Optical Properties of Graphite in the Region 1100 to 3000 Å*

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The optical properties of hot-pressed pyrolytic graphite were studied in the wavelength region from 1100 to 3000 Å. The real (n) and imaginary (k) parts of the complex index of refraction were obtained from reflectance measured at 20° and 70° incidence. The complex dielectric constant and the energy-loss function were determined from these values of n and k. The energy-loss function, $\mathrm{Im}(1/\epsilon)$, was found to exhibit a maximum at a wavelength of 1800 Å corresponding to an energy of 6.9 eV. This peak corresponds to the 7.5-eV loss in electron energy-loss experiments, where it has been attributed to the excitation of the conduction-electron plasma.

INTRODUCTION

THE electronic properties of graphite as determined by its molecular structure are of particular interest in biophysics because this material represents a "series limit" to the sequence of many ring aromatic molecules. That is, the geometrical arrangement of carbon atoms in rather widely spaced parallel planes within which the atoms are in hexagonal array gives a good representation of an organic molecule containing many benzene rings. Accordingly, we have measured the optical reflectance of hot-pressed pyrolytic graphite in the 1100- to 3000-Å spectral region and determined the energy loss function in an effort to obtain information on the predicted collective electron oscillation at 7.5 eV.[1,2]

The reflectance data have been analyzed by the CDC 1604 computer using a computer code based on Fresnel's equation[3] which solves for n and k from reflectances at two angles of incidence. In the analysis of the data presented here the simplifying assumption is made that the graphite is isotropic. Since the optical constants so obtained depend only slightly on the particular two angles chosen, it is believed this assumption introduces little error. This point will be investigated more thoroughly using polarized light, but it is not expected that the results will be affected significantly.

EXPERIMENTAL

The apparatus used for the reflectance measurements was essentially the same as that described by Berning, Hass, and Madden.[4] A brief description of the apparatus is given here. Unpolarized light from a hydrogen discharge lamp enters a Seya-Namioka monochromator which selects the wavelength of the incident beam. The graphite specimen located at the exit slit of the monochromator is rotated to various angles of incidence for the reflected intensity measurements or withdrawn from the beam to allow measurements of the incident intensity. The incident (I_0) and reflected (I) light are detected by an RCA 1P28 photomultiplier coated with sodium salicylate. The output from the photomultiplier is amplified by a Keithley dc micromicroammeter and the values of I and I_0 are read directly from the electrometer.

The hot pressed pyrolytic graphite used in our studies was manufactured by the Carbon Products Division of Union Carbide Corporation. The sample was taken from a half cylinder approximately $3\frac{1}{2}$ in. in diameter and $1\frac{1}{2}$ in. thick. The half cylinder was prepared by pressing several sheets of pyrolytic graphite in the c direction at a very high temperature. The structure of the material was determined by x-ray diffraction and electron transmission and diffraction studies. The "c" spacing was found to be 6.706 Å from the 004 reflection which is very close to the theoretical value of 6.708 Å. The crystallite size was estimated to be greater than 1000 Å in the "c" direction by x-ray diffraction and 1–3 μ in the "a" direction by the electron transmission studies. The orientation of the graphite planes was measured by an x-ray diffraction technique. The result of this measurement showed the 001 planes, which are

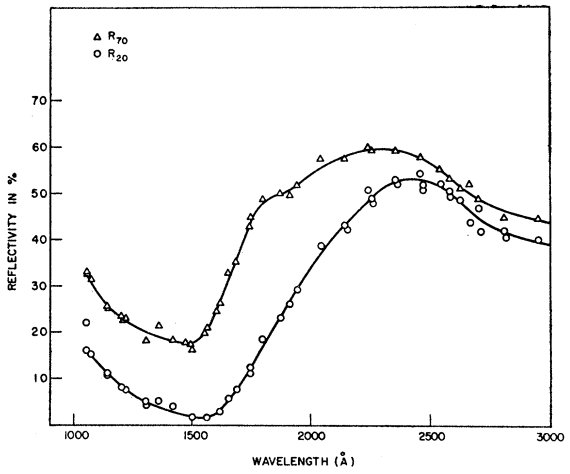

FIG. 1. Measured reflectance of unpolarized light from pyrolytic graphite for light incident at 20° and 70°.

