nature portfolio

Peer Review File

Optically-controlled phonon-specific phase transitions from graphite to diamond

Corresponding Author: Professor Sheng Meng

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This paper presents a computational study of the laser-driven structural transition of graphite to diamond. The authors use RT-TDDFT together with molecular dynamics to simulate the coupled electron-nuclear dynamics triggered by 50-fs laser pulses, and find that, if the laser fluence is sufficiently high (but not too high), graphite converts to the cubic or hexagonal diamond phase. About 30 trajectories are calculated, and a detailed analysis is provided in terms of the evolution of the band structure, the excited-state population, and the population and significance of various phononic states. From this, the authors conclude that there are realistic and achievable pathways towards purely optically controlled graphite-diamond transitions.

The topic of graphite-to-diamond phase transitions is an old and well-studied one, with an emphasis on high pressure and shock waves. Structural transformations via laser excitation are also a well-studied area in materials science. To my knowledge, a detailed theoretical study which explores concrete optical pathways for graphite-to-diamond seems indeed novel, and could be of significant interest in the sense of stimulating experimental research.

While I recognize that this is potentially interesting work, there are in my opinion significant problems with the analysis and interpretation of the results which prevent me from recommending publication.

1. The authors propose that the excited-state population distribution is dominated by two effects: Auger recombination and impact ionization. Auger recombination is an effect where electron-hole recombination energy gets transferred via Coulomb interactions to a third carrier, exciting it to a higher energy state. The ALDA does not capture Auger recombination since it is a many-body effect beyond the local approximation. Auger rates are typically obtained using Fermi's Golden Rule in the quasi-static case. However, Zhou, Lu and Prezhdo, Nano Lett. 21, 756 (2021) have shown that the Auger effect can also be incorporated into RT-TDDFT coupled with MD, but one needs to explicitly include Coulomb scattering matrix elements into the Hamiltonian. Therefore, based on ALDA-TDDFT results alone it is not possible to conclude that Auger recombination is responsible for the population of excited states shown in the instantaneous band structures in Fig. 3.

2. In that context, have the authors checked whether the total energy (electrons plus nuclei) is conserved (at least up to 400 fs, before the dissipation sets in)?

3. Also, the LDA gap of diamond is about 4.3 eV. The authors state that at 250 fs the gap is about 3.27 eV. Does the gap open up further after that?

4. Figure S4 shows the differential charge density, which is used by the authors to identify the formation of new bonds during the time evolution. A much better indicator of bond formation is the time-dependent electron localization functon(TDELF). Have the authors considered this quantity?

5. The authors then discuss the role of specific phonon excitations in the structural phase transition process. The phonons considered are those of the initial graphite structure. As the laser pulse hits the graphite, several of these phonon modes are excited. Figure 4 then shows how the projected intensity of the phonon modes grows over time, well into the second stage of the evolution (>160 fs). It is then discussed how the various phonon modes contribute to the structural change. In my opinion, this analysis is only meaningful in the early stages of the laser excitation, perhaps up until 50 fs or so. After that, the structure

of the system has changed so significantly that it makes no sense to project onto the graphite phonon eigenvectors, since the harmonic approximation would no longer be valid. In other words, it is fine to say that the laser triggers phonon modes corresponding to sliding and buckling motion, but once that motion goes towards a new structural phase, the phonon picture based on the initial phase is no longer meaningful. To see this, the projected phonon intensities in Fig. 4a should be expressed as amplitudes in units of the lattice constant or bond length, which would then show when the anharmonic regime would be reached.

6. Also, the authors mention phonon-phonon coupling, but no explicit illustration or analysis is given.

7. In the methods section, it is discussed how the time propagation up until 400 fs is done with the TDAP code using ALDA, and after 400 fs the CP2K package is used to do BO molecular dynamics based on the configuration and temperature at 400 fs, and using the BLYP functional. How can the authors be sure that these two methods match? Looking at Fig. 2b: the middle panel shows the buckling height Delta z, which is seen to decrease between 0.3 and 0.4 ps, but when the MD kicks in at 0.4 ps, Delta z suddenly increases. A similar behavior, although less pronounced, is seen in the other two panels of Fig. 2b. Are these artifacts of the computation? How much can the final relaxed state be trusted?

8. Lastly: the calculations are done using a 16-atom supercell. I can imagine that the computational effort that went into this paper was quite substantial. Nevertheless, this supercell seems quite small, given the massive structural changes that are being simulated here, where the system surely goes through various stages of disorder before reaching again an ordered phase. How can one be sure that the supercell size is adequate to capture this?

