

Radial Distribution Function of Amorphous Carbon

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(Received 5 July 1990)

The radial distribution function obtained by neutron diffraction on amorphous carbon films is compared to recent theoretical models. The first-neighbor peak is found to be quite broad for an amorphous semiconductor, in qualitative agreement with the predictions of molecular dynamics. However, the detailed shape of the first two peaks, including contributions in the minimum region, differs from all current models. Although the areas of the first two peaks indicate predominant threefold bonding, no evidence for a distinct peak associated with graphitelike, intrahexagon, third neighbors is observed. This distinguishes amorphous carbon from local two-dimensionally ordered graphitelike materials.

PACS numbers: 61.42.+h, 61.12.-q, 68.65.+g

An exceptional, if not unique, interest exists in the physical and chemical properties of the different phases of carbon. Quite special to carbon is the ability to exist under normal temperature and pressure conditions in a range of nonequilibrium crystalline and noncrystalline structures. Considerable interest exists in the structures of the latter, potentially very diverse range of disordered structures. These encompass both amorphous as well as partially ordered systems with intermediate character unique to carbon that are associated with the presence of intralayer order and interlayer disorder.¹ In this study we address the radial distribution function (RDF) of the amorphous phase of carbon for which several recent studies have been reported.^{2,3} The results provide a means of contrasting the order in amorphous carbon (*a*-C) with more ordered materials such as "glassy" and graphitelike, hard carbon films of considerable current interest.

Although a number of recent models have been proposed for the structure of *a*-C,²⁻⁴ reliable experimental data have not existed for comparison with theory. Previous radial distribution functions have been obtained by electron diffraction^{5,6} on materials which were not characterized as to purity, density, or whether possible partially ordered, microcrystallike constituents were present. In this study we report on the RDF of *a*-C prepared and studied under conditions that are appropriate for comparison with different structural models. The RDF of *a*-C is found not to exhibit a distinct peak associated with ordered sixfold ring structures that have been suggested in a number of quasi-two-dimensional, graphitelike models.⁷⁻⁹ While qualitative agreement is observed with recent fundamental structural calculations^{2,3} regarding predominant threefold bonding, important differences in RDF peak positions and form are observed. The RDF of *a*-C is also found to differ from other elemental amorphous semiconductors such as *a*-Si and *a*-Ge, in exhibiting a wide bond-length variation. This result is consistent with molecular-dynamics theory.³

Thick films of *a*-C were prepared by rf sputtering in a high-vacuum system of base pressure 1×10^{-7} Torr. A 5-in.-diam cathode was sputtered at a power of 400 W at an Ar pressure of 8 mTorr. Substrates of Cu were

placed in good thermal contact with a liquid-nitrogen-cooled plate to prevent film ordering due to heating. Such ordering is observed in the Raman spectra as distinct peaks or weak shoulders at approximately 1330 and 1580 cm^{-1} ; these features are also present in glassy carbon and most hard carbon films.¹⁰ In contrast,^{11,12} *a*-C exhibits a single broad high-frequency Raman peak at $\sim 1500 \text{ cm}^{-1}$ as well as additional low-frequency bands below 800 cm^{-1} that are common to density-of-states scattering in amorphous solids.¹³ To confirm the amorphous nature of deposited films, Raman measurements on a substantial number of samples of thickness 4 μm were performed. A total of 0.8 g of sample was employed for several neutron-diffraction measurements performed at 300 K at the SEPD instrument at the Argonne National Laboratory Intense Pulsed Neutron Source (IPNS). The films were removed from the substrate by using dilute HCl acid and cleaned thoroughly in deionized water. Low-angle scattering of these samples indicated ~ 3 at.% H, whose contribution was removed by an analysis of H scattering effects.¹⁴ A Lorch termination function $(\sin x)/x$, where $x = \pi Q/Q_{\text{max}}$, was used in the determination of the RDF. Measurements of the RDF of coarsely ground hexagonal graphite were employed to test the RDF accuracy of *a*-C and to estimate thermal-broadening contributions. The RDF of graphite yields values of the first- and second-neighbor distances and coordination numbers with $< 1\%$ deviation from their established results. The macroscopic density of the *a*-C films was estimated from weighing selected samples to be 2.0 g/cm^3 , while constraints on the RDF at low interatomic distances yield an *a*-C network density of $\rho_0 = 2.44 \text{ g/cm}^3$. This value is comparable to that employed in the model of Tersoff,² 20% greater than that assumed by Galli *et al.*,³ and 10% less than the C340 model of Beeman *et al.*⁴ Optical absorption and reflectance measurements yielded a Tauc gap of 0.57 eV, in agreement with the results of Hauser for dc sputtered *a*-C films deposited at low temperatures.¹⁵

