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# Variable step radial ordering in carbon onions

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ABSTRACT

We analyse the radial distribution of atoms in carbon onions optimised using a combination of classical molecular dynamics and density functional theory. X-ray diffractograms of thermally annealed nanodiamonds are also exploited together with high-resolution transmission electron microscopy data published elsewhere. The internal radial ordering of atoms inside the onions was determined showing a gradual change of intershell separation as a function of radius. This change may result in a twisted internal structure of the onions. The influence of atomic defects appearing in the shells altering their curvature on the formation of twisted onions is discussed.

## 1. Introduction

Open shell Carbon Onions (COs) may be useful structures with many applications such as hydrogen storage, new absorbers and targeted drug delivery vehicles [1] through the encapsulation of other molecules. They might also be precursors that occur in the nucleation of diamond [2]. Modelling the structural properties of COs is an alternative to expensive laboratory experiments which can throw new light on their geometry and physical and chemical properties. Recently, classical molecular dynamics (MD) simulations were performed by our group to investigate the heating of vacuum-suspended diamond nanocrystals of extremely small size [3] (1.3–1.4 nm). The spike heating was assumed to occur through the stochastic absorption of ultraviolet photons by the diamond nanoclusters in the interstellar medium [3]. It was found, depending on the heating temperature, that the nanodiamonds transform into nanoclusters with a diversity of shapes not previously mentioned in the literature. Namely, some of them were spirally twisted onions, resembling the structure of the marine mollusk *Rapana venosa* [3]. These obtained clusters occur in a chiral [3] form.

In this paper the coordinates of carbon atoms obtained by classical MD [3] for a spiral onion are relaxed using Density Functional Theory (DFT), with the code PLATO [4] to test stability. A further aim is the determination of the internal distribution function of atoms inside the cluster, as a function of the radial distance from the centre and to compare the results with experiments. To this end we analyse the most intense X-ray Diffraction (XRD) peak measured for COs in paper [5] and other results for the variation of the intershell distances measured directly from high resolution electron microscopy (HRTEM) images [2].

For the purpose of investigation of the XRD diffraction pattern, we elaborate on a model of broadening of the most intense XRD peak of COs, concentrating on the contribution of the variation of Bragg's angle to the resulting pattern. This broadening may occur due to the atomic ordering within the shells which have a specific distribution of intershell spacing.

## 2. Results and discussion

### 2.1. X-ray diffraction laboratory experiment

The Scherrer equation for the XRD profile, would interpret the smaller broadened peak *in* Fig. 1 as corresponding to a crystal of bigger size. As is seen from Eq. (1), the mean radius of coherent X-ray scattering associated with crystallite size is inversely proportional to the width of the XRD band measured at half its height. However from a comparison of the diffraction profiles of nanodiamonds and onions depicted in Fig. 1, this is not the case here. So the broadening mechanism associated with COs cannot be interpreted as due to the size of the onions. Therefore, it seems quite natural to assign the peak broadening to a variation in the “lattice spacings”, i.e. the distances between shells of onions. For a more rigorous analysis we shall present a formalism here.

This process of transformation of nanodiamonds to onions occurs with a decrease in the mass density of diamond to the value approximately equal to that of graphite. The transformation results in a corresponding increase in size of the onion child compared to the size of

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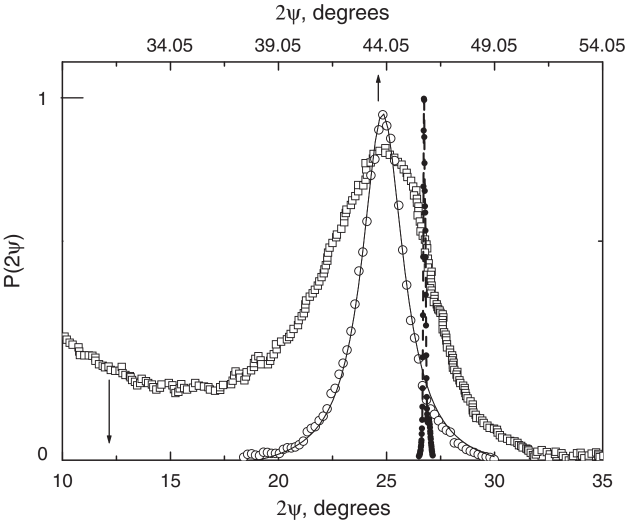

