Peer Review File

Manuscript Title: Synthesis of Paracrystalline Diamond

Redactions – Third Party Material

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

This paper reports on the synthesis of approximately one nanometer in diameter diamond crystals from C60 fullerene at a pressure of 30 GPa and temperature range of 1200-1800 K. The synthesized material is transparent to visible light and is termed as para-crystalline diamond. The authors have characterized the temperature range for synthesis of this material as going to lower temperature increases the sp2 or graphitic bonded carbon and going to higher temperature gives rise to well-known nanocrystalline diamond material. The authors have presented very intensive structural characterization and molecular dynamics simulations of this material, however, there are some unresolved issues with this manuscript.

(1) The authors indicate that "para-crystalline" content of their sample is limited to a maximum of 70%. It might be beneficial to indicate to a general reader on the remaining 30% whether the remaining carbon content is amorphous diamond.

(2) The Raman spectrum shows a significant rising background fluorescence with increasing wavelength in the material. Generally, in a wide band-gap material like diamond, the fluorescence is attributed to inclusion of impurities or defects in the lattice. It might be useful to include optical transmission and fluorescence data on millimeter size crystals that have been synthesized.

(3) The Youngs modulus and shear modulus of "para-crystalline" diamond is claimed to be superior to that of crystalline diamond. Such claims need to be substantiated by presenting error bars and providing side-by-side evaluation of both materials in Vickers hardness and nanoindentation testing. Ultrasonic determination of elastic constants of the synthesized material could strengthen the argument about superior mechanical properties.

(4) The changes in simulated structure factor S(Q) show very subtle differenced between p-d and a-D. Is there enough confidence in experimental measurements to observe these subtle differences. A direct experimental comparison of S(Q) for p-d and a-D might clarify the situation.

Referee #2 (Remarks to the Author):

The authors conducted both lab experiments and theoretical calculations to investigate the formation and physical properties of paracrystalline diamond at high pressure and temperature. Fullerene (C60) was used as the staring sample for the synthesis of the paracrystalline diamond at high pressure and various high temperatures. The recovered samples were characterized by a series of techniques and theoretical calculations are used to reveal the nature of the paracrystalline diamond.

Overall, the paper is well presented and quality of the research results is high. When I read the paper, my first reaction was that the authors were doing something similar to what Irifune et al. investigated. And, they would have cited and discussed nanopolycrystalline diamond (NPD) reported by Irifune et al. (Nature, 2003 and many other follow-up studies). Surprisingly, they did not even cite the paper and of course no comparison to this important work in the field. The authors focused on comparing their results to a-D (amorphous diamond instead). Without this, it's

difficult for me to judge the novelty of the study further. My own understanding is that the parapolycrystalline diamond is similar to polycrystalline diamond in nano scales.
Another key issue the authors should address is the kinetics and starting samples in their experiments. Their results as a function of temperature indicate that kinetics plays a major role in the formation of the nanocrystalline structures. Along this line of thought, starting sample which is fullerene here can also play a major role. It would be much more insightful if the authors use various starting carbon materials in their experiments to address this issue.

Referee #3 (Remarks to the Author):

This manuscript is a very interesting proposition in which the authors show that they have identified the structure of an sp3 carbon paracrystal consisting on sub-nm mixture of paracrystallites of hexagonal-diamond and cubic-diamond. They present this composite crystal as a "paracrystal", i.e., a material exhibiting short range organization and lacking long order organization. They call this material "Paracrystalline diamond", p-D and they entitle they article "Synthesis of Paracrystalline Diamond". This is up to my knowledge the first presentation of a paracrystalline sp3 carbon material and opens the path for the investigation of other forms of paracrystalline sp3 carbon, which may be materials exhibiting superior mechanical or stability properties to diamond. I think that this is a high quality work which will be of interest to a broad scientific community working on carbon materials, hard materials or science under extreme conditions. I do recommend the publication of this work after considering a number of questions and suggestions, listed below, which can contribute to further improve the quality of this work.

1) The material synthesized by the authors is certainly a paracrystal and I consider that the title chosen by the authors is fear. Nevertheless, the material they have obtained is not the only possible "paracrystalline diamond" and needs to be better described as one form of a new family of paracrystalline diamond materials. In fact, the authors need to estimate from their experimental TEM images and from their simulated structure the % of atoms in each one of the 3 components of the sp3 structure: cubic-diamond paracrystallites/ hexagonal-diamond paracrystallites/ amorphous-diamond (C % , H %, A%) . This information contributes, in addition to all other characterizations done by the authors, to describe the paracrystalline diamond phase that they have obtained. In fact there can be an infinity of forms of paracrystalline diamond obtained by changing the values of (C % , H %, A%) which may be reached by modifying the thermodynamic path, changing the precursor material, etc. This is an important point which deserves to be made clear. In fact, hardness, transparency or other physical properties may depend on the exact values of (C % , H %, A%) in p-D, as well as on the size of the paracrystallites. Underlining these points will certainly participate to stimulate the research on this area and to increase the impact of the author's work.

2) Fig. 1 shows that the synthesis of that C%H%A% p-D from C60 at 30 GPa is bounded in a temperature domain 1400 <T< 1800 K. I suggest that this is clearly stated in the manuscript.

