



## Examination of reactor grade graphite using neutron powder diffraction

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### A B S T R A C T

Graphite is of principal interest in Generation IV nuclear reactor concepts. In particular, graphite will be the moderator for the Very High Temperature Reactor. In support of experimental and computational investigations that aim at understanding the behavior of reactor grade graphite under operating conditions, neutron powder diffraction experiments have been performed at the North Carolina State University PULSTAR reactor. The collected diffraction patterns exhibit intense broadening of several of the reflections, characteristic of turbostratic stacking. In order to quantify this disorder structurally, a model combined with a Rietveld-like refinement approach was implemented, which includes several refinable parameters that aim at describing this type of structure. Stacking parameters representing the probabilities of a random and registered shift between stacking packages were defined. The results indicate that the studied reactor grade graphite specimens contain a small fraction of layer disorder. The inferred inter-layer spacing for the specimens is slightly larger than the theoretical value for graphite of 0.335 nm and the lattice constant is slightly less than 0.246 nm. The developed methodology is found to be successful in fitting the neutron diffraction patterns of reactor grade graphite.

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### 1. Introduction

Graphite has been of principal interest in nuclear reactor design since the operation of the first nuclear fission reactor (CP-1). More recently, Generation IV concepts, specifically the gas cooled Very High Temperature Reactor (VHTR), employ graphite as the moderator. In such reactors, a type of graphite known as “reactor grade graphite” is the form that will be used. This type of graphite is a polycrystalline material that exhibits a high degree of graphitization, high chemical purity to minimize the thermal neutron absorption in the moderator, and random bulk orientation. This latter characteristic results in dimensional stability under high neutron fluences. The manufacturing process is discussed in great detail elsewhere [1]. Structurally, this material may be considered as multiphase and composed of a petroleum-coke filler phase and a coal-tar pitch binder phase. The petroleum-coke achieves a high level of crystallinity upon heating the material to temperatures between 2800 and 3000 °C. The density is generally less than that of single crystal graphite and is in the range of 1.5–1.8 g/cm<sup>3</sup>, due to being a porous material.

Graphite has a crystalline structure that is composed of C atoms arranged in a hexagonal pattern and stacked in an ABABA... planar sequence. Within each plane, strong covalent bonds exist between the C atoms, while the bonds between the planes are relatively weak. Reactor grade graphite on the other hand has a less perfect structure than highly crystalline graphite [2]. The ABABA... stack-

ing sequence is lost and the planes may exhibit a random translation or rotation relative to each other. The term “turbostratic” has been used to describe this type of disorder [3,4].

The interest in reactor grade graphite has led to a considerable effort in the modeling of the fundamental properties of this material [5,6]. Thermal neutron scattering cross-sections, thermal expansion, thermal conductivity and heat capacity are just a few of the properties that are being investigated. All of these properties have been derived using either first principles or molecular dynamics techniques. These methods involve a detailed knowledge of the structure of the material on the atomic level. Nevertheless, so far the simulations have focused on perfect graphite structures and the effects that neutron damage may have on the properties of these structures. Thus, an experimental investigation of the atomic structure of reactor grade graphite can contribute to improving the fidelity of these computational methods and their potential impact on nuclear reactor design applications.

One technique of structure investigation is neutron powder diffraction. This technique can provide information on the crystal structure (lattice parameters, atomic species, etc.) of a material. A typical diffraction experiment (that is performed at a reactor neutron source) involves the use of monochromatic neutron beams incident on specimens that are powder-like. The neutrons scattered by the specimen are then collected by a detector and the counts (often normalized to a fixed number of beam monitor counts) are recorded as a function of the scattering angle  $2\theta$ . A diffraction pattern containing a series of peaks will then appear as a function of the scattering angle. The position of the peaks is related to the diffraction from atomic planes with different interplanar

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spacing. The collected diffraction patterns are subsequently analyzed by assuming a structural model and assessing its match to the measured data using Rietveld analysis techniques [7,8].

## 2. Model of reactor grade graphite structure

X-ray powder diffraction patterns of graphitic carbons can be calculated by assuming that the basic structure of the carbon is a two layer package with finite lateral extent and AB-registered stacking, which is the basis of the model introduced by Shi et al. [9]. In our work, this model has been adapted for the calculation of neutron powder diffraction patterns of reactor grade graphite.

In this model [9], the stacking of the two layer packages is controlled by introducing two layer disorder parameters,  $P$  and  $P_t$ . The parameter  $P$  represents the probability of finding a random shift between adjacent packages. A registered shift between the packages is determined by the probability  $P_t$ . This probability determines if the local order is AB/CA/BC etc. The probability that there is no shift is then given by  $(1 - P - P_t)$ . Setting  $P = 0$  and  $P_t = 0$  results in the ABAB stacking found in perfect graphite (see Fig. 1). If  $P_t = 1$  and  $P = 0$  then the ABC form is obtained.

