

LETTER TO THE EDITOR

A high-resolution neutron-diffraction study of the structure of amorphous hydrogenated carbon, a-C:H

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Abstract. Current structural models for amorphous hydrogenated carbon (a-C:H) are called into question on the basis of neutron-diffraction experimental work carried out at the ISIS pulsed neutron source (UK) on a-C:H. The nature of the neutron source allows the collection of data over an exceptionally wide dynamic range that ensures a real-space resolution sufficient to allow direct observation, for the first time, of contributions from the principal C-C bond types. The data also reveal details of the C-H correlations, and the presence of trapped molecular hydrogen.

The last two decades have seen a growth in our knowledge of the properties of amorphous materials, accompanied by continued technological exploitation. The complex nature of these materials maintains their position of fundamental as well as technological interest, and important questions concerning their properties remain unanswered. In fact, the range of questions only increases as new and more novel materials continue to be generated.

a-C:H is particularly interesting as it can be made harder, denser and more resistant to chemical attack than any other solid hydrocarbon, and this leads to a broad range of potential technological applications. The macroscopic properties of a particular material are critically dependent on the conditions under which it was produced. a-C:H can be prepared in forms varying from the soft polymeric or graphitic at one extreme to a so-called 'diamond-like' carbon form at the other. So, by altering the deposition parameters it is possible to vary, for example, properties such as the optical band gap and refractive index, giving a number of potential applications [1].

We are aiming in our work to relate these 'bulk' properties to the sub-microscopic, or atomic-level structure. However, the structure giving rise to these properties is not yet fully understood: current models involve clusters of sp^2 C linked via sp^3 C. A fuller account of these models can be found in reviews by Robertson [2] and Angus *et al* [3]. Attention should be paid to the crucial role that H has to play in determining and fully understanding the properties of a-C:H. Given the many possible variations in C-C bonding, and in addition the network-modifying role of H, it is essential that structural data of the highest quality are available; we offer here data on a-C:H of superior real-space resolution to any available hitherto and discuss the validity of current models in their light.

The a-C:H sample discussed here was prepared using a saddle-field fast-atom (i.e. neutral-particle) source [4] with propane as the precursor gas; the deposition conditions pertain to the hard form of the sample (an effective beam energy of 960 V, operating at

1.4×10^{-4} mbar system pressure). Knoop hardnesses of 2000 H_K have been measured [5] for this material (cf. 6000–11 000 H_K for diamond [3]), although hardnesses greater than 6000 H_K have also been observed. The macroscopic sample density was determined as 1.7 g cm^{-3} using a residual-volume technique, and the hydrogen content was determined as 32 at.% using a Carlo-Erba CHN combustion analyser. The total sample mass was $\sim 0.9 \text{ g}$, which ensured good statistical accuracy for the diffraction experiment.

Our overall experimental programme focuses on the use of neutron diffraction, together with complementary x-ray diffraction, inelastic neutron scattering and NMR measurements. The neutron work is centred on the pulsed neutron facility at ISIS at the Rutherford Appleton Laboratory (UK), which, because it allows a very wide dynamic range ($\sim 0.2\text{--}50 \text{ \AA}^{-1}$), results in high-resolution real-space data— $\Delta r = 2\pi/Q_{\text{max}} \simeq 0.1 \text{ \AA}$ —and is therefore particularly well suited for the study of covalently bonded amorphous materials.

The object of the neutron diffraction experiment is to determine the structure factor $S(Q)$, where for an amorphous material [6]

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

where ρ is the average number density of atoms in the material, $Q = k_f - k_i$ is the wavevector 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 λ is the incident neutron wavelength; $g(r)$ 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, which is itself directly related to the measured diffraction intensity. In a binary system such as a-C:H there are contributions to the total structure factor from each atom-type pair, which are weighted together to give a total structure factor. The corresponding function in real space is the total pair distribution function, $G(r)$, which is a weighted combination of partial pair distribution functions (according to the Faber-Ziman formalism [6]):

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

where c_α is the atomic fraction and b_α is the neutron coherent scattering length of element α , and where $g_{\alpha\beta}(r)$ represent the 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; there are three distinct $g_{\alpha\beta}(r)$ functions for a binary system. In contrast to x-ray or electron diffraction data, neutrons are sensitive to the correlations involving hydrogen (b_H is negative due to a phase shift on scattering; the C-H correlations therefore appear as troughs rather than peaks).

