

## Optical constants of arc-evaporated amorphous carbon in the far-infrared spectral region

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(Received 28 December 1983)

The optical constants  $n$  and  $k$  of arc-evaporated amorphous carbon films between 400 and 4800  $\text{cm}^{-1}$  were determined by measuring the transmittance and the reflectance of the films. Two broad bands with maxima at 703 and 1233  $\text{cm}^{-1}$  in the spectral dependence of the absorption index  $k$  are interpreted as a disorder-induced absorption due to tetrahedrally coordinated carbon atoms. A shoulder extending to about 1650  $\text{cm}^{-1}$  gives reason to believe that there is also a considerable amount of trigonally coordinated carbon atoms in the film.

## I. INTRODUCTION

Thin arc-evaporated amorphous carbon films<sup>1</sup> are widely used as substrates in electron microscopy and, in particular, in high-energy electron spectroscopy, because very thin films (down to a thickness of 7 nm) with a great mechanical stability can be prepared. The energy-loss spectra obtained by electron spectroscopy are usually interpreted in terms of the dielectric theory (see Ref. 2 for the plasmon region, and Ref. 3 for an example for surface phonons). Since a carbon film is frequently required to support the sample of interest, a sandwich system<sup>4</sup> is formed. Thus, for a proper analysis of the spectrum, the frequency-dependent dielectric constants of both the sample material and the carbon substrate must be known. The development of electron spectrometers with very high resolution, reaching now 2 meV for 30-keV electrons,<sup>5</sup> allows the energy-loss spectra to be extended to very small energy losses. In order to make the interpretation of the spectra feasible, the knowledge of the optical constants of the evaporated carbon films in the far-infrared spectral region is required. As far as the authors are aware, the optical constants of arc-evaporated carbon below 0.6 eV have yet to be published. The aim of this work was to determine the optical constants of amorphous carbon (*a*-C) between 400  $\text{cm}^{-1}$  (0.05 eV) and 4800  $\text{cm}^{-1}$  (0.6 eV), namely, the refractive index  $n$  and the absorption index  $k$ , which constitute the complex index of refraction  $\tilde{n} = n + ik$ .

The optical constants of arc-evaporated carbon above 0.6 eV have been measured by Arakawa, Williams, and Inagaki<sup>6</sup> and by Jungk and Lange.<sup>7</sup> Optical data of other types of amorphous carbon were published by Foster and Howarth,<sup>8</sup> Lévy-Mannheim and Méring,<sup>9</sup> and Bubenzer, Dischler, Brandt, and Koidl.<sup>10</sup> A survey is given in Table I.

There are many methods for determining the optical constants of a slab (see, for example, Meyer,<sup>11</sup> Wolter,<sup>12</sup> and Heavens<sup>13</sup>). We have applied here the classical method of measuring the optical transmittance and the reflectance of the films independently. The evaluation followed the method proposed by Murmann<sup>14</sup> (see also Refs. 11 and 12). Originally, this was a graphical method. The application of a computer, however, makes this method much more powerful since the desired numerical accuracy can always easily be obtained.

## II. EXPERIMENTAL

## A. Preparation and measurement

The carbon films were prepared by arc-evaporation of pointed carbon rods (spectrographic carbon, diameter 6.15 mm, impurities 20 ppm) onto a KBr substrate, 25 mm in diameter, at room temperature. The vacuum pressure during the evaporation was  $5 \times 10^{-5}$  Torr, the thickness of the films approximately 0.1  $\mu\text{m}$ . The film structure investigated is shown in Fig. 1(a). The ir detector was taken

TABLE I. Values of the optical constants  $n$  and  $k$  of amorphous carbon in the infrared, measured by various authors. The data are given for the lower energy limits  $\hbar\omega$  of their measurements, unless a range is named.