**Fig. 1.** The intensity profiles $P(2\psi)$ measured for the most intense bands of the experimental X-ray diffraction patterns for Cu–Kα radiation ($\lambda = 1.54059$ Å). The double diffraction angle $\psi$ for the narrow peaked curve denotes the result for detonational nanodiamonds [5]. The broad peaked curve relates to nanodiamonds annealed in vacuo for 10 min, at a temperature of 1500 °C, as reported in paper [5]. The solid line reproduces the Lorentzian fit (Eq. (4)) with the following set of parameters: $2\psi_B = 43.9°$, $w_L = 2.338 \pm 0.0419°$, $A_L = 7.325 \pm 0.127$ arbitrary units. Black spots show the reference data for graphite.

a parent diamond nanocluster. For example, taking the density of graphite as ~2.2 g/cm$^3$ and 3.515 g/cm$^3$ for diamond (see, e.g. [6]) we have for a parent a nanodiamond with a mean diameter of 5 nm, and a diameter of ~6 nm for a median child onion.

If there was a strong correspondence between the atomic spacing in the COs and the nanodiamonds, the XRD pattern formed due to the size distribution of the onions only would be similar to that for nanodiamonds (Fig. 1) and the shape of the peak of the diffraction pattern would be a rather sharp.

However, experiments show (see, e.g. [7,8]) that this transformation is accompanied with a significant broadening of the most intense XRD peak after annealing, compared to the peak for pristine nanodiamond (Fig. 1).

Excepting the contribution due to internal strain, the broadening of the diffraction pattern can occur through two basic mechanisms, namely broadening induced by the finite size of the nanoclusters and broadening induced by the variation in the lattice (intershell) spacings inside the clusters. From the well-known Scherrer formula the mean crystallite size, $\hat{D}$, is:

$$\hat{D} = \frac{K\lambda}{w_L cos(\psi_B)} \approx \frac{\lambda}{w_L} \tag{1}$$

here λ is wavelength of the X-ray radiation, $w_L$ is the full width of the contour measured at half height, $K \approx 1$ for spherical particles, and $cos(\psi_B) \approx 1$ because of the smallness of the Bragg angle $\psi_B$ taken for $n = 1$ from Bragg's law:

$$2\delta r \sin\psi_B = n\lambda \tag{2}$$

where $\delta r$ is lattice spacing.

For investigation of the line shape of the most intense diffraction peak of COs we have used two models. The first is based on an assumption that a set of uniform spheres with a certain size-distribution function may contribute to the diffraction pattern. The second one assumes a stochastic contribution of intershell distances to the pattern.

The principles of the first model are presented in paper [9] where direct calculation of the diffraction intensity profile by an ensemble of spherical particles with log-normal distributed sizes was performed and it was shown that for the case of a rather narrow distribution function of cluster sizes, the XRD profile associated with this distribution follows the Lorentzian (Cauchy) function [9]:

$$L(k) = \frac{2\hat{A}_L}{\pi} \frac{\hat{w}_L}{4k^2 + \hat{w}_L{}^2}. \tag{3}$$

Here $k$ is the wavenumber associated with the diffraction vector, $k = \frac{2(sin\psi - sin\psi_B)}{\lambda}$, and $\hat{w}_L$ is the FWHM. Assuming a small angle of diffraction, one may write $k \approx k' = \frac{(2\psi - 2\psi_B)}{\lambda}$ and rewrite Eq. (3) as follows:

$$L(\psi, \psi_B, w_L, A_L) \approx \frac{2\hat{A}_L}{\pi} \frac{\frac{w_L}{\lambda}}{k'^2 + \frac{w_L^2}{\lambda^2}} \approx \frac{2A_L}{\pi} \frac{w_L}{4(2\psi - 2\psi_B)^2 + w_L^2} \tag{4}$$

here $\hat{w}_L = \frac{w_L}{\lambda}$; $\hat{A}_L$ and $A_L$ are constants.

