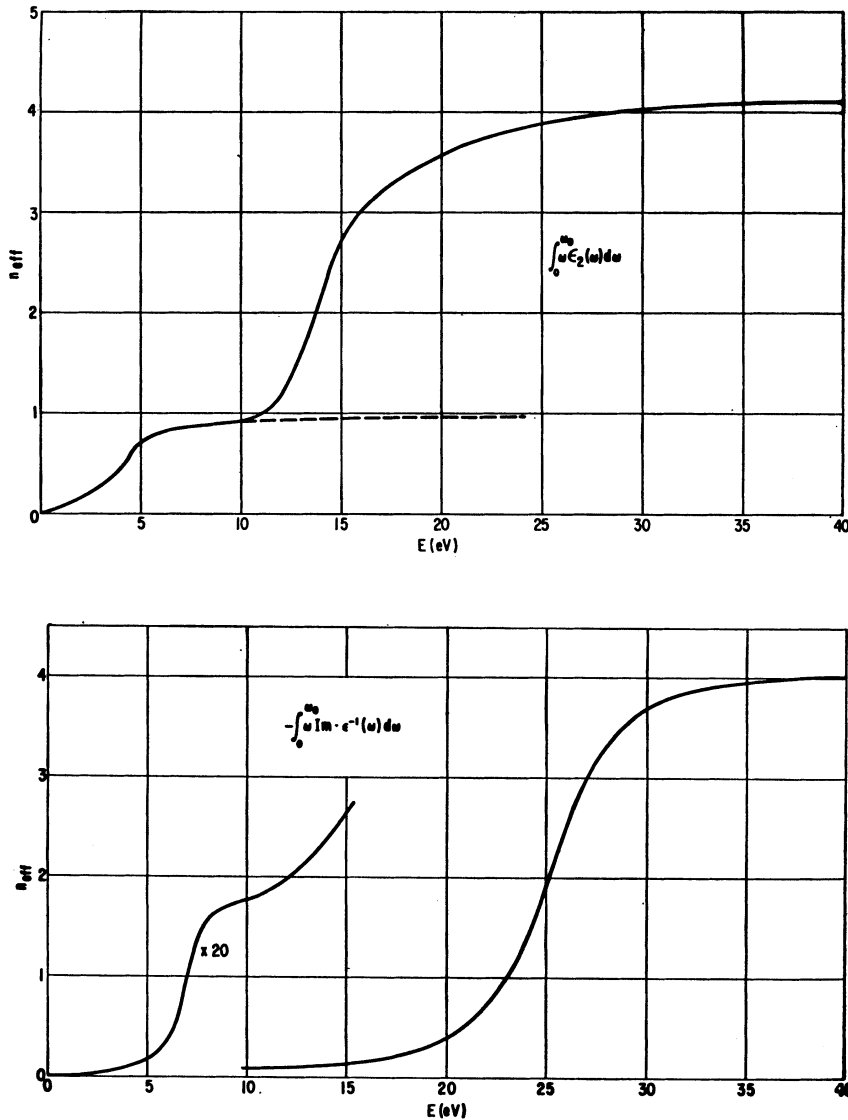


FIG. 4. The effective number of electrons per atom versus E obtained from numerical integration of experimental ϵ_2 and $-\text{Im}\epsilon^{-1}$. The n_{eff} are defined by Eqs. (3) and (4).

Justification for the point of view taken in this paper is obtained from an evaluation of the sum rule

$$\int_0^{\omega_0} \omega \epsilon_2(\omega) d\omega = (2\pi^2 N e^2 / m) n_{\text{eff}}, \quad (3)$$

where n_{eff} is the effective number of electrons per atom (in a crystal of atom density N) contributing to the optical properties in the range to ω_0 .^{5,21} Since transitions involving the core states can be neglected for energies in the range of the present experiments,²⁷ it is expected that n_{eff} should saturate near 4 electrons per atom (1 π plus 3 σ electrons) when the oscillator strengths for the combined π plus σ bands are exhausted. If, in addition, the oscillator strength for the π bands alone

²⁷ D. H. Tomboulian, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXX, p. 274.