Reviewer #2

(Remarks to the Author)
This manuscript presents a compelling computational study of ultrafast, laser-induced phase transitions from graphite to diamond, utilizing state-of-the-art non-adiabatic molecular dynamics (NAMD) simulations. The authors propose that light-driven, phonon-specific mechanisms govern the selective formation of either cubic or hexagonal diamond under non-equilibrium conditions. The work is timely and relevant to the fields of laser-matter interaction, phase transformation, and sustainable materials synthesis, with potential implications for energy-efficient diamond production.
The manuscript is generally well-written, and the simulations appear to be thoughtfully designed. However, several points require further clarification and discussion before the manuscript can be recommended for publication.
1.Experimental Validation of Simulation Results (Fig. 2): The manuscript would benefit from a more in-depth discussion of how the simulated light-induced phase transition pathways align with existing experimental observations. Are there published time-resolved studies such as ultrafast electron diffraction, X-ray diffraction, or transient absorption data, that support the key transitions proposed in Fig. 2? Discussing these connections will enhance the credibility and experimental relevance of the simulations.
2. Phonon Mode Analysis and Raman Correlation (Fig. 4): The authors emphasize the role of specific phonon modes (e.g., B_3g_1) in driving the transition. It would be useful to discuss whether any ultrafast Raman spectroscopy studies (published or ongoing) support the appearance or evolution of such phonon modes under pulsed laser excitation. Can any characteristic Raman shifts be associated with the phonon activity simulated in Fig. 4?
3. Cubic vs. Hexagonal Diamond Formation Conditions (Fig. 5): Under static HPHT conditions, it is well-known that hexagonal diamond tends to form at lower temperatures than cubic diamond. In Fig. 5, the light-induced phase diagram is intriguing, but lacks clear guidance on which laser parameters (e.g., fluence, pulse duration) favor hexagonal over cubic diamond. For experimentalists, a clearer interpretation of how these regimes are defined and how to tune laser conditions to selectively promote one phase over the other would greatly increase the practical utility of the figure.
4. Clarification of Fig. S9: In the supplementary figure S9, the authors compare cases with Q = 0 and Q = 1. However, the text mentions Q = 0.75, which is not shown in the figure. Please clarify whether this case was simulated and if so, include it in the figure or explain its absence.
5.Line 39 – Temperature-Dependent CD vs. HD Formation: The sentence referencing the temperature relationship between cubic and hexagonal diamond (CD and HD) formation needs clarification. Please revise for accuracy and consider citing experimental studies that establish this relationship under equilibrium conditions for comparison.

Reviewer #3

(Remarks to the Author)
This is a great work, very impressive and opening the doors to the future where diamond and other materials could be synthesized using lasers. The paper should be accepted. However, I have several questions that I hope can be addressed:

1. What does 4% electronic excitation mean? 4 percent of 4 valence electrons per atom are excited?
2. Simulations are done for a single crystal of graphite with a particular orientation of the polarization plane of the laser with respect to the crystal. How do the results translate to a polycrystal of graphite? Will more fluency be needed?
3. Simulations are done in a small 16-atom cell. Can the authors estimate size effects? For once, diamond formation may be hindered by the interfacial energy. Other allotropes might appear too.
4. For cold compression of graphite, the easiest allotrope to form is M-carbon (Li 2009; Boulfelfel 2012). Other candidates included carbon, bct4 carbon and dozens of other hypothetical forms (see paper by Haiyang Niu). Can the authors comment on their possibility to occur as a result of laser irradiation?
5. I'm surprised that laser fluence monotonically decreases with wavelength. Surely this trend must break at some wavelength, otherwise very weak radiowaves would make diamond from graphite :)

6. After electrons are excited to 2-4 eV above Fermi level, they should eventually relax back to the ground state, releasing energy as either light or more likely heat. So one will have very hot diamond at ambient pressure. Won't it revert back to graphite? This is what hot diamond usually does at ambient pressure.

Artem R. Oganov

Reviewer #4

(Remarks to the Author)
This work has identified and is focussing on a timely and interesting topic. The authors use cutting-edge simulation techniques to compute electron dynamics and coupling of electron and phonons. In principle this work has the potential to be of interest to the audience of this journal, however, the current manuscript does not meet this standard. The work is exclusively computational and, while that itself is not a problem, the work does not rigorously address this scientific question.

