n-diamond: an intermediate state between rhombohedral graphite and diamond?

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Abstract. A powder sample of n-diamond (new-diamond) synthesized from Fe-catalysed carbon black was investigated using the x-ray diffraction (XRD) technique. Based on the analysis and simulation of the peak position and intensity of the observed XRD pattern, the crystal structure of n-diamond was determined to be a $R3$ space group with cell angle $\alpha = 90^\circ$ and lattice parameter $a_0 = 3.5809$ Å. Using the experimentally determined space group and internal coordinates, first-principle calculations have obtained an equilibrium lattice constant that is close to the measured value. Assuming n-diamond as a transition state between rhombohedral graphite and diamond, the energetics on a path between rhombohedral graphite and diamond is computed and discussed.
1. Introduction

The ground-state crystalline phase of carbon is graphite, although it can transform to the metastable diamond phase under some circumstances [1]. Because of the unsurpassed hardness, excellent transport properties, transparency and inertness of diamond [1], there has been long-standing interest in synthesizing diamond from other allotropes of carbon. The first artificial diamond was synthesized under high-pressure and high-temperature conditions in 1955 [2–4]. Up to now, a variety of methods have been utilized to synthesize diamond materials from carbon in different forms, including high-pressure and high-temperature processes (bulk samples) [3, 4], explosive detonation (nanometre-sized powders) [5]–[7], chemical vapour deposition (CVD) with CH$_4$ or C$_2$H$_2$ as the carbon source (single crystal, microcrystalline and nanocrystalline films as well as thicker plates) [8], reduction–pyrolysis–catalysis route (nanoparticles) [9], etc. However, there are still many unclear issues in understanding the transformation process from the sp$^2$ or sp$^1$ allotropes to sp$^3$ diamond.

In 1991, Hirai and Kondo [10] developed a rapid cooling technique in the shock compression of graphite sheets and found a possible new allotrope of carbon. This new phase was referred to as ‘n-diamond’ (new-diamond), since its lattice parameter is close to that of diamond. Many reflections in its electron diffraction (ED) pattern match that of cubic (Fd$\bar{3}$m) diamond except for some additional forbidden reflections indexed at (200), (222) and (420). Subsequently, n-diamond has been found synchronously in a variety of processes to produce diamond [10]–[21], such as high-pressure and high-temperature processes [14], explosive detonation [15], CVD [12] etc. Indeed, the forbidden reflection at (200) was often seen in many experiments in diamond-like materials. However, the crystal structure and stability of n-diamond has not yet been determined, mainly due to the limited amount of samples and the tiny crystalline size in previous experiments [10]–[18]. Only transmission microscopy and ED were feasible for structural analysis in those experiments. Based on the ED data and electron energy loss spectrum, it was suggested that n-diamond is indeed a face-centred-cubic (fcc) crystal with space group Fm$\bar{3}$m and lattice parameter 3.57 Å [16, 17]. But recent first-principle calculations led to some controversies about the stability of fcc carbon [22]–[26]. If a carbon fcc crystal exists, the equilibrium lattice parameter would be about 3.08 Å, quite different from the observed lattice parameter for n-diamond (∼3.57 Å) [10].

Instead of the fcc structure, Hirai and Kondo [27] proposed that n-diamond is in fact a modified form of diamond, which is composed of hexagonal-ring-planes moderately puckered with the opposite direction to that of cubic diamond. Based on the observed ED pattern, four possible structural models were suggested for n-diamond [27], which has either cubic F$\bar{4}$3m or rhombohedral R3 space group with lattice parameter of $a_0 = 3.57$ Å and $\alpha = 90^\circ$. 

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For those three structural models with the $R3$ space group, the internal coordinates of the representative atoms can be expressed as $(0, 0, 0), (0.5, 0.5, 0), (x, x, x), (0.5 + x, 0.5 + x, x)$, where $x = 0.25$ and $0.5$ correspond to cubic diamond and simple cubic structure respectively. In Hirai’s models [27], several possible numbers of $x$ were proposed, such as $x = 0.333, 0.4$ and $0.416$. Recently, Buckmund et al [28] reported an alternative tetragonal carbon structural model for n-diamond, namely ‘glitter’, but the simulated XRD pattern from their model cannot reproduce the experiment well.

