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The structure of a C:H by neutron and X-ray scattering

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Abstract

Whilst the short-range order in a-C:H is of central importance in explaining its mechanical properties, it is order at intermediate distances that is likely to account more fully for the electronic and optical properties. The role of hydrogen would appear to be significant in promoting tetrahedral bonding — but no direct study of the hydrogen sites has been made. It is in this context that the preliminary results of neutron diffraction measurements, and of some novel synchrotron X-ray experiments, are presented and discussed. The X-ray diffraction studies were carried out using a technique which may prove useful for as-deposited films in which the angle of incidence is fixed at, or near, the critical angle. The results of a "reverse Monte Carlo" computer modelling study of the neutron data are presented.

1. Introduction

A hardness, density and resilience to chemical attack superior to those of most other solid hydrocarbons, together with a high degree of transparency in the infrared and histocompatibility, have led to many applications for amorphous hydrogenated carbon (a-C:H) materials (see, for example, ref. 1). In spite of this interest, a detailed knowledge of its structural characteristics has been slow in coming. Of the studies carried out, the results have tended to suggest the presence of aromatic clusters interconnected by diamond-like structures in a continuous random network, with the $sp^2:sp^3$ ratio varying between 1:2 and 2:1, depending on exact deposition conditions. The high degree of sp^2 clustering suggested by optical gap measurements indicates that intermediate- as well as short-range order is important. The reviews by Angus *et al.* [2] and Robertson [3] provide excellent outlines of this and other model structures.

There have been few diffraction experiments performed on hard a-C:H and these have been limited mainly to electron diffraction (*e.g.* McKenzie *et al.* [4]) and conventional laboratory-based X-ray diffraction in which the range of data available in k -space is too restricted to allow the extraction of high resolution real-space information. Neutron diffraction, especially from a

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pulsed source, overcomes this problem by allowing a significantly wider dynamic range. Neutron diffraction also probes the hydrogen environment in a direct way (neutrons scatter from atomic nuclei, the scattering is therefore isotope dependent; hydrogen has a relatively large cross-section for thermal neutron scattering).

X-ray diffraction using the short wavelengths (and therefore large k_{\max}) available at synchrotron sources provides complementary data, however, in the sense that it is dominated by the carbon scattering. We have begun to explore a novel use for the intrinsically highly parallel synchrotron X-ray beam at the synchrotron radiation source (SRS) (Daresbury Laboratory, U.K.) in which the angle of incidence is fixed at, or near, the critical angle for external reflection: we are therefore able to eliminate the effects of substrate scattering and may study the as-deposited material.

Neutron or X-ray diffraction from an amorphous material is spherically averaged and the data therefore yield a one-dimensional average of the actual three-dimensional structure and it is only possible to produce non-unique, model structures consistent with the data [5]. The recently developed "reverse Monte Carlo" (RMC) algorithm [6] offers the promise of a significant step forward in computer-based modelling, and we show preliminary results of its application to our diffraction data.

2. Experimental details

The a-C:H used in these experiments was produced using a saddle-field ion beam source (see ref. 7 for details). The sample, prepared from a propane precursor gas, was deposited onto copper (as a-C:H does not adhere to copper, this proved an ideal method for providing the large, about 2–5 g, powder sample required for neutron scattering experiments). A Carlo Erba CHN combustion analyser was used to determine the composition of the sample: hydrogen content was found to be 32 at.%. Infrared characterisation measurements were performed using a Mattson Instruments Alpha Centauri Fourier transform infrared device [8]. The gram atom density was determined, using a residual volume technique, to be 0.2.