	$\hbar\omega$ (eV)	$n$	$k$	Comments
Arakawa <i>et al.</i> <sup>6</sup>	0.6	2.42	0.95	Glassy carbon
		2.73	1.54	Evaporated <i>a</i> -C
Foster and Howarth <sup>8</sup>	0.124	1.9–2.4	0.6–1.2	Carbon-soot
Jungk and Lange <sup>7</sup>	1.25	3.4	0.82	Evaporated <i>a</i> -C
Lévy-Mannheim and Méring <sup>9</sup>	0.25	0.46	1.91	Evaporated graphite
Bubenzer <i>et al.</i> <sup>10,16</sup>	0.124–1.0	1.85–2.20	a	GD <i>a</i> -C:H
Present work	0.05–0.6	2.7–3.5	0.12–0.23	Evaporated <i>a</i> -C

<sup>a</sup> $\alpha = 15 \text{ cm}^{-1}$  at  $\nu = 3570 \text{ cm}^{-1}$ .

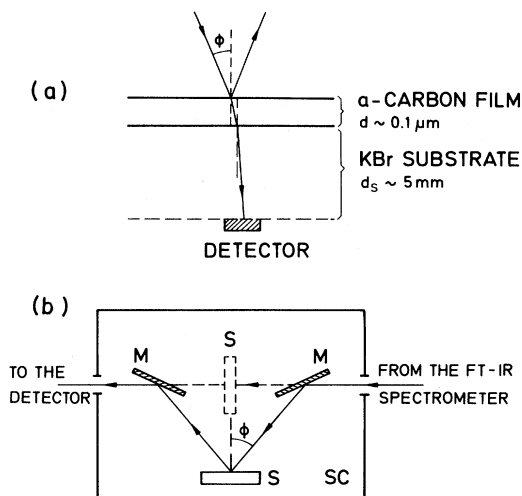


FIG. 1. (a) The layer structure investigated. (b) The trajectories of ray for the measurement of the reflectance (solid lines) and of the transmittance (dashed lines). *S*, sample; *M*, mirror; *SC*, sample compartment.

to be mounted directly onto the KBr substrate. The influence of the air gap between the substrate and the detector was ignored.

The thickness of the carbon films was measured by a quartz monitor and, after evaporation of an additional reflecting aluminum coating, by multiple-beam interferometry. The ir transmittance and reflectance of the carbon films were measured by means of a Nicolet ir Fourier spectrometer model no. MX1. The measurements were carried out at atmospheric pressure, since carbon does not oxidize at room temperature. The mirror system [Fig. 1(a)], which was necessary for the measurement of the reflectance, consisted of two mirrors. One deflected the ir beam to the sample, the other one led the light reflected from the sample back to the detector. In order to determine the reflectance of the sample, the sample was substituted in a first run by an Au mirror of the same sort as the other two of the reflection measuring system. The reflectance of these Au mirrors had been measured before.

The mirror system [Fig. 1(b)] did not allow a measurement at normal incidence for geometric reasons. Therefore, it had to be remembered that at oblique incidence the reflectance depended on the polarization of the light. Although the globar source of the spectrometer emitted unpolarized light, the beam splitter and the mirrors in the spectrometer partially polarized the light and, moreover, the polarization was dependent on the wavelength of the light. In order to minimize possible errors due to a partial polarization of the light, the angle of incidence measured to the normal of the sample was taken as small as possible, since in this case the difference of the reflectance of the two components of polarization, parallel and perpendicular to the plane of incidence  $R^{\parallel}$  and  $R^{\perp}$ , would be small.

At an angle  $\phi = 20^\circ$  the values of the reflectance amount to  $R^{\parallel} = 0.34$  and  $R^{\perp} = 0.30$  for  $n = 3.0$  and  $k = 0.20$ . The error caused by this difference could be reduced by taking

the average  $R = \frac{1}{2}R^{\parallel} + \frac{1}{2}R^{\perp}$ . Even if the intensity of the parallel component were double the intensity of the perpendicular component, the error introduced by this approximation would be only 3%.

### B. Evaluation of the data

Expressions for the transmittance  $T$  and the reflectance  $R$  of the layer system sketched in Fig. 1(a) can be derived from classical electrodynamics. The results are two lengthy formulas which can be found in Ref. 11. They are symbolized here by

$$T = T(n, k, n_s, k_s, d, \lambda, d_s) \quad (1a)$$

and

$$R = R(n, k, n_s, k_s, d, \lambda, d_s), \quad (1b)$$

where  $n$  and  $k$  mean the optical constants,  $d$  the thickness, and  $\lambda$  the wavelength of light. The subscript  $s$  labels the corresponding parameters of the substrate. All parameters except  $n$  and  $k$  must be known. The expressions (1) are so involved that they cannot be solved explicitly for  $n$  and  $k$ . The method used to determine  $n$  and  $k$  in this paper goes back to the graphic procedure described by Murmann.<sup>14</sup> This procedure was converted into a computer program.