Recently, we have successfully synthesized n-diamond in macroscopic amounts (in the order of tens of grams) from Fe-catalysed carbon black under atmospheric pressure and at high temperature [19]. Hence it is possible to employ some straightforward approaches like XRD to investigate the structure and stability of n-diamond. In this work, n-diamond synthesized from Fe-catalysed carbon black was analysed by the least-squares refinement method and XRD pattern simulation technology. A possible crystal structure of n-diamond as an intermediate state between graphite and diamond is proposed and first-principle calculations are conducted to study the corresponding energetics.

2. Experimental procedure, XRD simulation and crystal structure model

The details for synthesizing n-diamond have been described in our earlier publications [19]. In brief, colloidal Fe(OH)$_3$ as catalyst was prepared from the reaction between saturated FeCl$_3$ solution and saturated NaOH solution at room temperature, and then stirred into carbon black N231 powders using a blender. The admixture with 10:1 carbon to iron mass ratio was compressed into an open stainless steel tank. The tank was initially maintained at 300°C for 100 min, then heated up to 1100°C for 30 min, and finally cooled down to room temperature. The obtained powders were washed with distilled water and then dried in an oven at 110°C. The final powder sample of n-diamond was analysed with XRD using an XRD-6000 diffractometer with Cu-K radiation. The results are shown in figure 1(a). Co-existence of graphite, NaCl, α-Fe and n-diamond in the powder sample can be seen. The evidence for the presence of n-diamond has been discussed in our previous works [19].

To determine the crystal structure of n-diamond, CELREF$^5$ and CaRIne Crystallography 3.1 programs$^6$ were utilized to analyse the observed XRD pattern from experiment. Enlightened by Hirai’s models [27], an $R3$ space group with cell angle $\alpha = 90^\circ$ was assumed for n-diamond. CELREF analysis indicates the onset of four strong peaks at 43.729, 50.906, 75.069 and 90.881° for a crystal structure with the $R3$ space group and lattice parameter 3.58 Å, which were observed for n-diamond (figure 1(a)). Mean square deviation for XRD angles between experimental data and CELREF analysis by the least-squares refinement method is only 0.0033. In other words, within the $R3$ space group and cell angle $\alpha = 90^\circ$, CELREF analysis yields a refined lattice parameter 3.58 Å for n-diamond crystal. In our experiments, we have studied many samples synthesized under the same conditions and those results were identical and repeatable.

To further determine the internal coordinates of the carbon atoms, we simulated the x-ray diffraction (XRD) pattern for a crystal of $R3$ space group with lattice parameter $a_0 = 3.5809$ Å

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$^5$ CELREF is a crystal cell parameter refinement program for application to powder x-ray or neutron diagrams, using a least-squares refinement method.

$^6$ The CaRIne Crystallography 3.1 program is crystallographic software for research and teaching by C Boudias and D Monceau.
and $\alpha = 90^\circ$ using the CaRIne Crystallography 3.1 program. Comparison between experimental and simulated intensity for the XRD pattern can verify the guessed internal coordinates for the simulations. Four sets of internal coordinates proposed by Hirai and Kondo [27] have been tested but none of them matches with experiment very well (see table 1). Instead, the atomic

**Figure 1.** Comparison of experimental (a) and simulated (b) XRD pattern for n-diamond. ▼: n-diamond; ◊: graphite; □: $\alpha$-Fe; △: NaCl.
Table 1. Comparison of experimental and simulated XRD reflection intensities of the n-diamond. $d_{\text{obs}}$: the spacing of XRD reflection observed in the experiment; $I/I_{111}$: the intensity ratio of each reflection peak with regard to the (1 1 1) peak; $I/I_{200}$: the intensity ratio of each reflection peak with regard to the (200) peak; $d_{\text{cal}}$: the spacing of XRD reflection from simulation.