The neutron diffraction data were collected at the ISIS pulsed neutron source (Rutherford Appleton Laboratory, U.K.) using the LAD time-of-flight diffractometer [9]. A spallation neutron source, such as ISIS, produces a pulse of neutrons with a spread of velocities, and thus a spread of arrival times at any one detector. This gives a smooth variation of neutron wavelength as a function of time of flight ($\lambda \propto T/L$ where T is the time of flight over path length L). The LAD detectors are arranged on each side of the instrument at fixed scattering angles. A "white beam" diffraction method is thus used with spectra recorded separately, as a function of time of flight, for each detector, and also for monitors in the incident and in the transmitted beam. Spectra were recorded for each of the following: the sample, its associated empty container, the no-sample background and for a vanadium

rod. The vanadium rod is used as a "standard" and provides the information necessary to put the sample scattering on an absolute scale [5].

The exploratory shallow incidence X-ray diffraction experiments were undertaken using the "wiggler" beamline 9.1 at the SRS; a water-cooled Si{111} channel cut monochromator [10] provided a beam of $\lambda = 0.7 \text{ \AA}$. Angles of incidence in the region of 0.1° – 0.2° were used, with the associated evanescent mode decay depth being about 100 \AA . Diffracted intensity from the evanescent wave in the thin-film sample was recorded as a function of scattering angle 2θ in the range 0.9° – 130° (i.e. a k -space range of about 16 \AA^{-1}) using a conventional solid state detector. This sample was deposited from acetylene onto a polished silicon wafer to nominal thickness 1 \mu m .

3. Theoretical background and data analysis

3.1. Neutron diffraction

The object is to determine the structure factor $S(Q)$ where, for an amorphous material [5]

$$S(Q) = 1 + \frac{4\pi\rho}{Q} \int_0^\infty r[g(r) - 1] \sin(Qr) dr$$

where ρ is the average number density of atoms in the material, $Q = k_r - k_i$ is the wave vector transfer associated with the diffraction experiment — which for a liquid or amorphous solid is defined as $Q = (4\pi/\lambda) \sin \theta$, where 2θ is the scattering angle — and $g(r)$ is the pair distribution function, which is a measure of the atomic density at a distance r from a given atom at the origin. The pair correlation function may therefore be obtained by Fourier transformation of the structure factor.

In a multicomponent system, there are contributions to the total structure factor from each atom-type pair. For the binary alloy a-C:H this yields three terms, which are weighted thus to give a total structure factor $F(Q)$:

$$F(Q) = \sum_\alpha c_\alpha b_\alpha^2 + \sum_{\alpha, \beta} c_\alpha b_\alpha c_\beta b_\beta [S_{\alpha\beta}(Q) - 1]$$

where c_α is the atomic fraction and b_α the isotope-averaged coherent scattering length respectively of element α ; $S_{\alpha\beta}(Q)$ is the partial structure factor and represents the interference term arising from atom-type pairs. The first summation represents the "self" or "single-atom" scattering while the second is the "interference" or "distinct" scattering term and contains the basic information on atomic positions. A Fourier transformation of $F(Q)$ leads to the total pair distribution function

$$G(r) = \sum_{\alpha, \beta} c_\alpha b_\alpha c_\beta b_\beta g_{\alpha\beta}(r)$$

where the $g_{\alpha\beta}(r)$ represent the corresponding partial terms in $G(r)$ and describe the probability of finding an atom of type β at a distance r from an atom of type α at the origin. For this sample the weightings of individual terms in the structure factor and pair distribution function are: C—C, 0.300; H—H, 0.044; C—H, 0.338. The C—C and C—H terms will thus dominate the $F(Q)$ and $G(r)$. It is important to note that the coherent scattering length for hydrogen is negative: we observe dips, not peaks, for the C—H terms (the value of b for deuterium is, however, positive!).

The experimental data are subject to standard corrections for multiple scattering, container scattering and attenuation effects, and particularly for the effects of inelastic scattering which may be problematic for hydrogenous material. These procedures have been outlined elsewhere [8, 11].