First, I suggest the authors start by a schematic and quantitative figures that captures the relevant processes. This should estimate energies and time scales for the crucial steps that are relevant here. Are the initial and final states, as well as the pathways that connect both, quantitatively reasonable? At the same time, routes towards computational or experimental validation of the provided results are necessary.

Second, the simulation techniques and involved approximations come with error bars that are absent in this work. This needs to be explained and quantified, to better understand what is relevant and what is the accuracy in this work. The physics present and absent in these simulations, due to the used approximations, need to be explained. It also is necessary to connect these error bars to possible experimental validation of these simulations. The chosen pulse parameters in this work should be connected to experimentally achievable pulse parameters and discussed explicitly in the paper.

Third, I am wondering what technique is used to model electron-phonon coupling and how do the authors deal with the large difference in time scales between electrons and phonons.

Fourth, what is not clear to me is, is to which extent this work just presents a possible mechanism and what are other possible mechanisms. In real samples, many other effects contribute (defects, substrate, temperature, ...) and it is not clear to me, to what extent the idealized simulations here are providing a realistic picture that can be demonstrated in a real sample.

As it stands, I view the provided results as a proposal for a reaction mechanism, but that alone is not sufficient for the high standards of this journal.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have substantially revised their manuscript in response to four referee reports. I believe that the paper has been much improved, and I am overall satisfied with the response of the authors to my own questions and comments. I think the authors also did a good job with the other three referee reports.

One point remains, namely the issue of the ALDA's inability to properly describe the Auger effect. In the paper the authors just add the single short sentence "Since adiabatic TDDFT tends to underestimate the carrier-carrier interaction and the scattering rates in real systems to some extent^42, the real electron-electron scattering effects may be more pronounced than indicated by the present simulation results."

In their rebuttal, the authors have made a convincing case that their approach at least includes electron-electron scattering to some degree, for instance due to their use of a supercell, and mediation via lattice distortions. Also, they found evidence by tracking orbital occupations. I would like to suggest to the authors to include a couple of brief additional sentences in the paper where these arguments are explicitly discussed, to justify that the Auger mechanism can be invoked here in spite of using ALDA.

Apart from this, the paper is now ready to be accepted.

Reviewer #2

(Remarks to the Author)
The authors answered all of my questions, and I suggest accepting current version of the manuscript.

Reviewer #3

(Remarks to the Author)
I am satisfied with the responses of the authors and their revision.
The paper can be accepted now.

Artem R. Oganov

Reviewer #4

(Remarks to the Author)
The authors provided thoughtful answers to all reviewer questions. These answers, in particular those that connect the computational simulations and experiment, maintain my concern that the paper studies an interesting mechanism, but does not provide strong enough evidence that the simulations indeed study the previously reported situations. The conditions studied in this work are, in my opinion, far from experimentally achievable situations. The excitation of 4% seems huge, compared to what can be expected in experiment, without vaporizing the sample, if it can be achieved over significant volume (or surface) of the sample. Again, I think this is a very interesting model study, but it does not strongly enough connect experiment and theory and, thus, should be reported in a more specialized journal.

RESPONSES TO THE REVIEWER COMMENTS

First of all, we would like to express our gratitude to all the four reviewers for valuable comments, which are very helpful for us to further improve the quality of the manuscript. We are also very pleased that all the four reviewers recognize the significance and high quality of our work. The reviewer's comments are listed, followed by our responses and changes made in the revised manuscript.

Reviewer #1 (Remarks to the Author):

This paper presents a computational study of the laser-driven structural transition of graphite to diamond. The authors use RT-TDDFT together with molecular dynamics to simulate the coupled electron-nuclear dynamics triggered by 50-fs laser pulses, and find that, if the laser fluence is sufficiently high (but not too high), graphite converts to the cubic or hexagonal diamond phase. About 30 trajectories are calculated, and a detailed analysis is provided in terms of the evolution of the band structure, the excited-state population, and the population and significance of various phononic states. From this, the authors conclude that there are realistic and achievable pathways towards purely optically controlled graphite-diamond transitions.

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1. The authors propose that the excited-state population distribution is dominated by two effects: Auger recombination and impact ionization. Auger recombination is an effect where electron-hole recombination energy gets transferred via Coulomb interactions to a third carrier, exciting it to a higher energy state. The ALDA does not capture Auger recombination since it is a many-body effect beyond the local approximation. Auger rates are typically obtained using Fermi's Golden Rule in the quasi-static case. However, Zhou, Lu and Prezhdo, Nano Lett. 21, 756 (2021) have

shown that the Auger effect can also be incorporated into RT-TDDFT coupled with MD, but one needs to explicitly include Coulomb scattering matrix elements into the Hamiltonian. Therefore, based on ALDA-TDDFT results alone it is not possible to conclude that Auger recombination is responsible for the population of excited states shown in the instantaneous band structures in Fig. 3.