is exhausted before transitions involving the σ bands are energetically possible, then the plot of n_{eff} should show a plateau near $n_{\text{eff}}=1$ electron/atom. This situation is shown in the upper half of Fig. 4 where n_{eff} is evaluated from Eq. (3) using the experimental ϵ_2 given in Fig. 2. Near $\hbar\omega_0=9$ eV, $n_{\text{eff}}\approx 1$ electron per atom and then rises abruptly at higher energies when transitions involving the σ electrons set in.²²

The n_{eff} plot corresponding to the sum rule for the energy loss function $-\text{Im}\epsilon^{-1}$,

$$-\int_0^{\omega_0} \omega \text{Im}\epsilon^{-1}(\omega) d\omega = (2\pi^2 N e^2 / m) n_{\text{eff}}, \quad (4)$$

is also shown in Fig. 4. This graph does not distinguish separately the π and σ electrons since the function $-\text{Im}\epsilon^{-1} = \epsilon_2 / (\epsilon_1^2 + \epsilon_2^2)$, as evaluated in Fig. 2, contains

$\epsilon_1 = \epsilon_1^\pi + \delta\epsilon_1^\sigma$ whose π and σ components contribute for all energies. This sum rule is useful mainly in testing the internal consistency of the Kramers-Kronig analysis. Since the magnitude of $-\text{Im}\epsilon^{-1}$ is large at the higher energies, this plot is particularly sensitive to the extrapolation procedures used in this analysis. As seen in Fig. 4, the integral also saturates near 4 electrons per atom.

We can, however, make use of the results plotted in Fig. 3 to evaluate this sum rule in a manner more meaningful to the present discussion. For this purpose, we consider the graphite crystal as a superposition of two distinct media having dielectric constants $\epsilon^\pi = \epsilon_1^\pi + i\epsilon_2^\pi$ and $\epsilon^\sigma = (1 + \delta\epsilon_1^\sigma) + i\delta\epsilon_2^\sigma$, respectively. In Fig. 5 we plot the energy-loss function and show the corresponding n_{eff} curve for each of these media.²² The integral for $-\text{Im}(\epsilon^\pi)^{-1}$ saturates near 1 electron per atom, while that for $-\text{Im}(\epsilon^\sigma)^{-1}$ saturates near 3 electrons per atom.

We can utilize the above information to discuss more specifically the curve for $-\text{Im}\epsilon^{-1}$ shown in Fig. 2. Both interband transitions and collective electron effects can give rise to structure in the energy-loss function.⁶ It is often possible to distinguish between these by noting the behavior of $\epsilon(\omega)$ in the vicinity of the loss peak. Near the plasma resonance, ϵ_1 and ϵ_2 are small and have positive and negative slopes, respectively. Although it is not necessary for ϵ_1 to vanish near the plasma frequency, when damping is small the condition for collective excitations is closely approximated by $\epsilon_1(\omega_p) = 0$. The magnitude of the peak in $-\text{Im}\epsilon^{-1}$ is then $\approx \epsilon_2^{-1}(\omega_p)$. In Fig. 2, structure in the energy-loss function near 7 and 25 eV is clearly associated with plasma effects. The positions of these peaks agree well with the results of characteristic energy-loss experiments.⁷

In the absence of interband transitions involving the σ electrons, ϵ_1 would be given by ϵ_1^π . The plasma resonance would occur where $\epsilon_1^\pi = 0$ which according to Fig. 3 is near 11 eV. The corresponding peak in the energy-loss function is exhibited in Fig. 5. This "hypothetical" resonance has a simple interpretation. It is associated with the π electrons of density one per atom. Since the oscillator strength for the π bands is essentially exhausted in the region, the dielectric constant should also be given closely by its asymptotic form $\epsilon^\pi(\omega) = 1 - 4\pi n N e^2 / m \omega^2$ where m is the free-electron mass, and n corresponds to one π electron per atom (in a crystal having the graphite atom density N). The plasma frequency is $\omega_{p\pi} = (4\pi n N e^2 / m)^{1/2}$ and $\hbar\omega_{p\pi} = 12.6$ eV, a value reasonably close to that found above.

