Structural studies of multiwall carbon nanotubes by neutron diffraction

A. Burian
Institute of Physics, University of Silesia, ulica Uniwersytecka 4, 40-007 Katowice, Poland

J. C. Dore
School of Physical Sciences, University of Kent, Canterbury CT2 7NR, United Kingdom

H. E. Fischer
Institute Laue-Langevin, 38042 Grenoble, Cedex 9, France

J. Sloan
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

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We report on structural studies of multiwall carbon nanotubes by wide-angle neutron scattering up to a maximum scattering vector $Q_{max}=166\ nm^{-1}$. The derived reduced radial distribution functions of the nanotubes are compared to those determined for graphite and turbostratic carbon, providing evidence that the stacking pattern of graphene tubules in multiwall carbon nanotubes is intermediate between those of the other two carbon forms. The (002) and (004) peaks of the nanotubes appear at smaller angles than graphite, yielding the intertubule spacing of 0.341 nm. At small length scales ($\lesssim 0.5$ nm) the nanotube structure resembles that of graphite, including graphitelike interlayer correlations for at least a few adjacent layers. Beyond this range, a systematic decrease in peak amplitudes and deviation from the graphite structure is observed.
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The high degree of interest in detailed information about the structure of carbon nanotubes is greatly motivated by their peculiar properties and potential applications. Nanotubes were originally produced in very small quantities and knowledge of their structure was based mainly on high-resolution transmission electron microscopy (HRTEM) observations, accompanied by the digital analysis of HRTEM lattice images[1–5] and electron diffraction (ED) studies.[6–10] Only a few reports on x-ray diffraction (XRD) studies of nanotubes have appeared.[7,11–14] A carbon nanotube is normally represented as graphitic sheet with a perfect hexagonal network that is wrapped up into a seamless cylinder. Multiwalled nanotubes (or multiple walled nanotubes MWNT's) are built up of such concentrically stacked cylinders with intertubule spacings in the range of 0.340–0.362 nm.[1,2,4,5,7] Detailed knowledge of the structure of carbon nanotubes is especially important from the point of view of their extraordinary electronic properties. The relationship between structure and electronic properties was predicted theoretically in 1992 (see, for example, Ref. 15) and recently established experimentally.[16,17] Depending on the geometrical tube parameters, such as diameter and helicity, carbon nanotubes exhibit metallic or semiconductor behavior.

The intertubule distances are greater than the interlayer spacing found in graphite (*G*) (0.335 nm) and close to the value characteristic of turbostratic carbon (TC) for which single layers are randomly translated or rotated.[18] The hexagonal structure of a single tubule and the presence of helical atomic arrangements in carbon nanotubes have been well established by theoretical and experimental studies. However, the key question concerns the interlayer structure, e.g., to what degree, if any, the *-ABAB-* graphitic stacking sequence is retained for coaxial tubes. It is impossible to arrange all hexagons on the surface of cylinders while mantaining the ideal graphite interlayer correlations, because of a shortage of succesive layers and because of their curvature. Therefore, in the earlier reports turbostratic stacking of graphene sheets has been suggested.[1,6,7] Additional problems may arise with the presence of helical tubes in MWNT's, which have been addressed in Refs. 8 and 9. More recent and more detailed analysis of HRTEM, ED, and XRD data has provided evidence that this hypothesis of turbostratic stacking should be reconsidered. It has been shown that the glide defect of graphene sheets in which each sheet is shifted parallel to its neighbors occurs in MWNT's. Moreover, the existence of short-range interlayer stacking correlations of the graphite type has been reported based on careful and detailed interpretation of the XRD data.[12] The proportion of graphitic stacking in the investigated samples, containing 60% carbon nanotubes and 40% carbon nanoparticles, has been estimated to be about 18%. The presence of such ordered regions has been related to flat domains, which locally approximate graphite. These studies suggest that tubule stacking in MWNT's is intermediate between graphitic and turbostratic stacking regarded as the two extreme cases. Similar conclusions have been derived by Liu and Cowley[19] from the ED and HRTEM observations. The authors have reported the existence of interlayer correlations in MWNT's and have related graphitelike stacking to the presence of the planar regions, which may be ordered or disordered.