In Fig. 1 the structure factor $S(Q)$ for *a*-C is shown for an average over detectors at angles of $\pm 90^\circ$, $\pm 60^\circ$, $+30^\circ$, and -15° . At low Q values, small-angle scattering associated with voids yields a large peak. This has

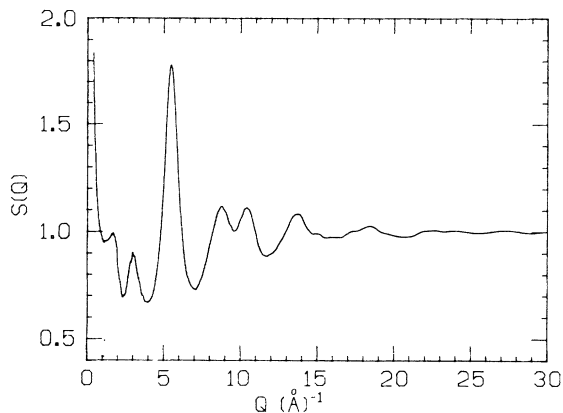


FIG. 1. Wave-vector dependence of the structure factor of *a*-C at 300 K. The dotted curve indicates the low- Q extrapolation employed for the RDF analysis.

been subtracted by a quadratic extrapolation to $Q=0$. Different extrapolation procedures at these low Q values were found to not influence the radial distribution functions. The form of the low- Q scattering indicates a distribution of void sizes, including a considerable fraction of small voids.

Fourier transformation of $F(Q) = Q[S(Q) - 1]$, terminated at a maximum wave vector $Q = 30 \text{ \AA}^{-1}$, yields the pair distribution function $G(r)$. The radial distribution function, $J(r) = rG(r) + 4\pi r^2 \rho_0$, and the network density were determined by imposing the constraint that $J(r)$ oscillate about zero intensity below the first RDF peak. Figure 2 indicates the modified pair distribution function $T(r) = J(r)/r$ for *a*-C for values up to 10 \AA along with that obtained on polycrystalline graphite. The $T(r)$ of *a*-C indicates four distinct peaks with rapid damping in form relative to other amorphous semiconductors. At r values of $\sim 6-7 \text{ \AA}$, $T(r)$ closely approaches the linear form $4\pi r \rho_0$. The detailed form of $T(r)$ in Fig. 2 differs in the form and positions of the first and second peaks from the results of Kakinoki *et al.*⁵ and Boiko, Paltnik, and Derevyanchenko.⁶ That our observed network density is found to be similar to the large estimated macroscopic density of the former is regarded as fortuitous.

Figure 3 compares the experimental $T(r)$ from 0 to 4 \AA with three different theories encompassing empirical-pseudopotential,² first-principles molecular-dynamics,³ and energy relaxed, hand-built models.⁴ These models have similar values for the percentage of diamondlike, fourfold bonds of $\sim 10\%$, 15% , and 14% , respectively. The theoretical $T(r)$ spectra have been convolved to correspond to the experimental resolution, determined from $Q(\text{max}) = 30 \text{ \AA}^{-1}$, by appropriate Q - r Fourier transforms. Although all theoretical models reproduce the main experimental features, they differ in detail. Table I compares various parameters associated with peak positions, most probable bond angles, densities, and integrated coordination numbers.

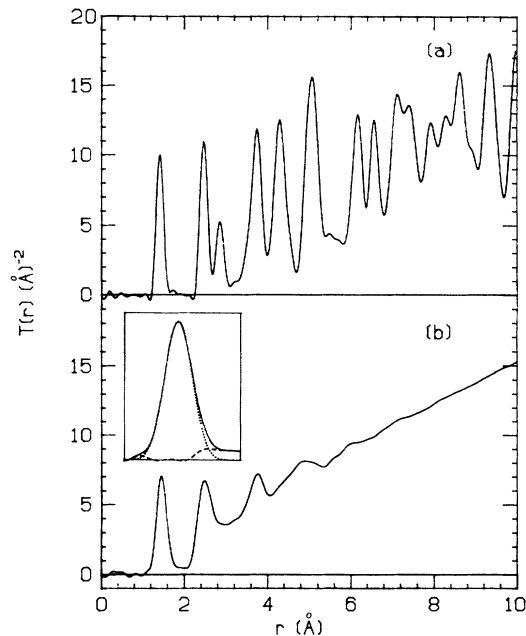


FIG. 2. Modified radial distribution function of (a) graphite and (b) *a*-C. Inset: The dotted line indicates a Gaussian fit of the first peak and the dashed line is the residual.