Before obtaining $S(Q)$, several corrections need to be applied, full details of which can be found elsewhere [7]. The major corrections are for background, container and multiple scattering, attenuation and the effects of inelasticity, which may be problematic for hydrogenous material. Although there was $\sim 20\%$ multiple scattering, this is mostly incoherent multiple scattering which takes the form of a smoothly varying function of Q and does not therefore lead to problems in the data analysis. To correct for the effects of inelasticity, an empirical method was successfully applied: this involved fitting a low-order polynomial to the data, which was then subtracted from the spectra without removing any of the structure. Vanadium, which is an incoherent scatterer, may be used as a calibrant to put the sample scattering on an absolute scale. $S(Q)$ and $G(r)$ are shown in figures 1 and 2

respectively. These may be compared with the neutron-diffraction data of Gaskell and co-workers [8] on mass-selected ion-beam-produced 'amorphous diamond': their small sample contains relatively little H and had some graphitic inclusions. Their diffraction experiment was also run on a reactor-source diffractometer ($Q_{\max} \sim 16 \text{ \AA}^{-1}$). The real-space resolution of the data presented here is therefore better by a factor of more than three.

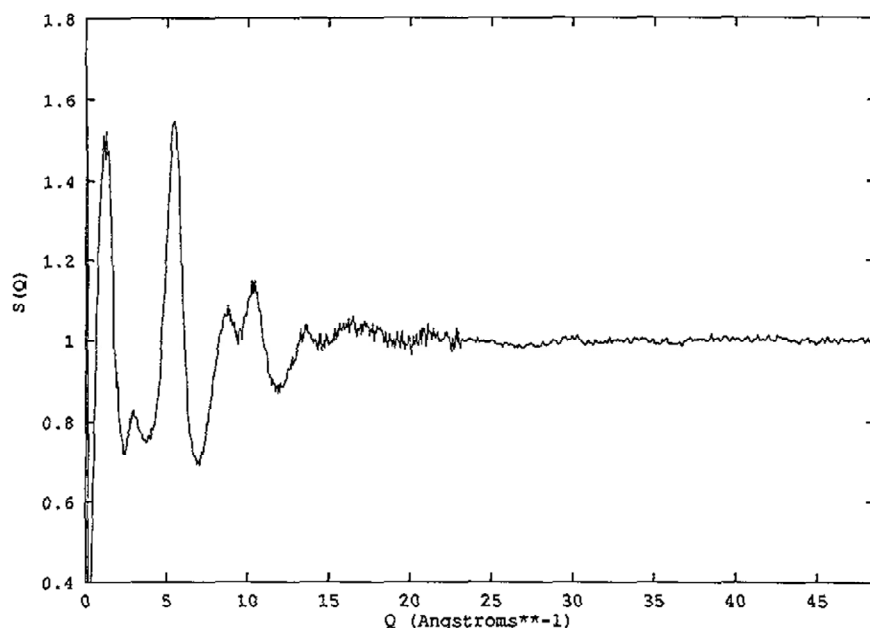


Figure 1. The structure factor $S(Q)$ for a-C:H.

The exceptional real-space resolution provided by the neutron data presented here allows, for the first time, comment in detail on the C bonding environments within the random network which makes up this complex material. The radial distribution function $4\pi\rho r^2G(r)$ has been fitted with a series of Gaussians (see figure 3), allowing both position and area to vary. Using this method, accurate values for bond lengths and coordination numbers have been obtained (see table 1). However, with such detailed data, it is possible to go beyond the straightforward assignments shown in the table. For instance, there is a clear indication that molecular hydrogen is present in relatively small quantities; this has been confirmed by inelastic neutron scattering experiments and is discussed more fully elsewhere [9]. It is also important to note the bond length of 1.34 \AA , corresponding to that of an olefinic environment: relative to graphite (1.41 \AA) and aromatic (1.39 \AA) environments, this unsaturated C=C distance is short and indicates that most of the sp^2 C present is olefinic.

Assuming this domination of the olefinic environment, it is possible to determine from the peak fits the proportion of C atom types as sp^3 (saturated) = 0.13, sp^2 (unsaturated) = 0.55, with the corresponding ratio of C-C single to double bonds being 2.4:1. Although we cannot completely rule out small contributions from aromatic or (rather less likely) graphitic groups on the basis of this data, it is evident that they can only be present at low concentrations. To a good approximation all remaining bonds are C-H; these are divided