3) To avoid any misinterpretation, I strongly advice the authors to better precise the synthesis conditions in the "Sample synthesis" part of methods:
- Please provide pressure values used for the pre-compression of the samples into Pt capsules. - Please precise how was done the compression up to 30 GPa : compression rate (GPa/s) and temperature at which the compression was done (300 K ?).

4) Lines 81 to 83. Sentence "Previous investigations ... and high temperatures[23-26]". I really suggest to include as reference the recent review work by B. Sundqvist [B. Sundqvist, Physics Reports, 909, 1 (2021)]

5) The p-D obtained by the authors shares many physical characteristics with the material

obtained in [Z. Zeng et al,. Nat. Commun. 8 (2017) 322] (some common authors with the present work) by laser heating treatment of glassy carbon: density, transparency, shoulder in the second peak of the S(q), EELS spectra. Unfortunately, in that work the HRTEM images were less resolved that in the present one. This should be discussed. Z. Zeng et al interpreted the obtained material as amorphous sp3 carbon (amorphous diamond). Could the authors discuss if, in view of the results presented in the present work, the sp3 carbon obtained by Z. Zeng may be interpreted or not now as a paracrystal?

6) Line 120. More details on the measure of the inclusive angles should be given, as number of measured crystals (all this can be given in the "Methods"). The authors measured inclusive angles should be given with errors bars or indication of their spread (visible in Fig. 2). I think that it will be useful to indicate the estimated strain on the paracrystallites which could be associated to the measured angles.

7) In Fig.3 the authors write "d, Structural model of p-D with 70% paracrystals". They should replace "paracrystals" by "paracrystallites". A paracrystal (the material the authors have synthesized and that they are studying) is made of paracrystallites embedded in an amorphous matrix.

8) Line 176. The authors should mention that the orientational correlation function definition can be found in the "Methods" section.

9) In lines 233 to 238 the authors present their hardness measurements and compare them with others forms of diamond. I really suggest to include a table of measured/calculated hardness in the Extended data comparing their results with other sp3 carbons including NPD (nano polycrystalline diamond) or carbon clathrates [X. Blase et al. Phys Rev Lett 92, 215505 (2004)]

10) In line 241 a reference is lacking after "NPD".

11) I strongly recommend to the authors to mention, as a perspective, that the known phase transformation of single-wall carbon nanotubes to diamond [A. Merlen et al, Carbon 47, 1643 (2009)] makes carbon nanotubes another path for the elaboration of new types of diamond paracrystals. This provides further research perspectives to their work increasing its impact.

12) Extended Data. Figure 9 legend. Please precise that the Raman experiment was done without pressure transmitting medium. The broad Raman peaks obtained at high pressure can be related to the non-hydrostatic conditions. I do not understand how the authors can then infer from these very broad Raman peaks that a polymerization or any buckyball deformation can be inferred. The sentence "suggesting polymerization and deformation of buckyballs" is not supported by the Raman data. They may not be in contradiction, but this will need to be demonstrated. Please modify the legend consistently.

Prof. Alfonso San-Miguel
University of Lyon, France

Referee #4 (Remarks to the Author):

This paper reports synthesis of paracrystalline diamond. The term "paracrystal" has been introduced in 1930s and has been occasionally used, but here paracrystalline state is found quite convincingly.
Before the paper can be published, I would like the authors to characterize the properties of their material properly (ideally both through experiment and ab initio calculations): the density, bulk modulus, shear modulus, Young's modulus, hardness, fracture toughness. Currently, only shear

and Young's moduli are reported - I find the values unconvincing and lacking proper explanation of how they were obtained and what the error bars are.

Author Rebuttals to Initial Comments:

Referee #1 (Remarks to the Author):

This paper reports on the synthesis of approximately one nanometer in diameter diamond crystals from C60 fullerene at a pressure of 30 GPa and temperature range of 1200-1800 K. The synthesized material is transparent to visible light and is termed as para-crystalline diamond. The authors have characterized the temperature range for synthesis of this material as going to lower temperature increases the sp2 or graphitic bonded carbon and going to higher temperature gives rise to well-known nanocrystalline diamond material. The authors have presented very intensive structural characterization and molecular dynamics simulations of this material, however, there are some unresolved issues with this manuscript.

(1) The authors indicate that "para-crystalline" content of their sample is limited to a maximum of 70%. It might be beneficial to indicate to a general reader on the remaining 30% whether the remaining carbon content is amorphous diamond.

Reply: We thank the referee for the constructive comment. In the revised manuscript, we have explicitly pointed out that the remaining 30% carbon content belongs to amorphous diamond (page 5).

(2) The Raman spectrum shows a significant rising background fluorescence with increasing wavelength in the material. Generally, in a wide band-gap material like diamond, the fluorescence is attributed to inclusion of impurities or defects in the lattice. It might be useful to include optical transmission and fluorescence data on millimeter size crystals that have been synthesized.