Author reply: We thank the reviewer for raising this important and insightful question. We agree with the reviewer that TDDFT calculations with conventional exchange-correlation functionals (*e.g.* ALDA) cannot perfectly describe the electron-electron scattering process. The approximate exchange-correlation functional may affect excitation energies and charge transfer rates. Compared to the actual situation, *ALDA*-TDDFT tends to underestimate the scatterings and energy transfer in real systems to some extent, as elucidated by Zhou, Lu and Prezhdo in Nano Lett. 21, 756, (2021). However, since we adopted the supercell calculations based on the multiple k points, some of the electron-electron scattering effects are naturally included in the localized regime due to the folding of k points. Moreover, electron-electron scattering mediated by the presence of lattice distortion (or virtual phonons) is also nicely incorporated in the present computational scheme. Therefore, while being fully respectful to the reviewer's comments, we do believe that Auger process can be approximately tracked in the present simulation settings as shown in Fig. 3c.

In details, we analyzed the variation of charge carrier occupancy corresponding to each molecular orbitals during the photo-induced phase transition process. Fig. 3c presents the temporal evolution of the distribution of the photogenerated charge carriers within each orbital, which indicates a small fraction of photoexcited electrons is indeed scattered to high-energy orbitals during evolution of electron wavefunction. Such an increasing charge carrier distribution in high-energy orbitals can be understood with Auger recombination, where the excess energy released by electron-hole recombination scatters electrons to higher energy levels. We further emphasize that the focus of this work is to provide insights into the electronic driving forces underlying the graphite-to-diamond phase transition, rather than to quantitatively describe the Auger scattering and fully reproduce the corresponding experimental results. Previous study in Faraday Discuss. 224, 382 (2020) has also illustrated that when the natural occupation numbers remain close to their initial values, ALDA yields reasonably accurate electron density evolution.

We have incorporated further discussions on this point in the revised manuscript:

"Since adiabatic TDDFT tends to underestimate the carrier-carrier interaction and the scattering rates in real systems to some extent[42], the real electron-electron scattering

effects may be more pronounced than indicated by the present simulation results." (Main text page 8)

2. In that context, have the authors checked whether the total energy (electrons plus nuclei) is conserved (at least up to 400 fs, before the dissipation sets in)?

Author reply: We thank the reviewer for this good suggestion. Indeed, we have checked that during the application of the Gaussian light field, the total energy of the system oscillates and exhibits an overall increase, corresponding to the injection of laser energy into the system. After the end of light field irradiation, the total energy of the system remains essentially constant, with only a small drifting (~0.0002 eV/fs per atom), due to the accumulation of numerical errors. We have verified that this drift diminishes if an even smaller timestep is used.

We have added the following information in the Methods in the revised manuscript:

"After the end of light field irradiation, the total energy of the system remains essentially constant, with only a slight drifting of ~0.0002 eV/fs per atom caused by the accumulation of numerical errors." (Main text page 15)

3. Also, the LDA gap of diamond is about 4.3 eV. The authors state that at 250 fs the gap is about 3.27 eV. Does the gap open up further after that?

Author reply: Yes, we have checked that the diamond structure, following the 8-ps-long dynamical evolution, exhibits a further widened band gap of 3.63 eV. This structure is a diamond-like structure formed by the relaxation of a metastable excited-state phase-transition structure to 300 K (room temperature), and its band structure properties can be compared with those of the perfect cubic diamond at 0 K, as shown in Fig. 1R.

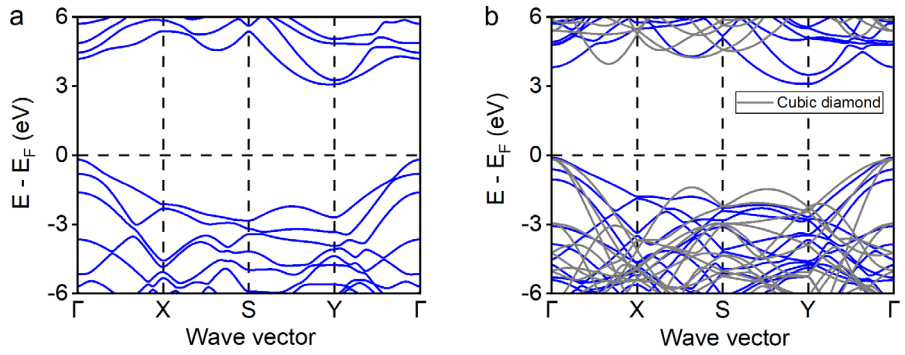

Fig. R1. Band structure of atomic structure (**a**) at 250 fs, and (**b**) at 8 ps, compared with that of cubic diamond.