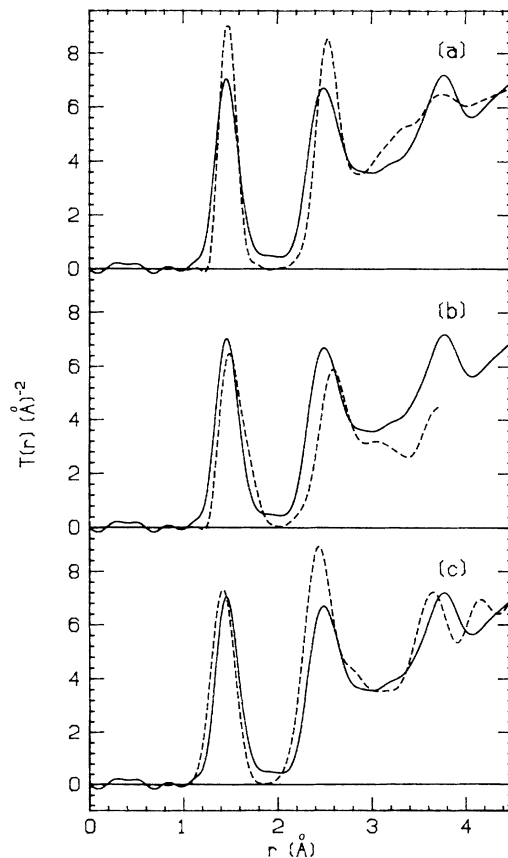


FIG. 3. Comparison of experimental $T(r)$ (solid line) and theoretical models of *a*-C (dashed). (a) empirical pseudopotential (Ref. 2); (b) molecular dynamics (Ref. 3); (c) relaxed hand-built C340 (Ref. 4).

TABLE I. Comparison of various parameters associated with peak positions, most probable bond angles, densities, and integrated coordination numbers. Tilde over symbol denotes peak value.

	<i>a</i> -C expt.	Ref. 2	Ref. 3	Ref. 4	Graphite
<i>T</i> (<i>r</i>):					
\tilde{r}_1 (Å)	1.46 ^a	1.48	1.49	1.43	1.42
\tilde{r}_2 (Å)	2.49	2.53	2.59	2.44	2.46
$\tilde{\theta}$ (deg)	117.0	117.4	120.7	118.4	120
<i>J</i> (<i>r</i>):					
ρ_0 (g/cm ³)	2.44	2.38	2.0	2.69	2.26
$z(r_{\min})$ (atoms)	3.34 ^b	3.07	3.20	3.28	3.00
$z(\tilde{r}_2) - z(r_{\min})$	1.04	1.04	0.88	1.26	1.00
$z(r_{\min})$					

^aA value of 1.45 Å is obtained for a cutoff, without a Lorch function.

^bThis value corresponds to $r_{\min} = 1.90$ Å. Other r_{\min} will give slightly different results.

The experimental *T*(*r*) of *a*-C yields a peak at 1.46 Å, a value 0.04 Å larger than that of graphite and 0.08 Å less than that of diamond. While this value is nearest to the empirical-potential model of Tersoff,² the peak is found to be substantially broader. The observed static-disorder, Gaussian width of ~6% of the first *T*(*r*) peak is much larger than the ~1% value obtained in *a*-Ge and *a*-Si.^{16,17} This large bond-length dispersion is qualitatively consistent with the molecular-dynamics model of Galli *et al.*,³ although the peak of this model occurs at 1.49 Å and has a substantially larger asymmetry to higher *r* values. In particular, the molecular-dynamics result exhibits a longer tail and a value of *T*(*r*) = 0 at ~2 Å, while the observed RDF exhibits a nonzero minimum between 1.8–2.0 Å.

As shown in the inset of Fig. 2(b), it is possible to fit the experimental *T*(*r*) reasonably well by a Gaussian, but only for *r* values up to ~1.58 Å. The area under the corresponding *J*(*r*) curve corresponds to ~3.04 atoms. Additional longer-bonded first neighbors not fitted by a Gaussian yield an integrated coordination number, $Z(r) = \int_0^r J(r') dr'$, of 3.34 atoms for $r = 1.90$ Å. These results clearly imply the presence of fourfold bonds, as suggested by previous studies.^{5,6} Preliminary NMR studies yield two distinct peaks which are related to threefold and fourfold bonding.¹⁸ While the values of *Z*(*r*) suggest predominant threefold bonding, the form of the first RDF peak precludes a precise quantitative estimate of the fraction of fourfold bonds.