Reply: To check the possible origin of the high background in the Raman spectra of p-D (Fig. 1c), we collected fluorescence spectra of the sample synthesized at 1600 K and 30 GPa. A significant fluorescence excitation is seen around 702 nm. We thus confirm that the significant rising background fluorescence with increasing wavelength is due to the fluorescence effect. We have now added the fluorescence spectrum of the sample synthesized at 1600 K in Extended Data Fig. 2 to justify the rising background of the Raman spectroscopy of p-D.

As the referee pointed out, the fluorescence in diamond is caused by impurities or defects in the lattice. The fluorescent nanodiamonds, with either foreign atom impurities or lattice imperfections, are well studied (e.g. *JACS* (2005): 17604-17605; *Adv. Mater.* (2010): 843-847). The fluorescence spectrum of p-D, however, shows quantitative differences from that of nanodiamonds, which may be attributed to many factors, such as, disordered structure (amorphous domains/boundaries and paracrystalline distortions), carbon vacancies in the clusters, and other defects. Because of the pronounced fluorescence signal of p-D, it seems rather useful to explore its applications in relevant fields such as biotechnology (*Nature Nano.* (2008): 284-288).

(3) The Youngs modulus and shear modulus of "para-crystalline" diamond is claimed to be superior to that of crystalline diamond. Such claims need to be substantiated by presenting error bars and providing side-by-side evaluation of both materials in Vickers hardness and nanoindentation testing. Ultrasonic determination of elastic constants of the synthesized material could strengthen the argument about superior mechanical properties.

Reply: In order to solidify our conclusions on the mechanical properties of p-D, we carried out more rigorous nanoindentation measurements, so that a direct side-by-side comparison between p-D and natural diamond was made available. Our new nanoindentation data was calibrated with natural diamond, which, to the best knowledge of the authors, was seldomly done in the nanoindentation literature. Our new mechanical data reveals that the hardness of p-D is comparable with natural diamond, but the Youngs modulus is slightly lower. The results are consistent with our *ab initio* modelling of the mechanical properties of p-D. For the experimental mechanical properties, error bars are now included in revised Extended Data Fig. 12. In the same revised figure, we also added a summary of the calculated and experimental hardness for typical full sp^3 carbons, e.g. p-D, diamond, hexagonal diamond, carbon clathrates, NPD and nanotwinned diamond (NTD).

In addition to nanoindentation and Vickers hardness, we strived to employ other techniques to validate the as-determined mechanical properties of p-D, as suggested by the referee. More specifically, we have engage the pulse-echo ultrasonic and Brillouin scattering techniques. To this end, we synthesized millimeter-sized p-D at 1600 K and 30 GPa to achieve better sample quality. However, due to large internal stress accumulated in the sample during recovery, despite our best effort, microcracks were still present in the end product, which prevents us from obtaining reliable and consistent mechanical data using both techniques. Since our work involves unprecedentedly high pressure for mm-sized sample synthesis, we aim to optimize our experimental protocols in the future such that monolithic samples can be obtained to enable reliable ultrasonic and Brillouin scattering determination of the mechanical properties of p-D.

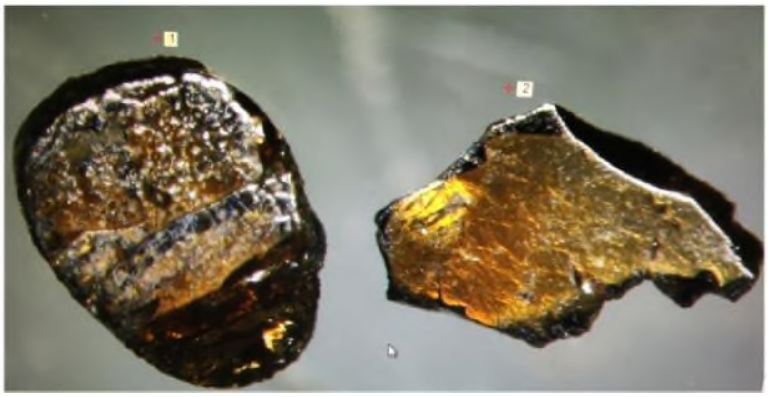

Figure R1. Optical micrographs (taken without backlight) showing the morphology of p-D samples synthesized at 1600 K and 30 GPa. Microcracks were found in the recovered samples.

(4) The changes in simulated structure factor S(Q) show very subtle difference between p-d and a-D. Is there enough confidence in experimental measurements to observe these subtle differences? A direct experimental comparison of S(Q) for p-d and a-D might clarify the situation.

Reply: We have great evidence that the subtle differences between the structure factors of p-D and a-D have been experimentally captured. Firstly, as shown in Fig. 2b of the main text, the changes of the structure factor of p-D with increasing volume fraction of paracrystallites show quantitively the same trend as the theoretical prediction.

To more clearly demonstrate the experimental differences of S(*Q*) for p-D and a-D, in Fig. R2 we present the experimental S(*Q*) of a-D and p-D (47.1% paracrystals) synthesized at 1500 K. The experimental S(*Q*) of a-D was provided by the authors of the article “Synthesis of quenchable

amorphous diamond" (Zeng, Z. *et al. Nat. Comm.* **8**, 322 (2017).). The hallmark feature differentiating p-D from a-D is the relative intensity of the first peak with respect to the second peak. One can clearly see that, for a-D, the intensity of the first peak is lower than that of the second peak (as marked by the red dashed line in Fig. R2c), whereas for p-D, a reverse trend is observed. In the main text, however, the experimental S(Q) of a-D was not directly included mainly because a different technique (laser heating in a diamond anvil cell) was used for the synthesis of a-D. Consequently, the optimization of the S(q) of a-D became highly challenging due to a much more involved background removal process as well as a limited q-range, which may lead to uncertainties in the shape of the optimized structure factors. By comparison, the structure factors obtained from our bulk p-D samples in this work have higher quality.