| $hkl$ | Experiment | Our model | Hirai’s model M1<sup>a</sup> |
|------|------------|-----------|----------------------------|
|      | $d_{\text{obs}}$ | $I/I_{111}$ | $d_{\text{cal}}$ | $I/I_{111}$ | $d_{\text{cal}}$ | $I/I_{111}$ | $d_{\text{cal}}$ |
| 111  | 2.068      | 100       | 2.067      | 100       | 2.061      | 100       |
| 200  | 1.792      | 41        | 1.790      | 38.3      | 1.785      | 69        |
| 220  | 1.267      | 21        | 1.266      | 21.9      | 1.262      | 25        |
| 311  | 1.081      | 17        | 1.080      | 30.6      | 1.0763     | 50        |

| $hkl$ | Experiment | Our model | Hirai’s model M2<sup>a</sup> | Hirai’s model M3<sup>a</sup> | Hirai’s model M4<sup>a</sup> |
|------|------------|-----------|------------------------------|------------------------------|------------------------------|
|      | $d_{\text{obs}}$ | $I/I_{111}$ | $d_{\text{cal}}$ | $I/I_{200}$ | $d_{\text{cal}}$ | $I/I_{200}$ | $d_{\text{cal}}$ | $I/I_{200}$ |
| 111  | 2.061      | 100       | 2.061      | 91.6      | 2.061      | 60.6       |
| 200  | 1.785      | 22.3      | 1.785      | 100       | 1.785      | 100        |
| 220  | 1.262      | 22.7      | 1.262      | 33.9      | 1.262      | 33.7       |
| 311  | 1.0763     | 25.1      | 1.0763     | 41.2      | 1.0763     | 30.4       |

<sup>a</sup>The crystal structure models (M1–M4) were from Hirai and Kondo [24], and the reflection intensities were calculated by the CaRIne Crystallography 3.1 program [27].

coordinates that match best with experimental XRD intensity are (0, 0, 0), (0.5, 0.5, 0), (0.355, 0.355, 0.355) and (0.855, 0.855, 0.355), i.e., $x = 0.355$ in Hirai’s model. The simulated XRD pattern is shown in figure 1(b), and the simulated intensities for each characteristic peak associated with n-diamond were compared with experimental data in table 1. It can be clearly seen that the present structural model with $x = 0.355$ matches with experimental data quantitatively. This agreement is better than the previously proposed ones [27]. Mean square deviations between experimental and simulated XRD intensities are 13.89, 43.46, 20.45, 65.60 and 73.31 for present model, and M1, M2, M3, and M4 models in [27], respectively. It is noticeable that the mean square deviation between experimental and simulated XRD intensities based on our model is not negligible. The remaining deviations imply that our model may not be the ultimate structural model for n-diamond. However, it matches with experimental data better than those models previously proposed.

Figure 2(a) shows the experimentally determined crystal structure of n-diamond in rhombohedral representation. With the same $R3$ space group (cell angle $\alpha = 90^\circ$), both diamond and n-diamond have four atoms in the unit cell and their internal coordinates can be expressed as $(0, 0, 0)$, $(0.5, 0.5, 0)$, $(x, x, x)$ and $(0.5 + x, 0.5 + x, x)$. For diamond, $x = 0.25$, while our present model yields $x = 0.355$. Namely, n-diamond can be considered as a modified form of diamond under rhombohedral representation with cubic lattice. Figure 2(b) shows the crystal structure of n-diamond in hexagonal representation. Similar to the rhombohedral graphite [29], n-diamond is composed of hexagonal-ring layers stacked by an $ABCABC \ldots$ sequence, while the
Figure 2. (a) Crystal structure of n-diamond determined from experimental XRD data with aid of simulation (in rhombohedral representation). It has a $R3$ space group with lattice parameter $a_0 = 3.5809 \text{ Å}$ and $\alpha = 90^\circ$, the internal coordinates for the four carbon atoms in the unit cell are $(0, 0, 0)$, $(0.5, 0.5, 0)$, $(0.355, 0.355, 0.355)$ and $(0.855, 0.855, 0.355)$. (b) Crystal structure of n-diamond in hexagonal representation. The hexagonal-ring-planes in the n-diamond stack by an $ABCA\ldots$ sequence.

