

# Neutron Diffraction Study of Amorphous Carbon with a Fast Data Acquisition System\*

B. K. Annis and A. H. Narten

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Z. Naturforsch. **43a**, 164–168 (1988); received November 19, 1987

A fast neutron data acquisition system involving a curved position-sensitive proportional counter is described. The system permits simultaneous measurement of diffraction data over an angular range of 130 degrees at moderate resolution. Data for amorphous carbon are compared with x-ray diffraction data. Structure functions derived from the different methods are in good agreement. Amorphous carbon is a useful standard for the comparison of diffraction data from different laboratories.

## I. Introduction

The structure of crystalline solid is specified by the symmetry of the space group and by the mean atomic positions in the unit cell, together with estimates of the amplitudes of thermal vibration of each of the nuclei. The periodicity of the lattice allows one to construct a model of the unit cell which is representative of the entire crystal.

In a non-crystalline (amorphous) solid, there is no such periodicity. The short-range ordering or structure found in these materials is completely described by probability functions of position and orientation. For monatomic materials such as carbon, the pair distribution function  $g(r)$  depends only on the scalar distance  $r$  between the atoms and is defined so that  $\rho g(r) dr$  is the average number of atoms in the volume element  $dr$  at a distance  $r$  from an origin atom. Hence, the function  $g(r)$  is a measure of the local particle density in the vicinity of any origin atom in a material of bulk number density  $\rho$ . The pair distribution function is related to a structure function  $a(k)$  by the Fourier integral

$$\hat{h}(k) = 4\pi \int r^2 h(r) j_0(kr) dr \quad (1)$$

with  $j_0(x) = x^{-1} \sin x$ ,  $h(r) = g(r) - 1$ ,  $k = (4\pi/\lambda) \sin \theta$  and  $2\theta$  the scattering angle in an experiment with radiation wavelength of  $\lambda$ . The pair distribution func-

tion of a monatomic material can thus be obtained from a single diffraction experiment using thermal neutrons, x-rays, or electrons.

Neutrons are scattered by the nuclei, x-rays by electrons, and electrons by both. Hence the question has been raised [1] whether the different techniques can be combined to obtain partial structure functions for materials with more than one kind of atom. Neutron and x-ray experiments with liquid gallium [2] and lithium [3] have answered this question by yielding structure functions which, for the two techniques, were identical within experimental error. The situation is not so clear for electron scattering: carefully performed electron and x-ray diffraction experiments with amorphous germanium have yielded rather different structure functions [4].

We here present the first comparison of neutron and x-ray diffraction data for an amorphous solid material, which confirm the conclusions reached from the study of liquids. We propose amorphous carbon as a convenient standard for the comparison of diffraction data from different laboratories and with different techniques.

## II. Experimental

### Materials

Samples of "Vitreous Carbon Grade V10" were obtained commercially [5]. According to the manufacturer, the material was obtained by "carbonization and subsequent thermal treatment of carbonaceous substances with strong transversal molecular bounds which, after carbonization, leave a coke in crystallo-

\* Research sponsored by the Division of Materials Science, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

Reprint requests to Dr. A. H. Narten, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37831 USA.

0932-0784 / 88 / 0200-0164 \$ 01.30/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

graphic disorder." The material has the appearance of black glass with a density of 1.50 to 1.55 g/ml.

### Fast Neutron Data Acquisition System

The neutron scattering facility of the Chemistry Division at the ORNL High Flux Isotope Reactor (HFIR) provides a uniform beam of very nearly monochromatic neutrons by reflection from a large Ge crystal. A cylindrical sample is completely bathed in the beam (maximum dimension  $5.0 \times 1.5$  cm). Scattered neutrons are recorded without energy analysis in a curved position-sensitive proportional counter (CPSPC) having a radius of 75 cm. The counter is interfaced to a dedicated DEC-11/23 computer, permitting the simultaneous measurement and on-line analysis of diffraction patterns over an angular range of 130 degrees.