In the present paper, we report neutron diffraction (ND) studies giving the reduced radial distribution functions (RRDF's) of purified MWNT's, using TC and *G* as the reference materials for comparison with different structural

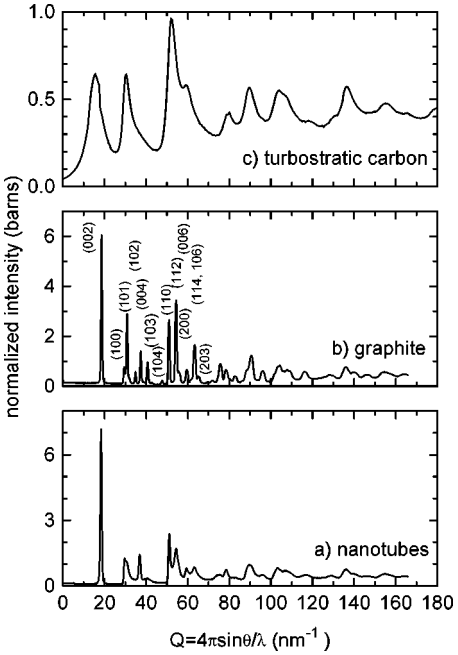

FIG. 1. Neutron diffraction intensities for multiwalled nanotubes (MWNT's) (a), graphite (G) (b) and turbostratic carbon (TC) (c).

models in both real and reciprocal space. The MWNT's were prepared and purified in the Inorganic Chemistry Laboratory at Oxford University.

A modified Krätschmer-Huffmann bulk preparation procedure was used, which involves the arc evaporation of a graphitic rod under dymanic pumping conditions with ~ 0.17 atm of helium using an arc generated by a dc voltage of 30 V and a current of ~ 180 A. The MWNT's accumulate on the cathode as a soft deposit covered by a hard cylindrical outer layer. The MWNT's can then be easily extracted from the soft inner core and the outer shell discarded.[20] The MWNT's were purified by heating in liquid bromine for four days, which selectively attacts the impurity nanoparticles (which contain more defects). The brominated sample is then heated to 530 °C under a flow of oxygen containing 4% helium for five days, after which the sample was composed mainly of pure nanotubes. The nanotube surfaces are apparently only slightly damaged and the majority of the tubes are open at both ends. The yields depended crucially on the flow rate of oxidant, the scale of the initial experiment, the manner of packing of the carbon, and the quality of the cathodic soot. The yields vary between 10–20 % (w/w), where (w/w) represents weight in weight concentration and the procedures have been described in more detail elsewhere.[21]

In order to address the structural questions related to atomic arrangement within a single layer and to the stacking nature of graphene layers in the MWNT's, the ND technique together with the RRDF method are applied in the present study. The intensities for the MWNT's and G were measured at room temperature using the D4 diffractometer at the Institut Laue-Langevin (Grenoble), operating at the wavelength of 0.07 042 nm up to the scattering vector $Q_{\max}$ of 166 nm^{-1} ($Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength). The RRDF is computed as the sine Fourier transform

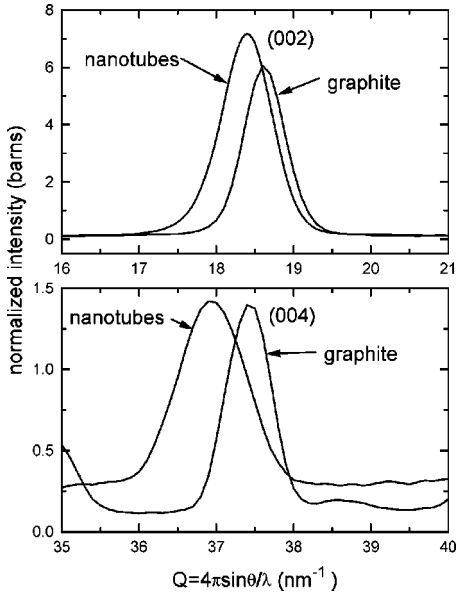

FIG. 2. Enlarged parts of Fig. 1 containing the (002) and (004) peaks for the MWNT's and G.

$$4\pi r[\rho(r)-\rho_0]=\frac{2}{\pi}\int_0^{Q_{\max}}\frac{Q[I(Q)-b^2]}{b^2}W(Q)\sin(Qr)dr,$$

where $I(Q)$ is the corrected and normalized intensity and b^2 is the square of the coherent scattering length of carbon. The Lorch window function $W(Q)=\sin(\pi Q/Q_{\max})/(\pi Q/Q_{\max})$ was used in the determination of the RRDF's. The data for TC were taken from our previous experiment.[22] The diffraction patterns are shown in Figs. 1 and 2 and the calculated RRDF's are presented in Fig. 3.