The Fourier spectrometer fed the computer the values of the reflectance and the transmittance of the carbon film on KBr at a given wavelength. In the first step a function  $n = f_R(k)$  was determined such that the substitution of these values  $n$  and  $k$  into Eq. (1b) yielded the measured reflectance. In the second step a second function  $k = f_T(n)$  was determined for the measured value of the transmittance  $T$ , Eq. (1b). The choice of the dependent and independent variables was guided by the slope of the corresponding curves. In the third step the two functions obtained were superimposed and the crossing was located by iteration. The coordinates of this crossing are the desired pair of optical constants  $n$  and  $k$  which, after substitution into Eqs. (1a) and (1b), give the measured values  $T$  and  $R$ .

In order to obtain the zeros of the functions, Newton's method was used. As mentioned above, the remaining parameters in Eqs. (1a) and (1b) had to be determined before by different ways. The refractive index  $n_s$  of the KBr substrate was taken from the literature,<sup>15</sup> and the absorption index  $k_s$  was measured. Interference fringes were not observed in the transmittance  $T_{\text{KBr}}$  of the KBr slab, therefore an average was taken over the interference terms in  $T_{\text{KBr}}$ .

### III. EXPERIMENTAL RESULTS

Figure 2 and Table II present the wave-number dependence of the indices of refraction and absorption for one of our  $\alpha$ -C films. The refractive index  $n$  is nearly constant between 4800 and 1600  $\text{cm}^{-1}$  and does not show any noticeable structure. In this spectral range  $n$  is between 2.5 and 2.8. From 1600  $\text{cm}^{-1}$  to lower wave numbers,  $n$  increases to 3.5. The course of the index of absorption is likewise rather flat down to about 2000  $\text{cm}^{-1}$  (note the ex-

TABLE II. The optical constants of arc-evaporated amorphous carbon. The whole set of data in steps of  $5 \text{ cm}^{-1}$  is available from the authors.

$\tilde{\nu}$ ( $\text{cm}^{-1}$ )	$n$	$k$	$\tilde{\nu}$ ( $\text{cm}^{-1}$ )	$n$	$k$
4801	2.86	0.127	1002	2.92	0.166
4001	2.75	0.139	901	2.97	0.159
3003	2.68	0.149	804	3.02	0.182
2000	2.68	0.126	703	3.12	0.229
1802	2.69	0.118	602	3.26	0.212
1465	2.72	0.170	404	3.48	0.180
1233	2.79	0.185			

tended scale for  $k$  on the right-hand side of the diagram). Between 2000 and  $400 \text{ cm}^{-1}$  two broad peaks are located at 1233 and  $703 \text{ cm}^{-1}$ . These two peaks are of interest in the following context.

Indications of any stretching modes of the hydrocarbon groups  $\text{CH}_x$  were not observed. From this it is concluded that the films are essentially free of hydrogen, and hydrocarbons from the residual vacuum are not incorporated. This is in contrast to films prepared by decomposition of benzene in a glow discharge, GD  $a\text{-C:H}$  films, where these  $\text{CH}_x$  bands (and others) are striking.<sup>16</sup>

The results of the present study are compared with the data of other authors in Table I. Our values for  $k$  are considerably lower than those of the other authors. They varied somewhat for the films prepared; the characteristic behavior as shown in Fig. 2 was always the same. The ir absorption in GD  $a\text{-C:H}$  films appears to be still lower<sup>16</sup> than in our arc-evaporated carbon films, presumably because in GD  $a\text{-C:H}$  films certain defect states, which contribute to the absorption in evaporated films, were passivated by hydrogen. The values obtained for the refractive index  $n$  are essentially consistent with those of Table I with the exception of Lévy-Mannheim's and Méring's results.<sup>9</sup>