The results of fitting the XRD profile for nanodiamonds using Eq. (3) is shown in Fig. 2 by the full line with the fitting parameters in the figure caption. Because the Bragg angles may fluctuate in the COs, it is natural to perform a decomposition of the most intense diffraction peak using the equation:

$$P(\psi) \approx \sum_{j=1}^{M} L\left(\psi, \psi_{Bj}, w_{Lj}, A_{Lj}\right). \tag{5}$$

Because there should be a strong correlation between the diamond and onion distributions, this correlation justifies the choice of Lorentzians in Eq. (5) keeping the same parameter $w_{Lj}$ but correcting it taking into consideration a slight inflation of size of the onions as a result of annealing. I.e., because this parameter defines the median diameter of the nanocrystallite, we slightly reduced its value for onions, taking into consideration that the reduction of density during the diamond–onion transformation is similar to that for diamond–graphite

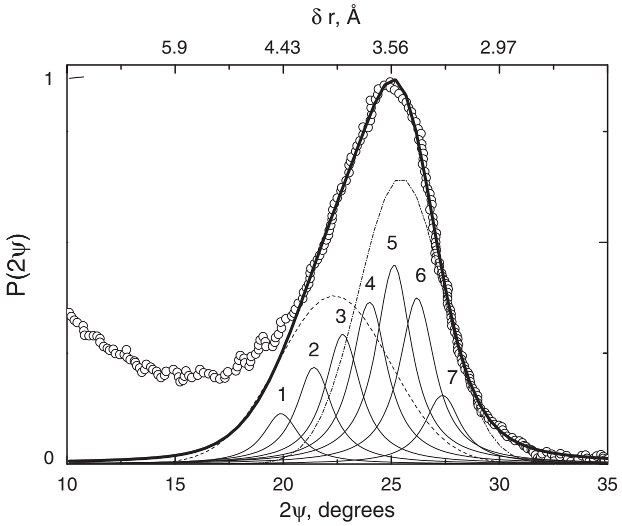

**Fig. 2.** The Lorentzian decomposition of the central part of the X-ray diffraction pattern $P(2\psi)$. Thin lines marked with numbers portray each of seven Lorentz contours used for the decomposition: the thick line shows the sum of all of the Lorentzians included (Eq. (5)). The best fit parameters are: $w_{L1} = w_{L2} = w_{L3} = w_{L4} = w_{L5} = w_{L6} = w_{L7} = 1.994°$; $2\psi_{B_1} = 19.900 \pm 0.023°$, $2\psi_{B_2} = 21.433 \pm 0.020°$, $2\psi_{B_3} = 22.753 \pm 0.020°$, $2\psi_{B_4} = 23.987 \pm 0.021°$, $2\psi_{B_5} = 25.114 \pm 0.020°$, $2\psi_{B_6} = 26.188 \pm 0.021°$, $2\psi_{B_7} = 27.368 \pm 0.024°$; $A_{L1} = 0.713 \pm 0.017$, $A_{L2} = 1.371 \pm 0.024$, $A_{L3} = 1.834 \pm 0.031$, $A_{L4} = 2.307 \pm 0.040$, $A_{L5} = 2.814 \pm 0.045$, $A_{L6} = 2.348 \pm 0.044$, $A_{L7} = 0.977 \pm 0.034$, normalised units. The parameters of the stochastic model, given in Eq. (6) for $i = 1$ (dashed line) and $i = 2$ (dash-dot line) are: $\psi_{o1} = 22.35 \pm 0.41°$, $w_1 = 5.162 \pm 0.30°$, $A_1 = 4.914 \pm 0.827$, $\psi_{o2} = 25.45^{\pm}0.079°$, $w_2 = 3.90 \pm 0.08°$, $A_2 = 6.309 \pm 0.822$.