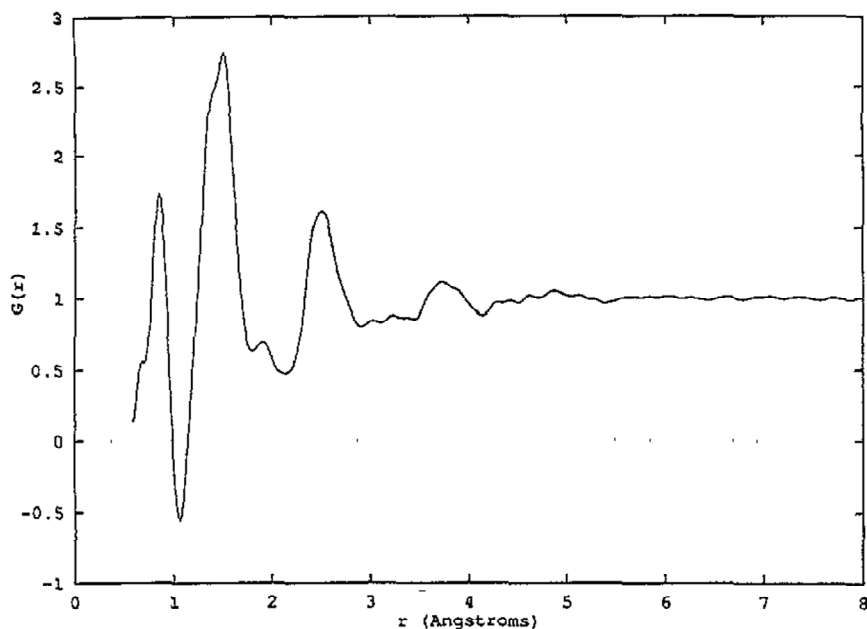


Figure 2. The total pair distribution function for a-C:H.

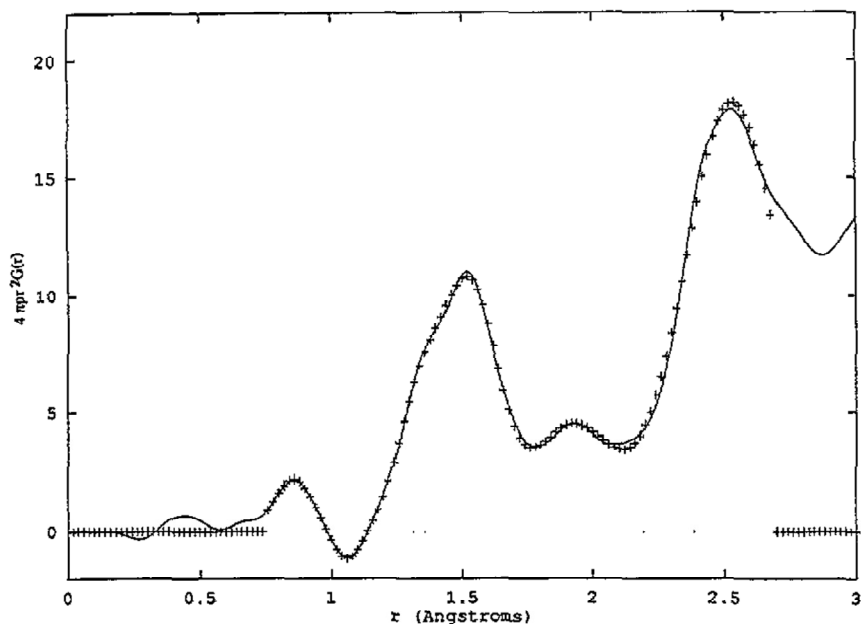


Figure 3. The peak fits (+) to the experimentally derived radial distribution function $4\pi r^2 G(r)$ (full curve).

into approximately equal numbers of CH and CH₂ groups, i.e. $\frac{2}{3}$ of the H is in CH₂ groups with relatively little bonded to sp² C [10].

We therefore see no evidence for the existence of the relatively large graphitic or

Table 1. Bond lengths and coordination numbers derived from neutron data.

Peak position ($\pm 0.01 \text{ \AA}$)	Peak area (atoms)	Assignment
0.86	0.41	H-H (molecular)
1.06	0.16	C-H and H-C
1.34	1.12	C=C (aromatic, double bond)
1.53	2.64	C-C (single bond)
1.7-2.2	—	H-C-H and C-C-H
~ 2.5	—	C-C-C

aromatic sp^2 clusters which lie at the heart of the most commonly used of the current structural models; indeed the data are such that we can quite clearly state that these models must be radically updated.

Some comment should also be made concerning the small peak at 1.92 \AA . This is possibly the result of a convolution of the large C-C second-neighbour peak at $\sim 2.5 \text{ \AA}$ with a 'negative feature' at 2.16 \AA , due to the C-H second-shell correlation, or it could be due to the H-C-H second-shell correlation (which one would expect to see at $\sim 1.8 \text{ \AA}$). Given the complexity of the second shell it is clear that quantitative assignments cannot be made. Using the C-C second-shell peak at $\sim 2.5 \text{ \AA}$, it is possible to generate the expected C bond angle distribution with a principal peak centred on the tetrahedral angle, but extending towards 120° , although precise statements on bond angles are problematic because the broad 2.5 \AA peak clearly has contributions from several C-C-C correlations.

This work is already being extended with a study of the effect of changing the precursor gas (i.e. changing the H content of the plasma), and most importantly by conducting experiments on a series of deuterated samples so that the partial pair distribution functions $g_{C-C}(r)$, $g_{H-H}(r)$ and $g_{C-H}(r)$ can be determined. Complementary NMR, x-ray diffraction and computer modelling/simulation studies are also well advanced. Full details of this work will be published in due course.

In conclusion, we reiterate that these high-real-space-resolution data have enabled a description of the atomic-scale structure of 'diamond-like' C in detail not available hitherto. The results lead us to question current structural models for this important system.

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