#### IV. DISCUSSION OF THE RESULTS AND CONCLUSIONS

Kakinoki *et al.*,<sup>17</sup> after a careful analysis of the electron-diffraction pattern of evaporated carbon films, came to the conclusion that the films consist of a random

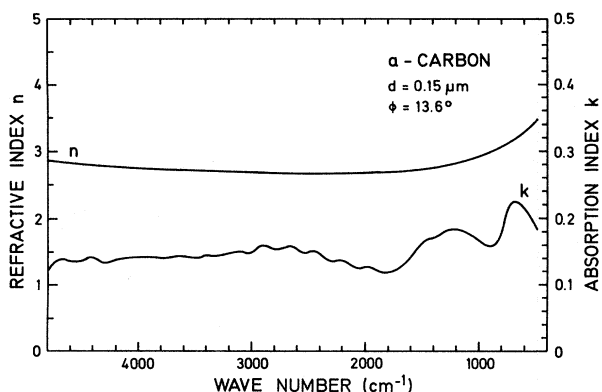


FIG. 2. Refractive index  $n$  and the absorption index  $k$  of an arc-evaporated amorphous carbon film. The weak modulation in the course of  $k$  between 2000 and  $3000 \text{ cm}^{-1}$  developed from the evaluation process and has no physical meaning.

network of graphitelike (threefold-coordinated) and diamondlike (fourfold-coordinated) configurations, each of several angstroms in size. According to the opinion of these authors this microstructure should be responsible for the high mechanical stability of the films and for the great hardness of the material. Stenhouse and Grout<sup>18</sup> found that by a renewed analysis of the electron scattering data of Ref. 17 a model containing partially ordered, layered domains of trigonally coordinated carbon atoms connected by a network of tetrahedrally coordinated carbon atoms would also be consistent with the experimental data. Fink *et al.*<sup>19</sup> concluded from a  $K$ -edge extended x-ray absorption fine structure study combined with electron energy-loss spectroscopy that their gd  $a\text{-C:H}$  film contains  $\frac{2}{3}$  of the carbon atoms in tetrahedral coordination and  $\frac{1}{3}$  in trigonal coordination. On the other hand, ESR, electron energy loss, and Raman spectroscopy studies made on amorphous carbon films prepared by electron-beam evaporation of graphite or sputtering do not support the possibility of tetrahedral coordination.<sup>20</sup>

Infrared absorption is forbidden for reasons of symmetry in the diamond lattice; two first-order infrared active modes exist, however, in graphite at  $1587$  and  $868 \text{ cm}^{-1}$  as shown by Nemanich *et al.*<sup>21</sup> The disorder in amorphous carbon is expected to relax the optical selection rules and a disorder-induced one-phonon absorption (see, e.g., Ref. 22) should be observed. Thus following Dawber and Elliott<sup>23</sup> we may write for the absorption coefficient  $\alpha(\omega)$

$$\alpha(\omega) = \frac{2\pi}{\lambda} k(\omega) \propto A(\omega)^2 g(\omega), \quad (2)$$

where  $A(\omega)$  is the dipole transition moment induced by the disorder, and  $g(\omega)$  is the one-phonon density of states. The course of the absorption coefficient is determined by the one-photon density combined with the frequency-dependent transition moment  $A(\omega)$ . If  $A(\omega)$  is constant for all lattice vibrations, or varies only weakly with the frequency, the maxima of the absorption index will correspond to the maxima of the phonon density of states. Nothing is known about the behavior of  $A(\omega)$  for evaporated carbon films, and their phonon density of states is also unknown. Assuming, however, in the first approximation the frequency dependence of  $A(\omega)$  to be smooth, we can compare the measured absorption index with the one-phonon densities of states of crystalline diamond<sup>24,25</sup> and graphite<sup>26</sup> (Fig. 3), since their main structure is determined by the short-range order, which is