The detector, filled with 2.6 atm or  $^3\text{He}$  and 1.4 atm of  $\text{CF}_4$ , has an efficiency of 70% for  $0.9 \text{ \AA}$  neutrons. The CPSPC was developed by the Instrumentation and Controls Division of ORNL. It has an anode line made of 0.2 mm tungsten wire carefully placed on a form in a spiral shape with 2.6 mm separation (Figure 1). The counter uses LC position encoding based on the shape of the neutron pulse obtained from each end of the detector. Due to the distributed inductance (L) and capacitance (C) of the anode-cathode configuration (Figure 1), the pulses from a single neutron detected along the arc of the counter have different shapes at each end of the detector. The time at which these pulses after amplification cross the base line (cross-over time) is used as a measure of the pulse shape, and the time difference between these cross-over signals from each end is proportional to the distance along the arc of the detector. These time signals start and stop a converter module which generates a digital address stored in a histogramming memory. The memory increments the address to record the neutron event. Thus, while a data run is being accumulated, no computer time is needed for the data acquisition process.

The CPSPC was designed for an angular resolution of 0.2 degrees. From the width of the measured Bragg peaks of polycrystalline powders, the overall resolution is estimated as 0.3 degrees. The counts are accumulated in arrays ranging from 256 to 4096 channels. The linearity of the detector is measured by measuring a pattern from Ni powder whose Bragg peak positions are accurately known. The observed channel numbers

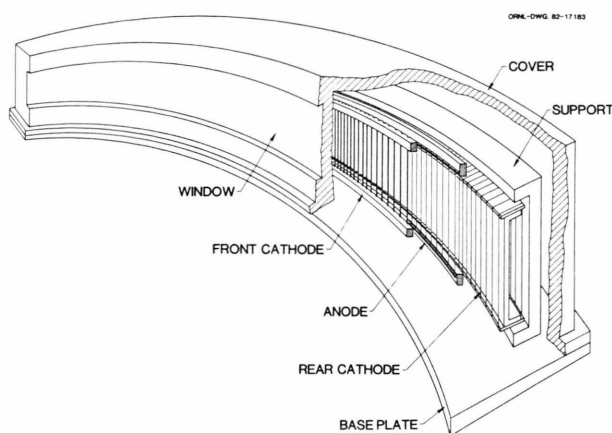


Fig. 1. Curved position-sensitive proportional counter for simultaneous detection of thermal neutrons over a range of 130 degrees.

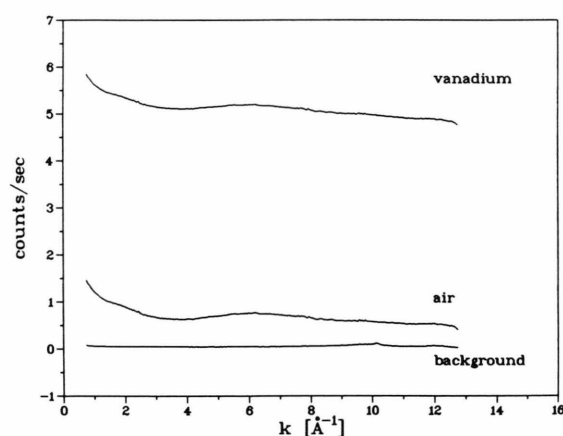


Fig. 2. Observed neutron diffraction pattern from a 6.5 mm vanadium rod.

for the peaks are least-squares fitted to the scattering angles, and the calibration parameters stored with the data runs. The scattering from a vanadium sample is measured with each sample and used as a sensitivity correction. The measured scattering from a vanadium sample is shown in Figure 2; a summary of the vanadium data is given in Table 1.

The useful angular range of the CPSPC is  $10 \leq 2\theta \leq 130$  degrees corresponding to an interval  $0.8 \leq k \leq 13 \text{ \AA}^{-1}$  in the momentum transfer coordinate  $k$  (for  $0.9 \text{ \AA}$  neutrons). For an equally spaced data set of increment  $\Delta k = 0.1 \text{ \AA}^{-1}$ , 123 points need to be measured; to collect 500,000 counts per data point

Table 1. Summary of data from vanadium run shown in Figure 2.