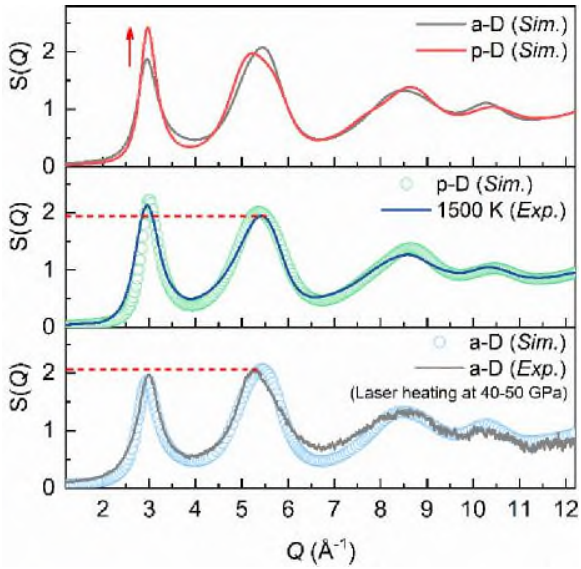

Figure R2. Comparisons of the structure factors of p-D and a-D. The experimental data for a-D was obtained from a different technique employing laser heating in a diamond anvil cell.

Referee #2 (Remarks to the Author):

The authors conducted both lab experiments and theoretical calculations to investigate the formation and physical properties of paracrystalline diamond at high pressure and temperature. Fullerene (C60) was used as the staring sample for the synthesis of the paracrystalline diamond at high pressure and various high temperatures. The recovered samples were characterized by a series of techniques and theoretical calculations are used to reveal the nature of the paracrystalline diamond. Overall, the paper is well presented and quality of the research results is high.

Reply: We thank the referee for the positive assessment of our results.

Comment A: *When I read the paper, my first reaction was that the authors were doing something similar to what Irifune et al. investigated. And, they would have cited and discussed nanopolycrystalline diamond (NPD) reported by Irifune et al. (Nature, 2003 and many other follow-up studies). Surprisingly, they did not even cite the paper and of course no comparison to this important work in the field. The authors focused on comparing their results to a-D (amorphous diamond instead). Without this, it's difficult for me to judge the novelty of the study further. My own understanding is that the parapolycrystalline diamond is similar to polycrystalline diamond in nano scales.*

Reply: We thank the referee for pointing out the pioneering work by Irifune and coworkers on the formation of nanopolycrystalline diamond (NPD), which is relevant to our discovery of paracrystalline diamond. We are sorry for missing out the paper. In the revised manuscript, we have cited the paper and made proper discussions in connection to our work.

In presenting the paracrystalline state of diamond, we put an emphasis on differentiating it from a-D mainly because it can be easily misinterpreted as a-D, for example, from the seemingly amorphous X-ray diffraction patterns and HRTEM images. Meanwhile, we were highly conscious of making clear distinctions between p-D and NPD as well (see, e.g., Extended Data Fig. 4). We demonstrated that our synthesized p-D consists of sub-nanometer-sized paracrystallites (0.5-1.0 nm) that are devoid of the LRO present in NPD (which has grain sizes typically greater than 5 nm). A tell-tale distinction between p-D and NPD lies in the degree of lattice distortion. The severe lattice distortion of p-D is on par with the grain boundary portion of the nano-grains of NPD (see discussions on page 5 of the main text and Extended Data Fig. 5). In a sense, the paracrystallites can be regarded as nanocrystals without "cores". The structural differences between p-D and NPD give p-D distinctive properties, such as Raman spectroscopy, thermophysical and mechanical properties.

Comment B: *Another key issue the authors should address is the kinetics and starting samples in their experiments. Their results as a function of temperature indicate that kinetics plays a major role in the formation of the nanocrystalline structures. Along this line of thought, starting sample which is fullerene here can also play a major role. It would be much more insightful if the authors use various starting carbon materials in their experiments to address this issue.*

Reply: Our line of thought aligns well with the referee's. In fact, we have considered different precursors to study the role of fullerene played in the formation of p-D and the details were presented in Extended Data 1.

More specifically, we compared fullerene, type-1 glassy carbon, and carbon onion as the starting material to study the possibility of p-D formation under the same experimental condition. In cases of

using type-1 glassy carbon and carbon onion as the starting material, crystallization precedes the complete conversion of sp^2 to sp^3 carbon at 30 GPa and 1400-1600 K, preempting the formation of fully sp^3-bonded p-D. Our experimental results demonstrate the importance of the structure of the starting material in the formation pathway of p-D. The formation mechanism p-D from fullerene was analyzed in great details in Extended Data Fig. 7-11 and Supplementary Note.