In Fig. 1, the measured powder diffraction patterns, plotted as a function of Q for the MWNT's, G, and TC are compared. Miller indices for G are also given. The measured

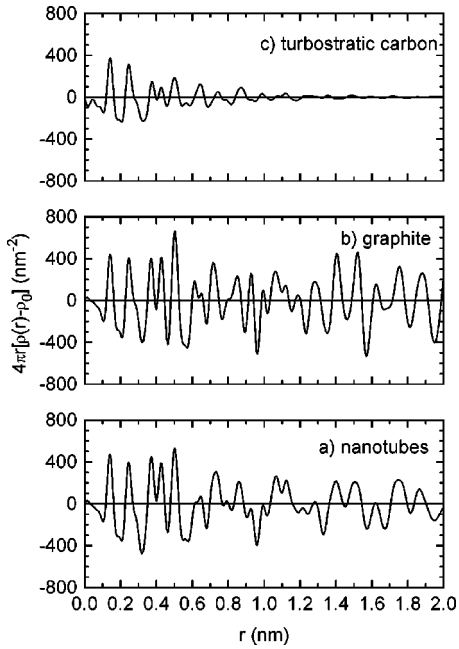

FIG. 3. Reduced radial distribution functions of the MWNT's (a), G (b), and TC (c).

ND pattern of the MWNT's differs appreciably from the previously reported x-ray results.[7,12,13] The main features seen in Fig. 1(a) are sharper and the ND pattern of the MWNT's exhibits lines with general (hkl) indices (indicative of interlayer correlations), that are similar to the -*ABAB*- graphite stacking sequence. The (hkl) peaks are broader than graphite's but not completely extinguished as for TC, in which graphitelike layers are stacked without geometrical correlations. In the case of TC only ($hk0$) and (00l) diffraction lines are observed. Since Fig. 1 suggests that there are interlayer correlations in the investigated MWNT's, we have analyzed the positions and shapes of the (002) and (004) diffraction lines in more detail to learn more about the stacking nature of the tubules. The enlarged parts of the MWNT's and *G* (002) and (004) diffraction profiles are shown in Fig. 2. One can clearly see that the MWNT peaks are shifted towards lower *Q* values, yielding an interlayer spacing of 0.341 ± 0.001 nm, which is greater than the value of 0.336 ± 0.001 nm obtained for *G*. An important observation of the (002) and (004) profiles is that their widths increases with *Q* in the case of the MWNT's and are almost constant for *G*. The estimated full widths at half maximum (FWHM) are 0.64, 0.69, and 0.78, 1.02 for the (002), (004) peaks of *G* and the MWNT's, respectively. For carbon nanotubes the FWHM may be related to particle size and lattice distortion broadening. The former is *Q* independent, the latter increases with *Q*. In order to separate precisely these two contributions the data having higher resolution in reciprocal space are necessary for which at least three orders of Bragg reflections should be present in the diffraction pattern (see, for example, Ref. 23). The present results suggest that an increase in the FWHM of the (00l) peaks for the investigated MWNT's is due to defective stacking of tubules. The nearest-neighbor interatomic distances, estimated from the positions of the (100) and (110) peaks are 0.141 ± 0.001 nm and 0.142 ± 0.001 nm for the MWNT's and *G*, respectively. These values are in agreement with the first-peak positions of the RRDF's shown in Figs. 3(a) and 3(b).

The conclusion concerning the resemblance of the local MWNT's structure to that of G is reinforced by comparison of the RRDF's shown in Fig. 3. In the *r* range of 0–0.5 nm the RRDF peaks of the MWNT's and *G* have practically the same positions, shapes, and amplitudes, in contrast to the TC peaks, which are broader and have clearly lower amplitudes. These features result from the lack of correlations in layer stacking in TC, for which the RRDF contains peaks only due to correlation within a single layer and interlayer correlations contribute in the form of the steplike or continious turbostratic term.[22] This comparison supports the conclusion based on the analysis of the ND data in reciprocal space, that there are the geometrical correlations between tubules, at least for three adjacent tubules. Moreover, the detailed analysis of the higher resolution radial distribution function, derived from the ND data extended to $Q_{\max}=237.5$ nm^{-1}, using the curve fitting method,[22] shows that each carbon atom has two neighbors, lying in adjacent layers, at $r=0.34$ nm.[24] The RRDF's of the MWNT's and *G* clearly differ in the range of 0.5–1.3 nm. Such behavior is related to curvature of graphite layers and stacking disorder leading to deviations from the perfect graphite structure. For $r>1.3$ nm the peak positions of the MWNT's and *G* are practically the same—the former are broader and have smaller amplitudes. In this structural region the correlations between atoms lying in the same layer (i.e., along the length of the nanotube) are the main contribution to the RRDF. We explain this feature by the size effect resulting from a limited diameter of individual tubules and broadening due to stacking disorder, which makes the interlayer correlations weak in a high *r* region.

In summary, the ND data of the MWNT's containing mainly pure nanotubes have allowed the structure of this form of carbon to be determined more precisely than previously. The perfect graphite hexagonal network is retained within a single layer when graphitic sheet is wrapped up into a cylinder. The obtained results provide direct evidence of the existence of short-range graphitic interlayer correlations in multiwalled nanotubes, which have been suggested previously in Refs. 12 and 19.

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