Incident wavelength	(Å)	0.894
Neutron flux at sample	(cm <sup>-2</sup> sec <sup>-1</sup> )	$2 \times 10^6$
Collimation at sample	(degrees)	
horizontal		0.3
vertical		1.0
Integrated count rates	(sec <sup>-1</sup> )	
vanadium rod 6.5 mm		3200
beam open, no sample		140
cadmium in front of		30
sample beam closed		10

takes about 5 hours for the *V* sample used in the analysis. This data acquisition time is representative of most liquid and amorphous solid materials. It is a major advance over conventional step scanning techniques.

#### Neutron Data Collection and Reduction

The scattering from a cylindrical carbon rod (3 mm 0.d.) was measured for a preset number of monitor counts and stored in 1024 channels equally spaced along the anode wire of the CPSPC. The average number of accumulated counts per channel was  $1.5 \times 10^5$ . The data were summed over a number of channels chosen such that the increment in the variable  $\Delta k$  was constant. The increment chosen was  $\Delta k = 0.05 \text{ Å}^{-1}$ . The data, corrected only for counter response, are shown in Figure 3. The absolute scale was established by the vanadium method. The cross sections were corrected for background, multiple scattering [6], absorption in the sample, and absorption and scattering [7] by air. The effective cross section thus obtained is shown in Figure 4. It may be written as

$$(d\sigma/d\Omega) = S_s(k) + S_d(k), \quad (2)$$

with  $S_s(k)$  the self scattering from independent atoms (solid line), and  $S_d(k)$  the distinct scattering from correlated atom pairs (points). The function  $S_s(k) = \sigma_T/4\pi + D(k)$  was calculated from the tabulated [8] total scattering cross section  $\sigma_T(5.555 \pm 0.03 \text{ barn})$  and the inelasticity correction [9]  $D(k)$ . The function  $S_d(k) = f^2 a(k)$  is simply related to the structure function  $a(k) = \varrho \hat{h}(k)$  defined in Eq. (1), with  $f(0.66464 \pm 0.00013 \text{ barn})$  the coherent scattering length and  $\varrho(0.0765 \text{ Å}^{-3})$  the number density of atoms. The function  $a(k)$  is independent of the scatter-

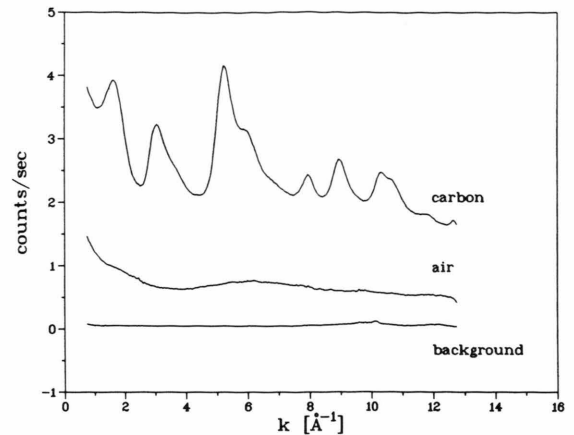


Fig. 3. Observed neutron diffraction pattern from a 3 mm amorphous carbon rod.

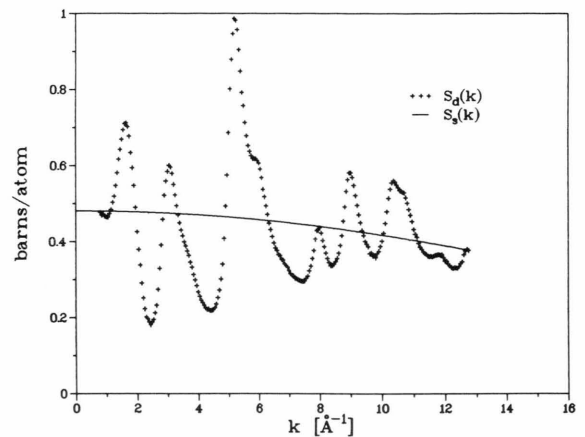


Fig. 4. Effective neutron cross-section of amorphous carbon derived from data shown in Fig. 3 and calculated self-scattering.

ing factors and hence of the kind of radiation used in the scattering experiment. We can therefore compare it with results obtained from x-ray diffraction.