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[1] N. R. Whetten, Bull. Am. Phys. Soc. **9**, 536 (1964).
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[3] R. H. Huebner, E. T. Arakawa, R. A. MacRae, and R. N. Hamm, (to be published).
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parallel to the plane of compression, to be very highly oriented with respect to each other. The spread in their orientation is best described as Gaussian with a width at half-maximum intensity of 1.4°. However, the planes are rotated randomly about the normal to the surface, that is, all (001) type directions are aligned parallel to the compression axis and all possible rotations about this axis are uniformly distributed. Thin strips 2 cm wide by 5 cm long of the pyrolytic graphite were peeled from the sample and attached to a holder. Reflectance was measured with the plane of incidence oriented perpendicular to the basal surfaces.

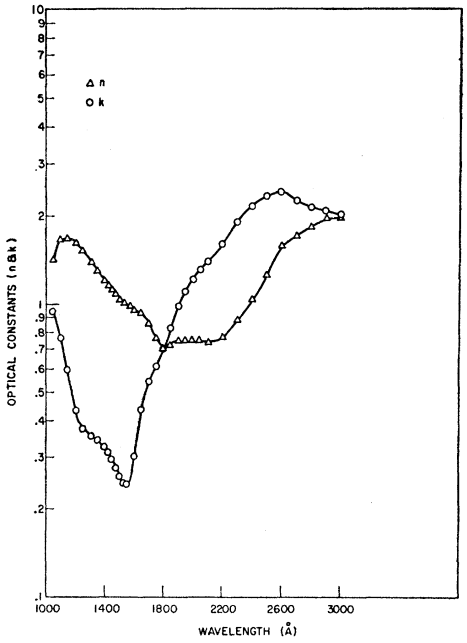

FIG. 2. The real and imaginary parts of the complex index of refraction for pyrolytic graphite.

RESULTS AND DISCUSSION

Reflectance curves for unpolarized light incident at 20° and 70° are shown in Fig. 1, where the basal surface is oriented perpendicular to the plane of incidence. In Fig. 2 the real (n) and imaginary (k) parts of the complex index of refraction obtained from Fig. 1 are presented for this orientation. The complex dielectric constant ϵ(where $\epsilon=\epsilon_1+i\epsilon_2$) is related to the complex index of refraction $(n+ik)$ by the equation $\epsilon=(n+ik)^2$. The real part, $\epsilon_1=n^2-k^2$, and the imaginary part, $\epsilon_2=2nk$, shown in Fig. 3, were calculated from the n and k values in Fig. 2. The condition for collective electron oscillation (i.e., the damping term ϵ_2 is small and ϵ_1 passes through zero) is satisfied at 1800 Å. The energy loss function, $\mathrm{Im}(1/\epsilon)$, is presented in Fig. 4 and can be seen to peak at about 1800 Å or at an energy of 6.9 eV. The simple plasma theory predicts that losses of 12.5 and 25 eV should be found in graphite on the basis of either one or four free electrons per atom, respectively.

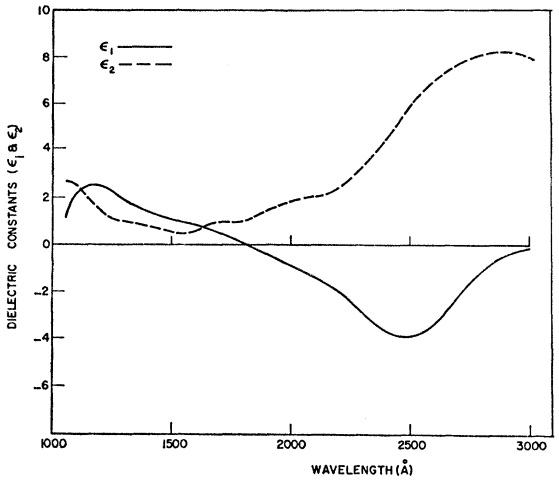

FIG. 3. The real and imaginary parts of the complex dielectric constant for pyrolytic graphite.

The shift in energy from 12.5 to 7.5 eV was accounted for by Ichikawa[5] and the latter value as well as the 25 eV were found in electron energy-loss experiments by Leder and Suddeth.[2] The anomalous dispersion of the smaller plasma energy noted by Watanabe[6] was also found to be in accord with Ichikawa's calculations. However, more recent theoretical studies of Ichikawa and Kobayashi[7] have questioned the earlier calculations of the first author and have placed the plasma resonance at less than 1 eV.