Referee #3 (Remarks to the Author):

This manuscript is a very interesting proposition in which the authors show that they have identified the structure of an sp3 carbon paracrystal consisting on sub-nm mixture of paracrystallites of hexagonal-diamond and cubic-diamond. They present this composite crystal as a "paracrystal", i.e., a material exhibiting short range organization and lacking long order organization. They call this material "Paracrystalline diamond", p-D and they entitle they article "Synthesis of Paracrystalline Diamond". This is up to my knowledge the first presentation of a paracrystalline sp3 carbon material and opens the path for the investigation of other forms of paracrystalline sp3 carbon, which may be materials exhibiting superior mechanical or stability properties to diamond. I think that this is a high quality work which will be of interest to a broad scientific community working on carbon materials, hard materials or science under extreme conditions. I do recommend the publication of this work after considering a number of questions and suggestions, listed below, which can contribute to further improve the quality of this work.

Reply: We thank Prof. Alfonso San-Miguel for his recognition of our work and insightful comments that help us to improve the paper. We have made necessary revisions following the suggestions.

1) Comment A: *The material synthesized by the authors is certainly a paracrystal and I consider that the title chosen by the authors is fair. Nevertheless, the material they have obtained is not the only possible "paracrystalline diamond" and needs to be better described as one form of a new family of paracrystalline diamond materials.*

Reply: In this work, we conceptually present the paracrystalline state of diamond. We agree with the referee that various forms of p-D exist, for example, with different types and compositions of crystalline MRO, contingent upon the starting material and synthesis condition. This was pointed out at the end of the revised manuscript (page 6) to help stimulate relevant research in this area.

1) Comment B: *In fact, the authors need to estimate from their experimental TEM images and from their simulated structure the % of atoms in each one of the 3 components of the sp3 structure: cubic-diamond paracrystallites/ hexagonal-diamond paracrystallites/ amorphous-diamond (C % , H %, A%). This information contributes, in addition to all other characterizations done by the authors, to describe the paracrystalline diamond phase that they have obtained. In fact there can be an infinity of forms of paracrystalline diamond obtained by changing the values of (C % , H %, A%) which may be reached by modifying the thermodynamic path, changing the precursor material, etc.*
This is an important point which deserves to be made clear. In fact, hardness, transparency or other physical properties may depend on the exact values of (C % , H %, A%) in p-D, as well as on the size of the paracrystallites. Underlining these points will certainly participate to stimulate the research on this area and to increase the impact of the author's work.

Reply: We agree with these comments. We believe that the three components of the sp^3 structure: CD-, HD-paracrystallites, and amorphous diamond in p-D can be controlled by changing the thermodynamic path (temperature, pressure, and annealing time), which determine the physical properties. Combining high-quality XRD and theoretical modelling, we were able to yield information about the percentage of paracrystallites in the as-obtained p-D (Fig. 3c) at different annealing temperatures. Computationally, our numerical analysis indicated that the volume ratio between CD-and HD-paracrystallites (Fig. 3d) is roughly 1.5:1.

To quantify the exact content of sub-nanometer-sized paracrystallites from TEM is rather tricky. We refrain from drawing firm conclusions from the TEM analysis alone. Experimentally, we attempted to use autocorrelation function (ACF) analysis, a statistical analysis of HRTEM images in real space, to evaluate the area fraction of paracrystallites. This technique has been used previously to analyze the content of ordered clusters in non-crystalline materials [Sarac, Baran, *et al*. *Nature communications* 9.1 (2018): 1-10; Fan, Guo-You, and J. M. Cowley. *Ultramicroscopy* 17.4 (1985): 345-355; Wang, Q., *et al*. *Scientific reports* 4.1 (2014): 1-5.]. Employing this method, we analyzed the images of the samples synthesized at 1400 - 1600 K (Fig. R3 a&b). The 1.0 x 1.0 nm^2 segmented regions were obtained from the original HRTEM images through an ACF process. If one-dimensional fringes or two-dimensional lattices were identified in a segmented cell, we say that this area has translational symmetry, suggesting locally ordered clusters. By this approach, we roughly estimate that the fractions of paracrystallites in the samples synthesized at 1400, 1500, and 1600 K are 25%, 46%, and 48%, respectively, which are close to the results (18.2%, 47.1%, and 52.4%) obtained from our computer simulation.

Nevertheless, it is more challenging to precisely distinguish cubic and hexagonal paracrystallites from the experimental TEM images. Although we were able to discern cubic-like or hexagonal-like lattices in some segmented regions (Fig. R3), a large number of frames contain only one-dimensional fringes that do not yield proper information of symmetry. To mitigate this problem, the state-of-the-art TEM technology (atomic electron tomography reconstruction method) recently developed by Yang *et al*. (*Nature* 592.7852 (2021): 60-64.) may offer better opportunities to separate the three components in p-D in the future.

In summary, we have experimentally estimated the ratio of paracrystallites and amorphous diamond in the samples through an ACF analysis and quantified the ratio of cubic-like and hexagonal-like paracrystallites in the theoretical model. The corresponding changes have been made in the seventh paragraph of the revised manuscript. Due to limited space, the details of the ACF analysis were not included in the manuscript.