#### Comparison with X-Ray Diffraction Data

The materials [5] used in the x-ray experiments were of the same grade (V10) but of different batches and shapes, namely flat plates of dimension  $25 \times 25 \times 2 \text{ mm}$ . The x-ray measurements were made using reflection geometry [10] and  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.7107 \text{ Å}$ ), with a crystal monochromator in the

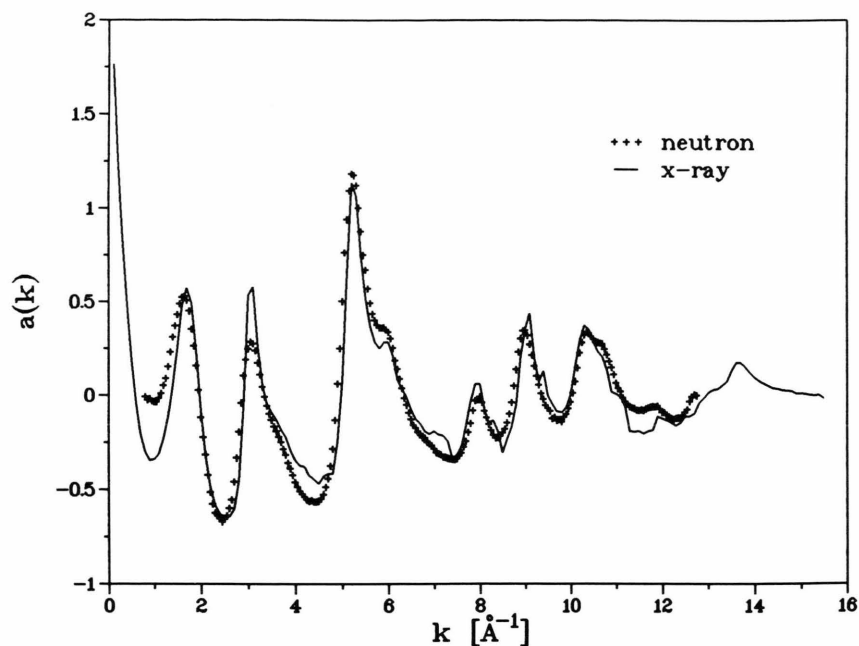


Fig. 5. Structure functions of amorphous carbon from neutron and x-ray diffraction.

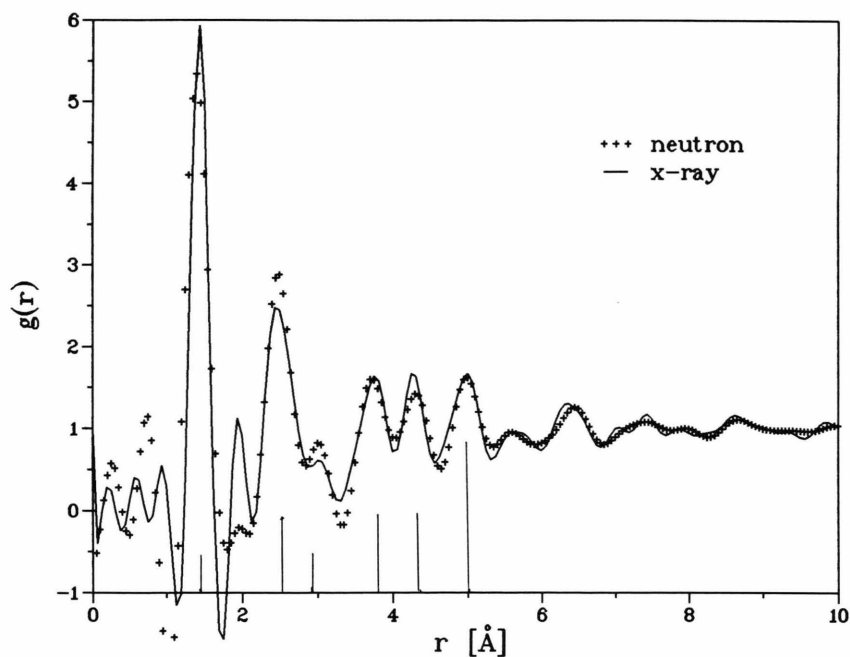


Fig. 6. Atom pair distribution functions of amorphous carbon obtained by Fourier inversion of the data shown in Figure 5.