In a recent paper J. W. McClure[8] remarks that although rather detailed and precise models of graphite have been worked out they have failed to include the correlation of electron motion due to the Coulomb interaction. It is clear that more work, both theoretical and

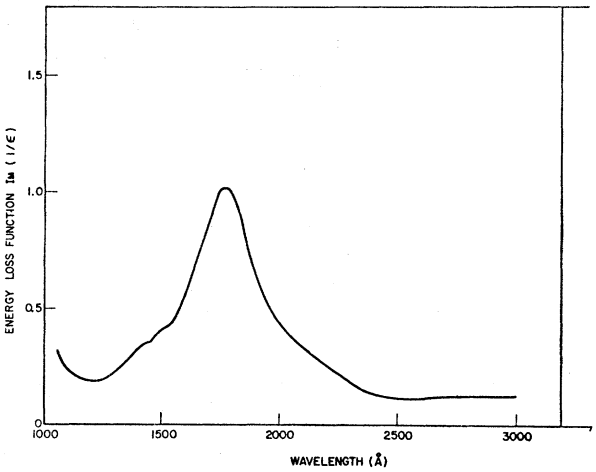

FIG. 4. The energy loss function $\mathrm{Im}(1/\epsilon)$ for pyrolytic graphite.

[5] Y. H. Ichikawa, Phys. Rev. **109**, 653 (1958).
[6] H. Watanabe, J. Phys. Soc. Japan **11**, 112 (1956).
[7] Y. H. Ichikawa and K. Kobayashi, Nihon University, Department of Physics, Report NUP-64-3 (unpublished).
[8] J. W. McClure, Bull. Am. Phys. Soc. **9**, 599 (1964).

experimental, is required. Our own optical studies are being extended to shorter wavelengths to determine if the 25-eV loss can be obtained from optical data. Efforts are also being made to extend the numerical analysis of reflectance data to anisotropic media.

ACKNOWLEDGMENTS

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Auger-Type Electron Ejection from the (111) Face of Nickel by Slow He^+, Ne^+, and Ar^+ Ions

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Experimental results concerning electron ejection from the atomically clean (111) face of nickel by singly charged ions of He, Ne, and Ar are reported. Total yield and kinetic-energy distribution of ejected electrons were measured as functions of ion energy in the range 4 to 100 eV. Revised experimental procedures have made it possible to extend the range of useful incident ion energies from the previous 10-eV lower limit down to 4 eV. Significant differences in the electron energy distributions are observed for ions whose energies differ by as little as 1 eV. The measured electron energy distributions were found to be markedly different from those observed for silicon and germanium as well as for tungsten and molybdenum. This is the result of differing state densities in the filled bands of these materials. The basic features of the results are only briefly discussed, since more extensive interpretive material will be subsequently reported. Data demonstrating the cleanness of the surface and the effects of adsorption of oxygen, carbon monoxide, and hydrogen are also presented.

I. INTRODUCTION

AUGER–TYPE electron ejection from clean surfaces of elemental semiconductors (silicon and germanium) as well as polycrystalline refractory metals (tungsten and molybdenum) by noble gas ions in the kinetic energy range 10 to 1000 eV has been studied and reported on previously.[1,2] In this paper we report the results of an experimental study of the electron ejection from the (111) face of monocrystalline nickel by He^+, Ne^+, and Ar^+ ions of incident kinetic energies K in the range 4 to 100 eV.

It has been well established that the principal electronic interaction of noble gas ions with solid surfaces in this kinetic energy range is of an Auger type. The ions are neutralized in a process (Auger neutralization) involving two electrons from the highest lying filled band in the solid. One electron tunnels into the ground state of the atom releasing energy to a second electron in the solid which becomes a fast internal secondary. Some of these latter electrons may cross the surface barrier and are detectable outside. The observed kinetic energy distributions from clean surfaces of those materials studied so far have been accounted for in terms of this mechanism with assumed functions for the state density in the filled band and relative transition probability through the band.[1,2] Work on polycrystalline tungsten using noble gas and other ions has recently been reported by Propst and Lüscher.[3]

One of our current reasons for studying Auger electron ejection is to look into the possibility of extracting at least the coarse features of the state density near the top of the filled band of the solid from the observed electron kinetic energy distribution. The transition metals are of particular interest in this regard, and nickel is one of the best of these with which to experiment since good quality single crystals are now available and the surface structures have been extensively studied by low-energy electron diffraction.[4,5] Thus our primary interest in the present study has been to observe the energy distribution of ejected electrons from the clean surface

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