In order to deal with fluctuations in layer spacing, a parameter corresponding to the average fluctuation in this spacing is introduced. The layer spacing is then given by  $d_{002} + \delta$  where  $\langle \delta \rangle = 0$  and  $\langle \delta^2 \rangle \neq 0$ . In the two layer model it is assumed that there are no interlayer spacing fluctuations within the packages but only between them. The probability of a given fluctuation is described by a Gaussian function given by:

$$p(\delta) = \frac{1}{\sqrt{2\pi\langle \delta^2 \rangle}} e^{-\delta^2 / (2\langle \delta^2 \rangle)} \quad (1)$$

where  $\sqrt{\langle \delta^2 \rangle}$  describes the fluctuation in the layer spacing. The quantity  $(\langle \delta^2 \rangle)^{1/2}$  represents the average layer fluctuation because half of the layer groups have no fluctuation. In the model, the number of two layer stacks is given by  $M$ . Therefore the number of layers in a crystallite is given by  $2M$ . Also since half of the layers are assumed to have AB stacking, the probability of finding a random shift between any two carbon layers is  $P/2$ .

## 3. Analysis of neutron powder diffraction patterns for disordered structures

Based on the structural model presented above, the diffraction intensity can be calculated by considering the reciprocal lattice for an ideal two dimensional graphite layer with finite extent. The reciprocal lattice is a series of rods which intersect the stacking plane. The calculation of the intensity at a certain scattering angle is a sum of all the contributions, averaged over all orientations in three-dimensions, from each  $hk$  rod in reciprocal space. The final intensity within an arbitrary scale factor can be calculated by:

$$y_{ci} = s \sum (I(\theta)_{00} + 6I(\theta)_{10} + 6I(\theta)_{11} + \dots) + I_b, \quad (2)$$

where  $s$  is the scale factor,  $I_b$  is the background correction, and  $I(\theta)_{hk}$  is the calculated intensity due to an  $hk$  reciprocal space rod. Since the highest scattering angle in most diffraction experiments never exceeds  $150^\circ$ , only the rods with  $\max h$  or  $k = 3$  are considered during the calculation. The calculated intensity can be directly compared to the counts (typically per a set number of monitor counts) measured in the detectors.

The average diffraction intensity due to a stack of graphite layers can be described by [10]:

$$i(s) = M |\Phi(\bar{s})|^2 G(\bar{s}), \quad (3)$$

where  $\Phi(\bar{s})$  is the scattering amplitude of a two layer package and  $G(\bar{s})$  is known as the modulation function and represents the effects of the layer stacking on the diffracted intensity. The modulation function can be written in terms of the average phase factor between two layers and is given as:

$$G(\bar{s}) = \text{Re} \left[ \frac{1+q}{1-q} + \frac{2}{M} \frac{q^{M+1}-q}{(1-q)^2} \right], \quad (4)$$

where  $q$  is the average phase factor. For a two layer package this factor can be written in terms of the various stacking probabilities and is given by:

$$q = \left\{ P \delta_{h0} \delta_{k0} + 1 - P + P_t \left[ \exp \left( \pi 4i \left( \frac{1}{3}h + \frac{2}{3}k \right) \right) - 1 \right] \right\} \times \exp \left( \pi 4i Z d_{002} - 2\pi^2 \langle \delta^2 \rangle Z^2 \right), \quad (5)$$

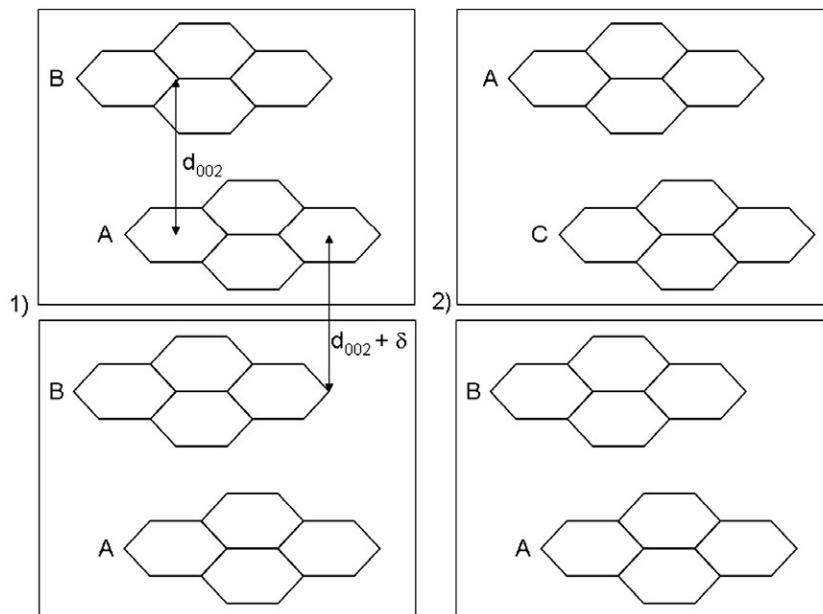


Fig. 1. Schematic showing the stacking sequence for (1) ABAB stacking and (2) ABC stacking in graphite. The boxed regions are two layer stacking packages.