diffracted beam. The range of scattering angles covered the interval  $0.6 < k < 16 \text{ \AA}^{-1}$ , and the accumulated counts ranged from  $10^4$  at the lowest to  $5 \times 10^5$  at the highest angles. Corrections for background, absorption [11], polarization, incoherent scattering [12], monochromator discrimination [10], and

multiple scattering [13] were applied. The corrected cross sections were normalized to the calculated self scattering from one carbon atom [12]. The X-ray cross sections were used to construct a structure function  $a(k)$  which is compared to the same quantity derived from neutron diffraction in Figure 5.

### III. Discussion

The structure functions derived from neutron and x-ray diffraction are shown in Figure 5. They were derived from experiments involving different scattering processes, geometries, and hence different corrections of sizable magnitude. We do not consider the differences between the two curves significant. The samples studied were of the same type but of different shapes and from different batches. Hence, these materials are very useful standards for the comparison of scattering data measured by different techniques and in different laboratories.

The x-ray data cover a wider range of momentum transfer and show sizable contributions at small angles. This is understood as a consequence of the porosity characteristic of this material [14], which has a much lower density (1.5 g/ml) than its crystalline modifications (2.25 g/ml for graphite). Fourier inversion of

the structure functions shown in Fig. 5 yields the atom pair distribution functions defined in (1). These curves, shown in Fig. 6, differ only in minor details caused by terminating the Fourier integral at different values of the variable  $k$ . The maxima in the functions  $g(r)$  agree very well with the in-plane distances calculated for a graphite network with a nearest neighbor distance of 1.42 Å (vertical bars in Figure 6). This result is in excellent agreement with earlier x-ray diffraction results [14, 15] on carbon black, and is another confirmation of the usefulness of this material as a standard in wide-angle diffraction experiments.

### Acknowledgements

The CPSPC was designed by Manfred Kopp, built by Joe Williams, and interfaced by David Smith. The help of Neal Skipper in the initial phase of its operation is appreciated.

- [1] P. A. Egelstaff, N. H. March, and N. C. McGill, *Can. J. Phys.* **52**, 1651 (1974).
- [2] A. H. Narten, *J. Chem. Phys.* **56**, 1185 (1972).
- [3] H. Olbrich, H. Ruppersberg, and S. Steeb, *Z. Naturforsch.* **38 a**, 1335 (1983).
- [4] F. Paasche, H. Olbrich, G. Rainer-Harbach, P. Lamarter, and S. Steeb, *Z. Naturforsch.* **37 a**, 1215 (1982).
- [5] Atomerig Chemetals Co., 100 Fairchild Ave., Plainview, NY 11803.
- [6] I. A. Blech and B. L. Averbach, *Phys. Rev.* **137** (1965).
- [7] H. H. Paalman and C. J. Pings, *J. Appl. Phys.* **33**, 2635 (1962).
- [8] V. F. Sears, *Thermal Neutron Scattering Lengths and Cross Sections for Condensed Matter Research*, Atomic Energy of Canada Ltd. Report AECL-8490, Chalk River, Ontario 1984.
- [9] L. Blum and A. H. Narten, *Adv. Chem. Physics* **34**, 203 (1976).
- [10] A. H. Narten and H. A. Levy, in "Water: A Comprehensive Treatise," F. Franks (ed.), Plenum, New York 1972, Vol. I, p. 314.
- [11] H. A. Levy, P. A. Agron, and M. D. Danford, *J. Appl. Phys.* **30**, 2012 (1959).
- [12] Atomic scattering factors for C were taken from "International Tables of X-Ray Crystallography," Kynoch, Birmingham 1974, Vol. IV. Compton scattering factors were taken from D. T. Cromer and J. B. Mann, *J. Chem. Phys.* **47**, 1893 (1967).
- [13] B. E. Warren and R. L. Mozzi, *Acta Crystallogr.* **21**, 459 (1966).
- [14] G. D. Wignall and C. J. Pings, *Carbon* **12**, 51 (1974).
- [15] S. Ergun, *Carbon* **6**, 141 (1968).