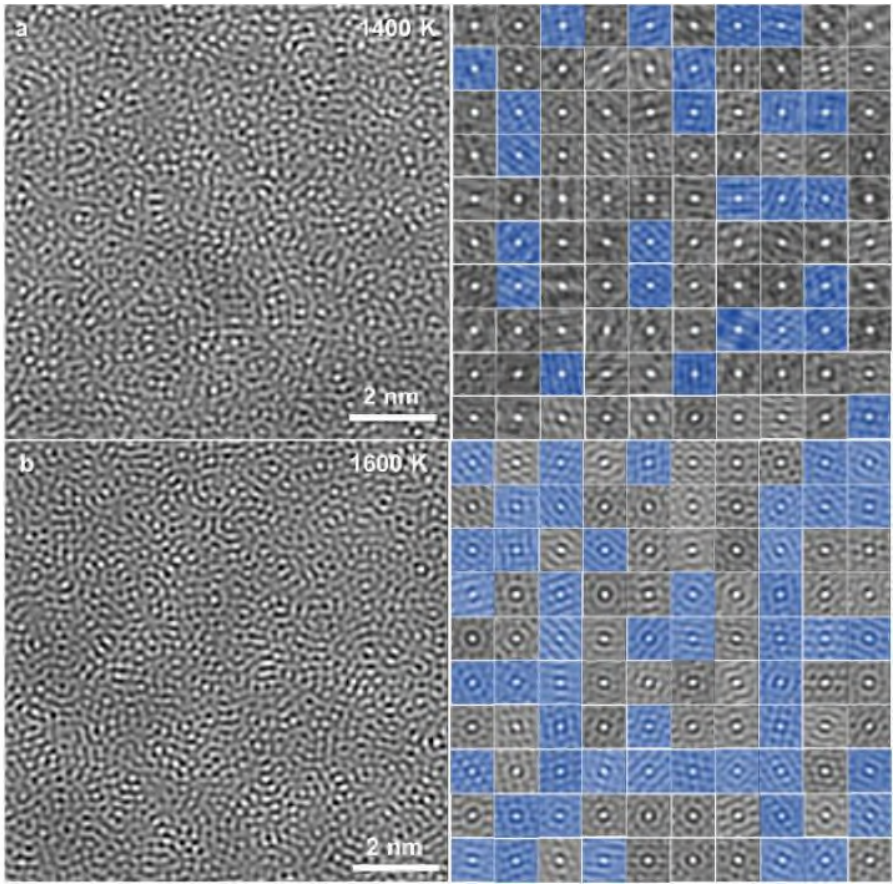

Fig. R3 a and b, HRTEM image and corresponding autocorrelation function (ACF)-processed images of samples synthesized at 1400 K and 1600 K, respectively.

2) Fig. 1 shows that the synthesis of that C%H%A% p-D from C60 at 30 GPa is bounded in a temperature domain 1400 <T< 1800 K. I suggest that this is clearly stated in the manuscript.

Reply: This has been explicitly stated in the revised manuscript (page 5).

3) To avoid any misinterpretation, I strongly advice the authors to better precise the synthesis conditions in the "Sample synthesis" part of methods:
- Please provide pressure values used for the pre-compression of the samples into Pt capsules. - Please precise how was done the compression up to 30 GPa: compression rate (GPa/s) and temperature at which the compression was done (300 K ?).

Reply: We have provided more details of the synthesis conditions in the revised manuscript.

4) Lines 81 to 83. Sentence "Previous investigations ... and high temperatures[23-26] ". I really suggest to include as reference the recent review work by B. Sundqvist [B. Sundqvist, Physics Reports, 909, 1 (2021)]

Reply: We have added the reference as suggested.

5) The p-D obtained by the authors shares many physical characteristics with the material obtained in [Z. Zeng et al,. Nat. Commun. 8 (2017) 322] (some common authors with the present work) by laser

heating treatment of glassy carbon: density, transparency, shoulder in the second peak of the S(q), EELS spectra. Unfortunately, in that work the HRTEM images were less resolved that in the present one. This should be discussed. Z. Zeng et al interpreted the obtained material as amorphous sp3 carbon (amorphous diamond). Could the authors discuss if, in view of the results presented in the present work, the sp3 carbon obtained by Z. Zeng may be interpreted or not now as a paracrystal?

Reply: Both p-D and a-D are fully sp^3-bonded and yield similar signals in structural characterization approaches (e.g, XRD, TEM, Raman spectroscopy, etc.). Nonetheless, the atomic arrangements in the two states are distinct from each other (see, e.g., Fig. 3d). This underlies the reason why the description of the atomic arrangements in amorphous materials has been an outstanding problem.

Concerning the sp^3 carbon obtained by Zeng *et al.*, our conviction is that it belongs to amorphous diamond. Leaving HRTEM images aside (because their HRTEM images are less resolved), the primary evidence comes from (a) the structure factor and (b) ab initio modeling. From the optimized structure factor (please refer to our reply to referee 1 as well as Fig. R2), it is found that the intensity of the first peak is lower than that of the second peak, which is a distinguishing feature of a-D. Moreover, the theoretical modeling that adopted a simulation protocol similar to the laser-heating experiment yields completely sp^3 bonded CRN type of carbon, i.e., amorphous diamond, which is different from the simulation results obtained in the present work.