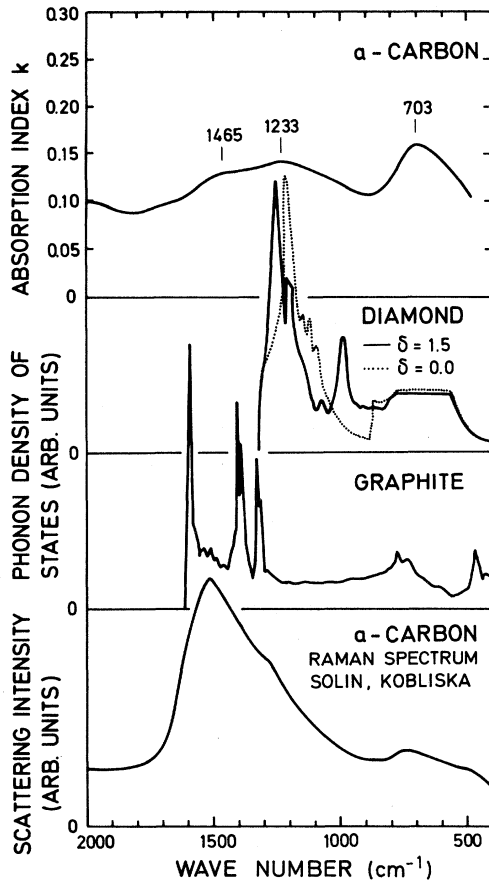


FIG. 3. Comparison between the wave-number dependence of the absorption index  $k$  of  $a$ -C between 400 and 2000  $\text{cm}^{-1}$ , the phonon density of states of diamond (Ref. 25) and graphite (Ref. 26), and the Raman spectrum (Ref. 27) of  $a$ -C prepared by electron-beam evaporation of graphite.

preserved in the amorphous modification.

The phonon density of states of diamond exhibits a sharp peak at 1255  $\text{cm}^{-1}$  with a secondary maximum at 1213  $\text{cm}^{-1}$ , a weaker peak at 993  $\text{cm}^{-1}$ , and a flat plateau due to the TA modes between 573 and 776  $\text{cm}^{-1}$ . If the antisymmetric second-neighbor constant  $\delta$  is set equal 0, a deep minimum appears at 922  $\text{cm}^{-1}$  and the peak at 993

$\text{cm}^{-1}$  vanishes. The main maximum shifts to 1205  $\text{cm}^{-1}$ . The phonon density of states of graphite shows maxima at 466, 775, 1340, 1420, and 1610  $\text{cm}^{-1}$ .

The measured frequency dependence of the absorption index of arc-evaporated carbon compares to these density-of-state distributions as follows: In general the experimental curve more closely resembles the density of states of diamond than that of graphite, since the maxima at 703 and 1233  $\text{cm}^{-1}$  would agree well with a somewhat broadened density-of-states distribution of diamond. The distinct minimum at 920  $\text{cm}^{-1}$  gives reason to believe that the density of states of the amorphous modification in question is better described by setting the second-order parameter  $\delta=0$ . Although a considerable contribution to light absorption seems to originate from diamondlike tetrahedrally bonded carbon atoms, the shoulder around 1470  $\text{cm}^{-1}$  and its spread up to about 1650  $\text{cm}^{-1}$  suggest that the contribution of graphitelike trigonal bonds must not be neglected.

The Raman spectrum of amorphous carbon deposited by electron-beam evaporation or by dc sputtering shows an asymmetric strong band with the maximum between 1500 and 1580  $\text{cm}^{-1}$  (Solín and Kobliska,<sup>27</sup> Wada, Gaczi, and Solín,<sup>20</sup>) (see Fig. 3), which agrees well with the broadened one-phonon density of states of graphite. Also the two humps on the low-energy tail of the spectrum correspond fairly well to the weak maxima of the acoustical modes within the density of states. Thus the authors<sup>20</sup> conclude that their amorphous carbon contains solely trigonally coordinated carbon atoms.

This is in contrast to the results of our infrared-absorption measurements for arc-evaporated carbon films. These films contain, as estimated with the understanding that the vibrational modes of trigonally and tetrahedrally coordinated atoms have the same oscillator strength, at least equal contributions of carbon atoms in tetrahedral and in trigonal coordination.

#### ACKNOWLEDGMENTS

Financial support of the Stiftung Volkswagenwerk is gratefully acknowledged. Thanks are due to Dr. M. Essig and Dr. B. Schröder for useful discussions and to H. W. Gress for providing the Au mirrors.

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