3.2. Shallow incidence X-ray diffraction

The central characteristics of the technique have been described by Lim *et al.* [12] as part of a study of crystalline iron oxide layers on glass substrates. Using the SRS we have been able to exploit the naturally parallel synchrotron X-ray beam to avoid the serious aberrations that occur with focussed laboratory sources, and to be able to use relatively hard X-rays: scans in 2θ yield the structural data whilst the angle of incidence is used to control, via the evanescent mode, the depth of the film from which the diffraction arises. Ignoring the effects of anomalous dispersion, the critical angle α_c for total reflection is given, in radians, by

$$\alpha_c = (2\delta)^{1/2} = 1.6 \times 10^{-6} \lambda d$$

where d is the density in kg m^{-3} and δ is related to the refractive index n by $\delta = 1 - n = 1.3 \times 10^{-9} \lambda^2 d$. For angles of incidence α less than α_c the penetration depth t is given by

$$t = \lambda / [2\pi(\alpha_c^2 - \alpha^2)^{1/2}]$$

For $\alpha > \alpha_c$ the corresponding depth depends only on the coefficient for linear attenuation μ_1 : $t' = 2\alpha/\mu_1$. One can therefore, in principle, control the characteristic penetration depth (from tens to hundreds of ångströms) by varying α . One further point to note is that, at $\alpha \approx \alpha_c$, the effects of refraction on the diffraction peak positions are significant; this corresponds to an effective shift in the zero angle of $\Delta(2\theta) = 2\delta/\sin(2\theta_{\text{true}}) + \delta/\alpha$. The data we present here — the first, we believe, for an amorphous film — are of a preliminary nature and much work remains to be done on the details of the data analysis procedures required for background subtraction, absorption effects, Compton scattering and normalization to the form factor. The raw data have merely been normalized to an incident beam monitor, "refraction"-shifted by $\Delta(2\theta) = 8^\circ$, and divided by a low-order polynomial to approximate the underlying form factor, etc. The resulting curve is therefore a first approximation to the structure factor only and must be treated with due caution.

3.3. RMC modelling

To elucidate further the structural conformations present in our samples of a-C:H we have begun a programme of computer modelling studies. Rather than use the "ball-and-stick" approach, we have investigated the so-called RMC method [6] which provides a method of generating an atomic model that is consistent with available experimental data. It is a development of the standard Metropolis Monte Carlo algorithm but, instead of minimizing the energy of the system, it minimizes the function

$$\chi^2 = \sum_i [S_E(Q_i) - S_M(Q_i)]^2 / \sigma_i^2$$

where $S_E(Q_i)$ is the experimental structure factor, $S_M(Q_i)$ the structure factor calculated from the model and σ_i the experimental error. In general, for a multicomponent system, the simulation can be carried out provided the partial coefficients $c_\alpha b_\alpha c_\beta b_\beta$ are known. The $S_M(Q)$ is generated, via a model $G_M(r)$, from a "box" of "atoms" having the appropriate c , b and ρ values. At each pass an "atom" is moved at random subject to the constraint that it does not overlap with its neighbours (*i.e.* a hard-core radius is supplied) and the new χ^2 calculated. The new configuration is accepted if χ^2 has been decreased; this is subject to a probability factor which follows a normal distribution of width σ and which ensures that local minima do not become traps. For the work introduced here boxes of edge about 33 Å were used which contained about 5000 "atoms".

Having generated a box, or more usually an ensemble of boxes with conformations consistent with the experimental data, it is then possible to examine the nature of the model pair distribution functions $g_{C-C}(r)$, $g_{C-H}(r)$ and $g_{H-H}(r)$, to analyse bond angle and length distributions etc.

4. Results

4.1. Neutron diffraction

Angus *et al.* [2] suggest that, for a hard carbon film, a gram atom density greater than about 0.2 is required. On the basis of this criterion our sample would appear to lie at the borderline; however, unpublished measurements by the Hull group suggest hardnesses up to 6000 kg mm⁻². It should be noted in this context that our infrared data [8] indicate the presence of small quantities of CH₃ and olefinic (*i.e.* ethene-like) CH₂ groups, which appear in polymeric films — however, inelastic neutron scattering data [8] show that some of the hydrogen may exist as interstitial molecules which would have little effect on the network structure although contributing to the atomic density.