conventional graphite is stacked by $ABAB$ hexagonal-ring graphene layers. The major difference between n-diamond and rhombohedral graphite is the interlayer distance. In rhombohedral graphite, the distance between graphene layers is about $3.36 \text{ Å}$, while the interlayer distance between hexagonal-ring-planes in n-diamond are much closer, i.e., only $2.07 \text{ Å}$. Moreover, the
hexagonal-ring layers of n-diamond are slightly non-planar. From a topological point of view, it would be easier to transform from rhombohedral graphite with sp\(^2\) hybridization to n-diamond and then to diamond with sp\(^3\) hybridization. Therefore, we suggest that the n-diamond is indeed an intermediate state between sp\(^2\) carbon and sp\(^3\) carbon.

After 1-, 90- and 180-days-ageing treatments at room temperature and in vacuum, the primal powder sample of n-diamond was analysed with XRD again. With the evolution of treatment time, the absolute intensities of XRD patterns for each peaks associated with n-diamond were significantly weakened, and the relative intensity ratios between different reflections of XRD were changed with the treatment time. With increasing treatment time, the ratio \(I_{200}/I_{111}\) for the intensities of (200) reflection and (111) reflection was weakened, while the ratio \(I_{220}/I_{111}\) was enhanced. No clear trend was found for the other peaks during the ageing process. The observed changes of intensity ratio such as \(I_{200}/I_{111}\) and \(I_{220}/I_{111}\) imply that n-diamond is metastable and might gradually transform towards other structural phase during the ageing process. To understand this observation, XRD patterns of Hirai’s model with different \(x\) values (\(x = 0.355, 0.354, 0.353, 0.352, 0.351\)) were simulated using a CaRIne Crystallography 3.1 program (see footnote 6). If we associate the time-evolutional change of the relative intensity ratios of XRD reflections with decreasing \(x\) values in Hirai’s model, the simulated results agree quantitatively with experimental observation. With decreasing \(x\) values, the simulated \(I_{200}/I_{111}\) is weakened and the \(I_{220}/I_{111}\) is enhanced, both of which are consistent with the time-evolutional trend of n-diamond in the ageing-treatment experiments. The qualitative agreement between experimental results and our simulations suggest that n-diamond is metastable and it transforms towards diamond very slowly (with decreasing \(x\) values) during the ageing process. In addition, our experiments of the electrical conductivity for the sample can be circumstantial evidence for the transformation from n-diamond to diamond. The experiments revealed that the electrical conductivity of the sample was reduced with the increasing ageing treatment time. Thus, we guess that the n-diamond transforms towards the insulating diamond instead of the conducting graphite. To further understand these phenomena, first-principle computations were conducted, and a transformation path from cubic diamond to rhombohedral graphite by n-diamond was suggested, which will be presented in the next section.

3. First-principle computations

In this work, the structural stability of n-diamond was investigated computationally using density functional theory (DFT) and plane-wave pseudopotential technique implemented in the CASTEP package [30]. The ion–electron interaction was modelled by norm-conserving pseudopotentials [31], and a high cut-off of 800 eV was used for the plane-wave basis. The generalized gradient approximation (GGA) with the PBE exchange-correlation functional [32] was used. The Brillouin zone of the reciprocal space for the n-diamond solid is sampled by a \(6 \times 6 \times 6\) \(k\) point set.

First, we adopted the experimentally determined \(R3\) space group (with cell angle \(\alpha = 90^\circ\)) and internal coordinates for n-diamond and the total energy as a function of lattice parameter can be obtained, as shown in figure 3. The computed equilibrium lattice parameter of n-diamond corresponding to the minimum of the curve is 3.63 Å, in reasonable agreement with the experimental value of 3.58 Å. From our calculation, the cohesive energy of n-diamond within our structural model is 1.06 eV atom\(^{-1}\) lower than that of diamond, but 3.62 eV atom\(^{-1}\) higher than carbon fcc crystal (with equilibrium lattice parameter \(a_0 = 3.08\) Å). This result demonstrates...
that the present structural model is energetically more favourable than the previously proposed fcc structure, whereas it is still a metastable phase of carbon and less favourable than both diamond and graphite. The existence of a minimum in the curve of total energy versus lattice constant in figure 3 further implies that the n-diamond is metastable.