6) Line 120. More details on the measure of the inclusive angles should be given, as number of measured crystals (all this can be given in the "Methods"). The authors measured inclusive angles should be given with errors bars or indication of their spread (visible in Fig. 2). I think that it will be useful to indicate the estimated strain on the paracrystallites which could be associated to the measured angles.

Reply: The inclusive angles shown in Fig. 2g&h were not a statistical mean from multiple paracrystallites, but instead correspond to the regions (presumably containing single paracrystallilltes) marked in Fig. 2e&f. The inclusive angles were directly measured between the strongest spots in the FFT image, associated with the inclusive angles of the crystal planes in the conspicuous paracrystallites in Fig. 2e&f. Our main purpose was to demonstrate (1) Paracrystallites have two different structural configurations (cubic-like and hexagonal-like), which agrees with our computational modelling and (2) Compared with the ideal crystal, the paracrystallites are structurally distorted.

We agree with the referee that the deviation of the inclusive angles reflects the strain on the crystals. However, the correlation between the "diffraction spots" and lattice distortion may concern many factors, for instance, the size of the paracrystallites and the atomic arrangements of surrounding paracrystallites, etc. We believe that more involved analytical methods, such as reverse Monte Carlo, can be developed to resolve this issue and would like to work on this in the future.

7) In Fig.3 the authors write "d, Structural model of p-D with 70% paracrystals". They should replace "paracrystals" by "paracrystallites". A paracrystal (the material the authors have synthesized and that they are studying) is made of paracrystallites embedded in an amorphous matrix.

Reply: We concur with the referee about the terminology of paracrystallite. In the revised manuscript, we have made necessary changes wherever appropriate.

8) Line 176. The authors should mention that the orientational correlation function definition can be found in the "Methods" section.

Reply: This has been indicated in the revised manuscript.

9) In lines 233 to 238 the authors present their hardness measurements and compare them with others forms of diamond. I really suggest to include a table of measured/calculated hardness in the Extended data comparing their results with other sp3 carbons including NPD (nano polycrystalline diamond) or carbon clathrates [X. Blase et al. Phys Rev Lett 92, 215505 (2004)]

Reply: We have added a table showing the experimental and calculated hardness of typical sp^3 carbon of p-D, diamond, hexagonal diamond, carbon clathrates, NPD and nanotwinned diamond (NTD), as a subgraph of the Extended data Fig. 12. Moreover, we have also added the fracture toughness K_{IC} of the p-D in Extended Data Fig. 12a, obtained by the indentation method [Huang, Quan, *et al. Nature* 510.7504 (2014): 250-253.]. The corresponding Methods section has been revised.

10)In line 241 a reference is lacking after "NPD".

Reply: Thanks for carefully reading our work. The onset oxidation temperature of NPD was actually measured in the present work, and we cited the reference for the NPD (~13 nm) used for this test.

Previously, Solozhenko *et al.* reported that the onset oxidation temperature of NPD is ~950 K (Solozhenko *et al. Advanced Materials, 2012, 24(12): 1540-1544.*). However, the heating rate (10 K/min) they selected is higher than that (5 K/min) in our research, which cannot be used as a reference. The onset oxidation temperature increases with increasing heating rate (Dallek, Steven *et al. Thermochimica acta* 192 (1991): 321-326.).

11)I strongly recommend to the authors to mention, as a perspective, that the known phase transformation of single-wall carbon nanotubes to diamond [A. Merlen et al, Carbon 47, 1643 (2009)] makes carbon nanotubes another path for the elaboration of new types of diamond paracrystals. This provides further research perspectives to their work increasing its impact.

Reply: We thank the referee for the insightful suggestion. Indeed, the bundled single-wall carbon nanotubes (SWCNT) with good orientations of carbon bonds have abundant and homogeneous sp^3 bonding under high pressure, which may serve as another precursor for the synthesis of p-D. This has been discussed in the revised manuscript (page 6).

12) Extended Data. Figure 9 legend. Please precise that the Raman experiment was done without pressure transmitting medium. The broad Raman peaks obtained at high pressure can be related to the non-hydrostatic conditions. I do not understand how the authors can then infer from these very broad Raman peaks that a polymerization or any buckyball deformation can be inferred. The sentence "suggesting polymerization and deformation of buckyballs" is not supported by the Raman data. They may not be in contradiction, but this will need to be demonstrated. Please modify the legend consistently.

Reply: It is possible that the broadening of the Raman peaks under high pressure was affected by the non-hydrostatic conditions. However, under hydrostatic conditions (with various types of pressure transmitting medium), Tolbert *et al.* reported similar behavior of Raman spectra of C_{60} as a function of pressure (*Tolbert et al. Chemical Physics Letters 188.3-4 (1992): 163-167.*) (see Fig. R4, for a

comparison between Tolbert's work and ours), suggesting that the non-hydrostatic pressure condition has a relatively weak influence on the changes of the Raman peaks.