Examination of the pair distribution function $G(r)$ (Fig. 1) reveals a split C—C first-shell peak at 1.39 and 1.52 (± 0.02) Å. Comparison of the peak positions with known C—C bond lengths (see Table 1) shows that the 1.52 Å peak is unambiguously the single-bond length and that the 1.39 Å peak

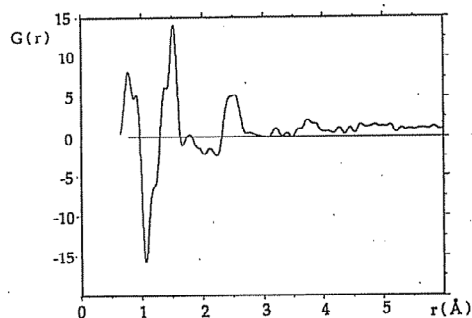


Fig. 1. The total pair distribution function $G(r)$ derived from neutron diffraction.

TABLE 1

Bond lengths associated with C-H systems

Bond	System	Length (Å)
C—C	Diamond	1.54
C—C	Graphite	1.42
C—C	Benzene	1.3954
C—C	Ethene	1.34
C—H	Methane	1.094
C—H	Ethene	1.074
H—H	Hydrogen	0.754

corresponds closest to that found in aromatic compounds (although it could be due to a C—C double bond apparently shifted to higher r by contributions from the 1.52 Å peak). The ratio of bonds 1.39 Å:1.52 Å has been found to be approximately 1:4 and the lower-bound estimate for the average number of carbon atoms bonded to each carbon atom is 2.5. The ratio of $sp^2:sp^3$ for carbon is unknown, although the predominance of single bonding and the relatively high average C—C coordination both suggest a high sp^3 concentration. Further analysis of the data is in progress.

The other features in the $G(r)$ can be ascribed to a C—H bond (1.07 Å), with a coordination number of 1 (owing to the close proximity of all C—H bond distances it is not possible to identify the dominant hydrogen location, although further study using deuterated samples may help), and an H—H peak at 0.8 Å which is either molecular hydrogen or from neighbouring CH_n groups (it is hoped that modelling will cast more light on this in the near future).

Moving beyond the first coordination shell, the broad feature between 2.3 and 2.7 Å is a combination of sp^2 and sp^3 C—C—C distances, with an average carbon coordination number of 4. Resolving the individual contributions has not been possible because of the proximity of the two distances, and their likely spread as bond angles vary between local configurations.

Preliminary analysis of the diffraction data from a sample produced from acetylene shows that the structure factor is very similar to that for a sample

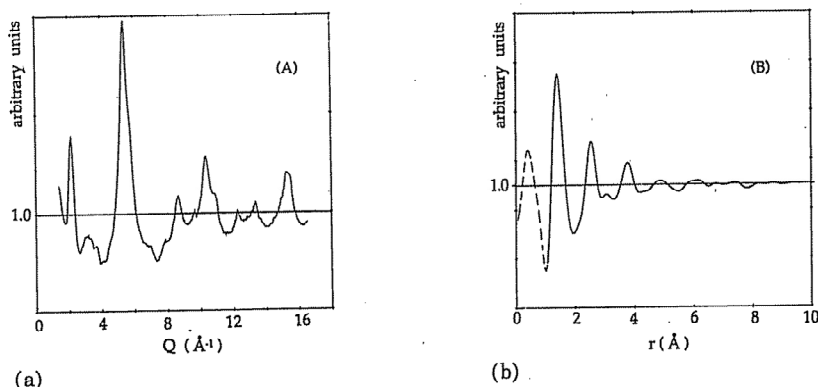


Fig. 2. (a) The first-approximation structure factor and (b) the pair distribution function for a-C:H derived from shallow incidence X-ray diffraction.

produced from propane. The only difference seems to be low Q , which would correspond to differences in the intermediate-range order in the continuous random network. A full analysis of this system, including inelastic neutron scattering studies, will be completed in the near future.

