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Extent of stacking disorder in diamond

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ABSTRACT

Hexagonal diamond has been predicted computationally to display extraordinary physical properties including a hardness that exceeds cubic diamond. However, a recent electron microscopy study has shown that so-called hexagonal diamond samples are in fact not discrete materials but faulted and twinned cubic diamond. We now provide a quantitative analysis of cubic and hexagonal stacking in diamond samples by analysing X-ray diffraction data with the DIFFaX software package. The highest fractions of hexagonal stacking in materials previously referred to as hexagonal diamond are below 60%. The remainder of the stacking sequences is cubic. We show that the cubic and hexagonal sequences are interlaced in a complex way and that naturally occurring Lonsdaleite is not a simple physical mixture of cubic and hexagonal diamond. Instead, it is structurally best described as stacking disordered diamond. The future experimental challenge will be to prepare diamond samples beyond 60% hexagonality and towards the so far elusive 'perfect' hexagonal diamond.

1. Introduction

The common form of diamond is cubic. Yet, a metastable hexagonal polymorph has been identified in fragments of the Canyon Diablo meteorite from the northern Arizona desert and other impactites [1,2]. To honour the achievements of the crystallographer Kathleen Lonsdale, hexagonal diamond has been named Lonsdaleite [1]. Synthetically, hexagonal diamond can be prepared, for example, by heating graphite in the 15–20 GPa range [3–8]. There is a considerable current interest in the targeted preparation and physical properties of hexagonal diamond as it has been predicted to display superior mechanical properties, such as hardness and compressive strength, compared with its cubic counterpart [9,10]. Furthermore, cubic and hexagonal diamonds are expected to have different band gaps and dielectric properties [11].

Cubic and hexagonal diamonds both consist of sp^3 hybridized and therefore tetrahedrally-bonded carbon atoms. Both allotropes contain puckered layers of carbon atoms with six-membered rings in the armchair configuration. The difference between cubic and hexagonal diamonds lies in how these layers are stacked on top of each other to build up the three-dimensional crystal structure (*cf.* Fig. 1). In cubic diamond, identical layers are stacked on top of each other with a shift half way across the diagonal of a six-membered ring. In hexagonal diamond, on the other hand, each layer is the mirror image of the previous layer [12]. The structural consequence of these different stacking recipes is that the six-membered rings *linking* the various layers are in the armchair conformation in cubic diamond but boat-type in hexagonal diamond. Consequently, cubic diamond consists of only armchair rings whereas hexagonal diamond is a 50:50 mixture of rings in the armchair and boat conformations, respectively.

The diamond structures are isostructural with ice if only the oxygen atoms in ice are considered. For ice, the hexagonal polymorph (ice I*h*) is the most stable at ambient pressure and a metastable cubic form (ice I*c*) has been thought to exist [13]. The field has progressed in recent years and it has been shown that what was previously considered to be cubic ice is in fact stacking disordered ice (ice I*sd*) containing variable fractions of both hexagonal as well as cubic stacking [14–18]. The 'perfect' cubic ice, containing only cubic stacking, has so far not been identified. As predicted for diamond, the differences in stacking have pronounced effects on the physical properties of ice including the vapour pressure [19], crystal shapes [20], spectroscopic properties [21] and potentially surface chemistry [22].

Originally, it was assumed that hexagonal and cubic diamonds often coexist which helped in understanding the observed X-ray diffraction data [1,2]. Yet, very recently, it has been shown by using high-resolution electron microscopy that what has been originally classified as hexagonal diamond is in fact not a discrete material but "faulted and twinned cubic diamond" [8].

Following our recent work on ice, we show here how stacking disorder can be characterised quantitatively in diamond samples on the basis of X-ray diffraction data using the DIFFaX software package [23]. We thereby take so-called memory effects, where the stacking depends on the previous stacking history, into account. The aim is to fully describe the stacking disorder in the various samples of hexagonal

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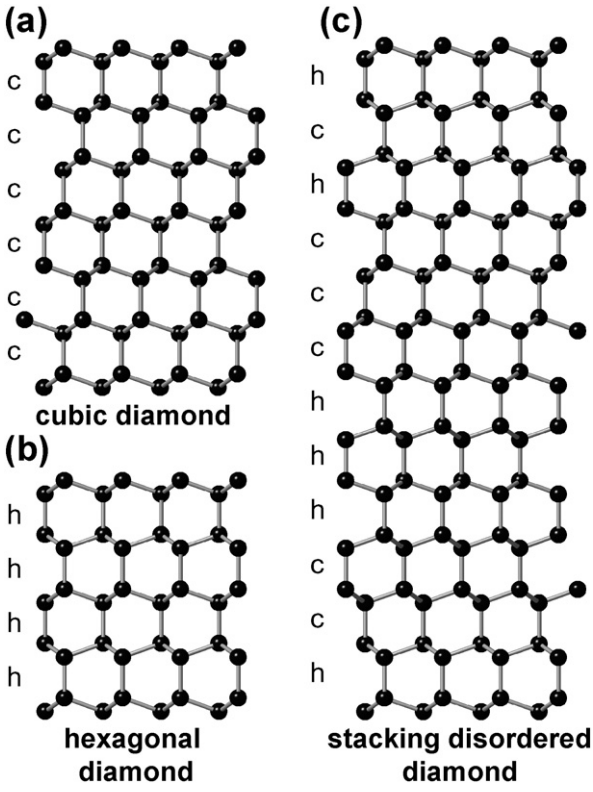

Fig. 1. Crystal structure projections along the hexagonal *a* axis for (a) cubic diamond, (b) hexagonal diamond and (c) stacking disordered diamond.

diamond that have been made so far and to show which experimental recipes lead to the most hexagonal stacking in diamond.