On the other hand, by means of *in situ* X-ray diffraction and X-ray Raman scattering, Serebryanaya *et al.* and Kumar *et al.* demonstrated the polymerization and formation of sp^3 bonds of buckyballs under high pressure without pressure transmitting medium (Serebryanaya, N. R., *et al. Solid state communications* 118.4 (2001): 183-187; Kumar, Ravhi S., *et al. Diamond and Related Materials* 16.4-7 (2007): 1250-1253.), which is highly consistent with our experimental results. Thus, we believe that the changes of Raman profiles of C_{60} under high pressure is mainly due to the polymerization of buckyballs. We have revised the legend of Extended Data. Figure 9 to ensure enough clarity.

[Redacted Figure]

Fig. R4. (Left panel) Raman spectra of C_{60} under high pressure with pressure transmitting medium (methanol). (*Tolbert et al. Chemical Physics Letters 188.3-4 (1992): 163-167.*). **(Right panel)** *In situ* Raman spectra of C_{60} under compression (up to ~32 GPa) without pressure transmitting medium, conducted in this work.

Referee #4 (Remarks to the Author):

This paper reports synthesis of paracrystalline diamond. The term "paracrystal" has been introduced in 1930s and has been occasionally used, but here paracrystalline state is found quite convincingly. Before the paper can be published, I would like the authors to characterize the properties of their material properly (ideally both through experiment and ab initio calculations): the density, bulk modulus, shear modulus, Young's modulus, hardness, fracture toughness. Currently, only shear and Young's moduli are reported - I find the values unconvincing and lacking proper explanation of how they were obtained and what the error bars are.

Response: We are very grateful for the referee's recognition of our work. We have considered the reviewer's suggestions regarding the mechanical properties of p-D and conducted more experiments and *ab initio* simulation to address the deficiencies.

To ensure the credibility of the data, the mechanical properties are averaged from more than effective 5 tests. In the revised manuscript and Extended Data Fig. 12, we have added the error bars of all the tested values and revised the description about the data acquisition of mechanical properties in the "methods" section. We now present the experimental density, bulk modulus, shear modulus, Young's modulus, hardness, fracture toughness in the revised manuscript.

Computationally, we carried out DFT-based *ab initio* modelling to evaluate the bulk modulus and Youngs of p-D samples. To this end, the starting configuration was obtained from our classic MD simulation protocol stated in the Methods section, but with a smaller ensemble size (240 atoms). The as-obtained configuration was subject to isothermal annealing using VASP (30 GPa, 2000 K), followed by structural relaxation to ambient condition. The well-relaxed p-D configuration was then isotopically compressed at 0 K using the conjugate-gradient minimization method to obtain the pressure-volume relationship of p-D, from which the bulk modulus (387.4±2.7 GPa) of the p-D was estimated based on the third -order Birch equation of state. Likewise, a strain-stress curve of p-D was obtained in *ab initio* modeling by subjecting the system under uniaxial loading, from which the Youngs modulus (952.5±4.9 GPa) was obtained. The theoretical Youngs modulus and bulk modulus were provided in the table for comparison.

Experimentally, we presented the mechanical properties of Young's modulus E, shear modulus G and hardness in the original manuscript and Extended data Fig. 12. p-D has highly isotropous Vickers hardness H_V of 116.1±3.6 GPa and nanoindentation hardness H_N of 102.1±1.4 GPa, measured by both Vickers and Berkovich diamond indenters. The Young's modulus (E) was derived from the loading/unloading-displacement curves according to the Oliver-Pharr method [Oliver, *et al. J. Mater. Res.* **7**, 1564–1583 (1992).]. The shear modulus G (437.9±4.7 GPa) was derived through a formula $G = E/[2(1+\nu)]$, where the elastic modulus E (937.2±10.1 GPa) was experimentally measured (shown in b) and ν is the Poisson's ratio (0.07) of diamond.

We measured the bulk modulus K and fracture toughness K_{IC} of p-D. The bulk modulus K is 363.3±3.9 GPa, derived through a formula $K = E/[3(1-2\nu)]$. We evaluated the fracture toughness by indentation method at a large load of 9.8 N. An equation $K_{IC} = \frac{0.016(E/H_V)^{0.5}F}{C^{1.5}}$ was added in Methods for calculating the fracture toughness [Huang, Quan, *et al. Nature* 510.7504 (2014): 250-253.].

In revised Extended data Fig. 12, we compiled the calculated and experimental hardness of typical full sp^3 carbon of p-D, diamond, hexagonal diamond, carbon clathrates, NPD and nanotwinned diamond (NTD) for completeness.

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

The authors have addressed the four main issues in the earlier version of the manuscript regarding the composition of para-crystalline diamond, background fluorescence from defects/crystal imperfections, mechanical properties/elastic constants, and subtle differences in the x-ray derived structural information. The investigators have satisfactorily addressed most issues, however, crystalline quality does not allow for ultrasonic or optical scattering determination of elastic constants.

Referee #3 (Remarks to the Author):

The authors took into account all the referees' requests and answered the various questions and remarks. Their manuscript has gained in quality and I recommend its publication in Nature..

Referee #4 (Remarks to the Author):

I am satisfied with the current version of the manuscript and consider it acceptable for publication.

Artem R. Oganov