As we suggested above, n-diamond could be viewed as a metastable intermediate state between rhombohedral graphite with sp$^2$ hybridization and n-diamond with sp$^3$ hybridization. We constructed a two-step path from rhombohedral graphite to n-diamond and then to diamond. The computed total energies for the crystal structures on such a path are shown in figure 4. We started from a rhombohedral graphite structure with $a = b = 5.06$ Å, which is the experimental lattice constant of n-diamond in its hexagonal representation. But the lattice constant $c$ is much longer, i.e., $c = 9.62$ Å, determined from the minimum on the relation of energy versus $c/a$ ratio. In the first step, we fixed the lattice constants $a$ and $b$ and compressed the rhombohedral graphite uniformly by reducing the magnitude of $c$ from 9.62 to 6.20 Å. Such compression transforms rhombohedral graphite into n-diamond observed in experiment. It is noteworthy to point out that we assume non-planar hexagonal planes in rhombohedral graphite for simplicity. The effect of non-planarity could play some role but is not dominant in the current case. The energy path from rhombohedral graphite to n-diamond with decreasing $c/a$ ratio is presented in the right panel of figure 4. A monotonic and smooth increase of total energy with decreasing $c/a$ ratio can be seen. When we reach the middle of figure 4, i.e., the intermediate n-diamond state, we switch from hexagonal presentation to the rhombohedral presentation with lattice constants $a = 3.58$ Å and $c = 90^\circ$. Then we fixed the cubic lattice and reduced the internal coordinate parameter $x$ from $x = 0.355$ (for n-diamond) to $x = 0.25$ (for diamond). The energetics of this step is shown in the right panel of figure 4. The total energy of the carbon crystal gradually decreases, indicating the enhanced stability in the transformation from n-diamond to diamond. Therefore, our present experimental and theoretical results suggest a possible transformation mechanism from sp$^2$ graphite to sp$^3$ diamond through n-diamond as an intermediate state. Indeed, our experiments

Figure 3. Relative total energy per atom versus lattice constant for the n-diamond crystal structure with fixed space group and internal coordinates from experiments.
show that the existence of the Fe catalyst is crucial for the synthesis of n-diamond. It is noteworthy that the lattice constant ($\sim$3.65 Å) [29] of the cubic $\gamma$-Fe (iron at high temperature) is close to that of diamond and n-diamond. Thus we suspect that the $\gamma$-Fe as catalyst serves as seeds for growth of n-diamond from sp$^2$ carbon, which helps the sp$^2$ carbon overcome the energy barrier and reach the intermediate n-diamond state. In other words, the existence of the $\alpha$-Fe catalyst might lead to some local minimum in the energy curve, in particular for the nanoparticles synthesized.

We have also investigated electronic structures of the n-diamond. Our calculations show that the n-diamond is a good conductor with substantial density of states at the Fermi level, consistent with our own observation and the experimental results by others [14, 15]. Thus it might be used as electromagnetic absorption materials. Our preliminary experiments show promising performance in microwave absorption of the synthesized n-diamond samples in X and Ku bands. The details will be presented elsewhere.

4. Conclusion

To summarize, powder samples of n-diamond in macroscopic amount have been synthesized and their structural properties were characterized using the least-squares refinement method and XRD pattern simulation. The crystal structure of n-diamond was determined as a $R3$ space group with a lattice parameter $a = 3.58$ and $\alpha = 90^\circ$. DFT calculations further suggest that n-diamond is an intermediate state between diamond and graphite. The excellent metallicity of n-diamond from electronic structure calculations implies application as an electromagnetic absorption material.
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