2. Methodology

Diffraction patterns of a cubic diamond sample in a 0.6 mm diameter glass capillary were collected on a Stoe Stadi-P diffractometer (Cu Kα, λ = 1.540598 Å) with a Mythen area detector. Additional diffraction data was taken from [6–8]. All diffraction patterns were background-corrected using shifted Chebyshev polynomials. For the calculation of diffraction patterns of stacking disordered diamond structure, we used the DIFFaX software package [23] as previously employed for ice samples [16,18]. To refine the *a* and *c* lattice constants, stacking probabilities, profile parameters (*u*, *v*, *w* and GL ratio) and zero-shift, we used our own MCDIFFaX programme[1] which embeds DIFFaX in a least-squares environment [18]. A typical refinement started with the optimisation of the lattice constants and the peak profile parameters. This was followed by refining the various stacking probabilities. Typically, several tens of thousands of individual DIFFaX calls were needed before the refinements converged. To prevent false minima, MCDIFFaX uses a Monte-Carlo-type parameter that allows a defined fraction of unfavourable moves to take place.

3. Results and discussion

The characteristics of stacking disorder in diamond are conveniently summarised with a so-called stackogram as shown in Fig. 2(a). In such a diagram, 1st order memory effects are taken into account; these are described with two independent stacking probabilities. The probability of cubic stacking following a cubic event is given by Φ_{cc} whereas Φ_{hc} describes the probability of a cubic event after hexagonal stacking.

[1] Salzmann CG, www.ucl.ac.uk/chemistry/research/group_pages/salzmann_group.

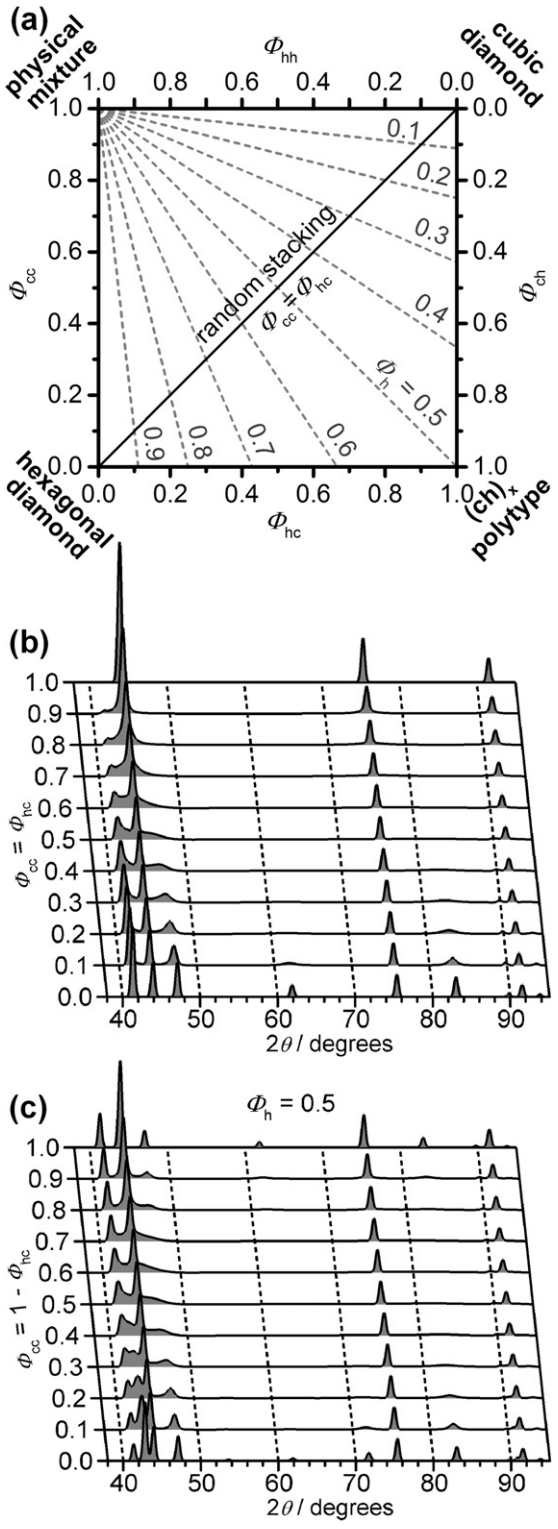

Fig. 2. (a) Stackogram used for the structural description of stacking disorder in diamond including 1st order memory effects. The black solid line indicates structures with random stacking whereas the dashed lines describe structures with a constant hexagonality. (b,c) Calculated powder diffraction patterns (Cu Kα) along the random stacking as well as the 0.5 hexagonality line.

Since the stacking can only be either cubic or hexagonal, it follows that $\Phi_{ch} = 1 - \Phi_{cc}$ and $\Phi_{hh} = 1 - \Phi_{hc}$. The stackogram is a plot of Φ_{cc} against Φ_{hc} and the corresponding dependent probabilities, Φ_{ch} and Φ_{hh}, have also been included. The four corners of this diagram define the end-member states. If Φ_{cc} and Φ_{hc} are both zero, the