When the contribution $\delta\epsilon_1^\sigma$ is considered, this simple picture is no longer valid. Since $\delta\epsilon_1^\sigma$ is positive in this region, it displaces the position of $\epsilon_1 = 0$ towards lower energy. It occurs near 7 eV according to Fig. 2. This can also be seen using the asymptotic form given above. We seek the solution of

$$\epsilon_1(\omega_p) = [1 - (\omega_{p\pi}^2 / \omega_p^2)] + \delta\epsilon_1^\sigma(\omega_p) = 0$$

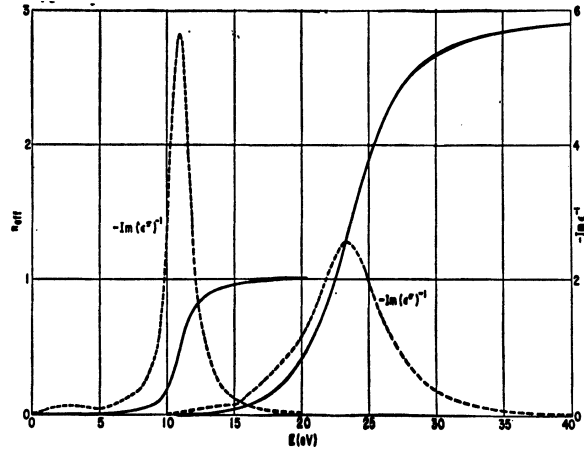


FIG. 5. The energy-loss function $-\text{Im}\epsilon^{-1}$ for two media having dielectric constants $\epsilon^\pi = \epsilon_1^\pi + i\epsilon_2^\pi$ and $\epsilon^\sigma = (1 + \delta\epsilon_1^\sigma) + i\delta\epsilon_2^\sigma$, respectively (dashed curves). The n_{eff} plots for each of these media are given by the solid curves.

and find

$$\hbar\omega_p = \hbar\omega_{p\pi} / [1 + \delta\epsilon_1^\sigma(\omega_p)]^{1/2} = 7.4 \text{ eV}$$

in good agreement with the experimental value of 7 eV. Since ϵ_2^π is reasonably small here, the plasma resonance is relatively undamped and a peak is observed in $-\text{Im}\epsilon^{-1}$. The position and amplitude of this peak is seen to depend not only on the energy for the onset of transitions involving the σ electrons, but also on the strength of these transitions (factors which determine the frequency dependence of $\delta\epsilon_1^\sigma$). If, for example, $\delta\epsilon_2^\sigma > 0$ for energies much below 9 eV, this resonance may not show up at all. Although the peak at 7 eV has been termed the π resonance,⁶ it is more accurately a hybrid resonance since it involves the cooperative behavior of both the π and σ electrons. It can be viewed as due to the π electrons screened by the frequency-dependent dielectric constant associated with the σ electrons. The resonance is thus similar in nature to the one observed in Ag near 4 eV.⁸

At higher energies a second peak is observed in $-\text{Im}\epsilon^{-1}$ which is associated with collective electron effects involving the combined π plus σ electrons. Since the oscillator strength for these bands is nearly exhausted in this region, according to Fig. 4, and transitions from the core states do not set in until much higher energies,²⁷ the dielectric constant should be well approximated by the asymptotic form given earlier where n now corresponds to 4 electrons per atom. The result $\omega_{p(\pi+\sigma)} = 25.2$ eV is in good agreement with the position $\epsilon_1 = 0$ and the peak in $-\text{Im}\epsilon^{-1}$.

It is expected that the position of this loss peak in other allotropic forms of carbon should depend mainly on the specimen density.⁷ For glassy carbon, having a density of 1.5, the peak in $-\text{Im}\epsilon^{-1}$ is near 21 eV. For diamond, it occurs near 30 eV.⁷ The position of the lower energy loss, observed in materials having π wave

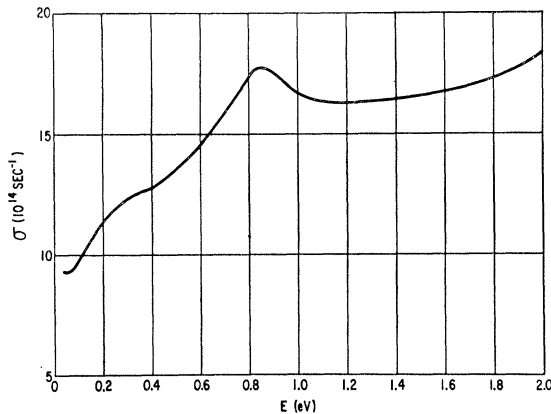


FIG. 6. The conductivity, $\sigma = \omega\epsilon_2/4\pi$ for graphite in the spectral region below 2 eV.