A comparison of the second *T*(*r*) peaks of Fig. 3 indicates that the experimental peak at 2.49 Å and its leading edge occur at substantially lower values than the empirical-potential and molecular-dynamics predictions. The most probable value of the bond angle obtained from the first two peaks of 117° is lower than the models of Fig. 3, as well as that of graphite. To obtain informa-

tion about the relative contributions of threefold and fourfold bonding to the RDF, it is useful to compare the ratio of the area of the lower half of the second peak of *J*(*r*) and the area of the first peak. This ratio in graphite has a value of 1 and in diamond of 1.5. The corresponding ratio obtained here of 1.04 is thus considerably closer to that for graphite and agrees well with the empirical-pseudopotential model which contains ~10% fourfold atoms. The hand-built and molecular-dynamics models with 14% and 15% fourfold atoms, respectively, yield 1.26 and 0.88 for this area ratio. In contrast, a relaxed hand-built model⁴ with 48% fourfold bonds has a ratio of 1.7. These results clearly suggest that a small fraction of fourfold bonds are present in our *a*-C samples. This predominant threefold bonding differs from an analysis of earlier RDF studies.⁵ It is possible that a reasonable fraction of the fourfold atoms might account for the longer bonding distances observed in the minimum between the first and second peaks of Fig. 3. Theoretical analysis of the transition from rhombohedral graphite to diamond suggests that longer-bonded diamondlike orbitals occur at these distances.¹⁹

In the region between the observed second and third *T*(*r*) peaks of Fig. 3 no distinct feature is observed between ~2.8 and 3.0 Å. In graphite a peak corresponding to a third-bonded intrahexagon distance of twice the first-neighbor distance occurs in this region (2.84 Å). The experimental results in *a*-C thus imply the absence of a significant fraction of ordered sixfold rings. This is consistent with the predictions of the empirical-pseudopotential model of Fig. 3(a). The presence of small features of 2.8 Å in the hand-built model and at 3.1 Å in the molecular-dynamics model is not consistent with experiment. The absence of a *T*(*r*) peak corresponding to that of graphite in Fig. 2(a) at ~4.15 Å is further evidence for the lack of ordered hexagonal ring structures. These results also clearly demonstrate that other models of *a*-C based on arrays of ordered graphitelike sixfold rings⁷⁻⁹ with a high degree of intermediate-range order are not correct. These models may, however, describe the structure of glassy C, as its RDF does exhibit a distinct intrahexagon peak,²⁰ as well as additional features that demonstrate that two-dimensional graphitelike order exists in this material. In contrast to *a*-C, which may be viewed as being "amorphous" in three dimensions, glassy carbon exhibits two-dimensional microcrystalline order along with disorder between layers. The Raman scattering spectra of glassy carbon, C films deposited without appreciable cooling, or annealed *a*-C above 300°C are similar, suggesting that these are not appropriately specified as "amorphous C." This includes many hard carbon films, without H, whose Raman spectra are qualitatively similar to glassy C.¹⁰

The absence of ordered hexagonal rings in *a*-C is consistent with the theoretical models of Fig. 3 which exhibit bond-angle disorder, the presence of five- and seven-atom rings, and rather distorted nonplanar character³ of

threefold sites. The observation of a broad third peak in $T(r)$ at 3.8 Å corresponds to third-bonded, chainlike configurations that are present within such a disordered a -C network. Evidence for this is based on the very good agreement between the ratio of the third and first peak positions of a -C and corresponding graphite distances. That is, the third peak in a -C at ~ 3.77 Å corresponds to the fourth-neighbor, intralayer distance at 3.69 Å in graphite [Fig. 2(a)]. The larger a -C value is due to an increase in the most probable first-neighbor distance relative to graphite. The observation of similar extended radial correlations in other amorphous semiconductors^{16,17} with limited or no intermediate-range order is also associated with chain configurations. These radial correlations arise from constraints on the widths of the first-neighbor distance and bond angles.

In summary, the present RDF results on well characterized, sputtered a -C exhibit qualitative agreement with a number of basic models, indicating predominant threefold bonding. However, the RDF obtained differs in detail with all existing theories, demonstrating the need for further modeling. The observations of a larger average first-neighbor distance than graphite and a broad first-neighbor peak differ qualitatively from the RDF's of other group-IV amorphous semiconductors. The absence of a specific peak at the graphite intrahexagon distance indicates that structural models with such intermediate-range correlations are not correct for a -C. Such hexagonal correlations, which are present in glassy carbon and by implication in sputtered hard carbon films, distinguish fully three-dimensionally amorphous carbon from these locally more two-dimensional ordered systems.

This work was supported by U.S. DOE Grant No. DE-FG02-84ER45095 as well as U.S. DOE support of the IPNS facility at Argonne National Laboratory. We wish to thank Dr. K. Volin for experimental assistance, Mr. Hongjun Pan for communicating information on the preliminary NMR spectra, Dr. J. Fortner for useful information on the data analysis, Dr. J. Tersoff and Dr. G.

Galli for useful discussions, and Dr. D. Beeman for providing theoretical data.

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