4.2. Shallow incidence X-ray diffraction

The first-approximation structure factor and pair distribution function are shown in Fig. 2. No detailed interpretation of the data is possible at present, but a comparison with the neutron data in Figs. 1 and 3 provides a very clear indication of the viability of this novel experimental approach. In making the comparison it is important to recall the X-ray diffraction is related to the electron density distribution in the sample. For a-C:H this ensures the dominance of the C—C partial terms. The resolution associated with the X-ray data is also necessarily limited relative to the neutron data.

4.3. RMC modelling

The experimental structure factor obtained for the propane sample, together with that calculated from the RMC method, are shown in Fig. 3; it is clear that a very good fit has been achieved. From the RMC data the $g_{\alpha\beta}(r)$ have been obtained and these are shown in Fig. 4. For $g_{C-C}(r)$ the first peak occurs at 1.4 Å, while the dominant second peak at 1.5 Å suggests the expected presence of diamond-like conformations. The narrowness of the second-shell peak at about 2.5 Å is indicative of a well-developed continuous random network and, with further study, may provide clues on intermediate-range ordering. The partial $g_{C-H}(r)$ shows a peak at 1.1 Å, in agreement with the accepted value for the C—H bond length and a broad or perhaps split peak at about 2 Å, while $g_{H-H}(r)$ implies the presence of molecular hydrogen by the peak at 0.75 Å.

We have already been able to augment this basic work with a preliminary examination of C—C—C, H—C—C and H—C—H bond angle distributions.

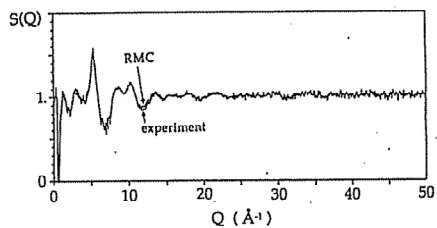


Fig. 3. The experimental and RMC-modelled structure factor for a-C:H.

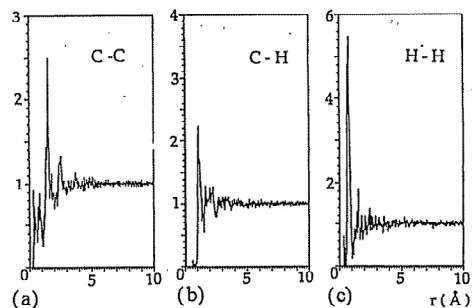


Fig. 4. The partial pair distribution functions for a-C:H derived from the RMC model: (a) C—C; (b) C—H; (c) H—H.

Only in the C—C—C distribution did we observe a definite feature; this suggested angles in the range 114° – 127° . It has also been possible to examine the distribution of C—C and C—H coordination numbers in the "box"; average values derived from these are entirely consistent with the experimental data. The RMC results will be discussed more fully elsewhere.

5. Conclusion

From the diffraction data it may be deduced that the single bonds from the bulk of the random network, with a smaller but nonetheless significant proportion of double or aromatic bonds. Molecular hydrogen is almost certainly present.

We have shown that a novel synchrotron X-ray diffraction technique, in which scattering is confined to the volume of the as-deposited film, is viable and offers potential. We have also sought to illustrate the benefits of a detailed RMC computer modelling study of the diffraction data — particularly of high real-space resolution neutron diffraction data which are sensitive to the presence of hydrogen. Future modelling work will include the combined use of X-ray, neutron and other (*e.g.* NMR) data as RMC constraints. Experiments using deuterated samples are also planned.

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