functions may not necessarily be so simply related to density since it depends, in part, on the nature of higher energy absorption processes which conceivably differ in other forms of carbon. The hybrid π resonance occurs near 5.6 eV in glassy carbon.²⁸

The band structure of graphite is rather well known for energies near the Fermi energy.¹ The band parameters²⁹ of the Slonczewski-Weiss model³⁰ for graphite have recently been determined accurately from magnetoreflexion and other experiments.² The present optical measurements are not of much help in elucidating the nature of intra- and interband transitions at these energies. In the first place, the reflectance data do not extend to low enough energies. Hence, the results derived by Kramers-Kronig analysis of the curve for R may not be very accurate here. Secondly, the separation of ϵ (actually ϵ^π) into intra- and interband parts, as accomplished in the cases of Al^4 and the noble metals,⁸ is more difficult for graphite since interband effects set in at very low energy. These transitions are

²⁸ The reflectance spectrum for unannealed pyrolytic graphite and glassy carbon is similar to that of graphite in the region near 15 eV. Absorption processes for these materials are thus similar in this energy range. We note $(7.0/5.6)^2 = 1.55$, which is close to the density ratio of graphite and glassy carbon. See also Ref. 7.

²⁹ J. W. McClure, Phys. Rev. **108**, 612 (1957).

³⁰ J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).

associated with the rise in ϵ_1 to positive values from the inherently negative values associated with intraband transitions.¹⁹

Weak structure in the reflectance curve is observed near 0.8 eV. This feature shows up as a peak in the plot of $\sigma = \omega\epsilon_2/4\pi$ shown in Fig. 6. Additional detail is seen in this curve near 0.3 eV which coincides roughly with structure in the emissivity measurements of Boyle and Nozieres.³¹ They interpret their data using a simplified version of the energy-band model of Slonczewski and Weiss. In this approximation, the parameters Δ and γ_2 , which describe the band overlap near the Fermi level,²⁹ are set equal to zero. This is just the Wallace structure³² where absorption processes are determined by γ_1 , the parameter which describes the maximum splitting of the bands at the zone edge HKH . They obtain $\gamma_1 = 0.14$ eV. This value is significantly smaller than the result $\gamma_1 = 0.27$ eV deduced from the analysis of the diamagnetism of graphite.³³ The magnetoreflexion data of Dresselhaus and Mavroides² give $\gamma_1 = 0.395$ eV. It appears reasonable, in light of these more recent experiments, to relate structure in the curves for R and σ near 0.8 eV ($\approx 2\gamma_1$) with the onset of transitions from the E_2 to the E_3 bands at the point K . Ergun³⁴ also reports $\gamma_1 \approx 0.4$ eV from preliminary measurements of the absorption spectrum of graphite.

Much of the oscillator strength for transitions involving the π electrons is relegated to absorption processes in the energy range 3 to 6 eV. The peak in ϵ_2 just below 5 eV has been associated with the maximum in the joint density of states of the π valence and conduction bands.^{1,17} Coulson and Taylor estimate this energy to be about 5 eV.²⁴

Note added in proof. J. G. Carter, R. H. Huebner, R. N. Hamm, and R. D. Birkhoff [Phys. Rev. **137**, A639 (1965)] have recently published values for the optical constants of hot-pressed pyrolytic graphite in the energy range 4 to 11 eV. Their experimental results are in reasonable agreement with those we present.

³¹ W. S. Boyle and P. Nozieres, Phys. Rev. **111**, 782 (1958).

³² P. R. Wallace, Phys. Rev. **71**, 622 (1947).

³³ J. W. McClure, Phys. Rev. **119**, 606 (1960).

³⁴ S. Ergun, Sixth Conference on Carbon, June 1963, as cited by J. W. McClure, IBM J. Res. Develop. **8**, 255 (1964).