We have shown the Fig. R1 in the insets of Fig. 2a in the revised manuscript, and added the following statements:

"As shown in Fig. 2a, through the annealing relaxation, the metastable sp^3-hybridized carbon lattice further evolves into a stable CD crystal structure, exhibiting a band gap that is further widened to 3.63 eV, and its electronic band structure can be directly compared with that of perfect CD." (Main text page 5)

4. Fig. S4 shows the differential charge density, which is used by the authors to identify the formation of new bonds during the time evolution. A much better indicator of bond formation is the time-dependent electron localization function(TDELF). Have the authors considered this quantity?

Author reply: We appreciate the valuable suggestion. Electron localization function (ELF) is a widely used analytical method for identifying chemical bond formation, serving to characterize electron localization and elucidating bonding details. We now performed new calculations of the ELF at the corresponding time points using the wavefunctions extracted from the non-adiabatic evolution in TDDFT simulations. The results successfully capture the transition of chemical bonding from sp^2 to sp^3 hybridization, as illustrated in the Fig. R2.

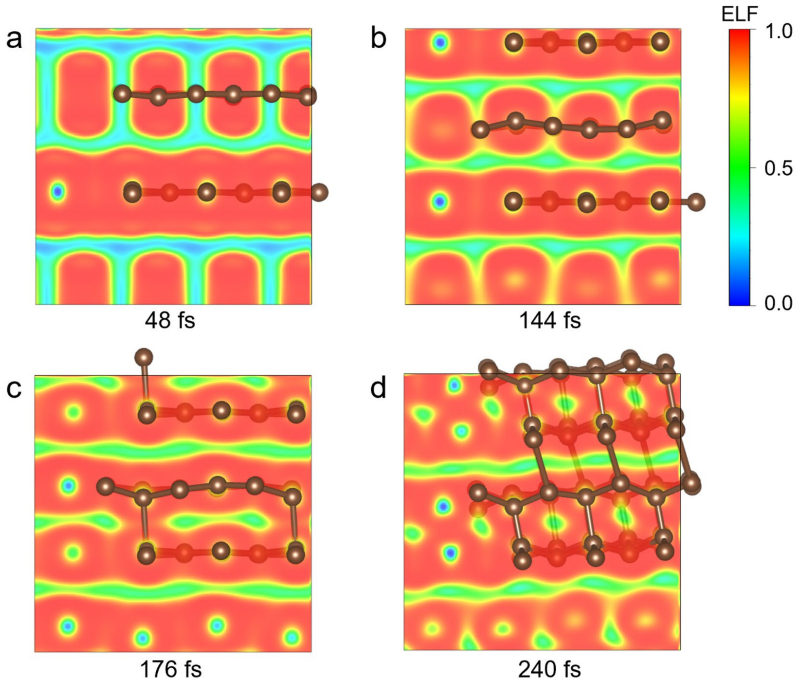

Fig. R2. Time-dependent electron localization function (TDELF) analysis at (a) 48 fs, (b) 144fs, (c) 176 fs and (d) 240 fs during the phase transition process.

We have added the following discussion in the revised manuscript and put Fig. R2 as Fig. S4 in the Supplementary Information (SI):

"The analysis of time-dependent electron localization function and differential charge density, as shown in Fig. S4 and S5, provide further electronic evidence for the formation of sp^3 bonds." (Main text page 6)

5. The authors then discuss the role of specific phonon excitations in the structural phase transition process. The phonons considered are those of the initial graphite structure. As the laser pulse hits the graphite, several of these phonon modes are excited. Fig. 4 then shows how the projected intensity of the phonon modes grows over time, well into the second stage of the evolution (>160 fs). It is then discussed how the various phonon modes contribute to the structural change. In my opinion, this analysis is only meaningful in the early stages of the laser excitation, perhaps up until 50 fs or so. After that, the structure of the system has changed so significantly that it makes no sense to project onto the graphite phonon eigenvectors, since the harmonic approximation would no longer be valid. In other words, it is fine to say that the laser triggers phonon modes corresponding to sliding and buckling motion, but once that motion goes towards a new structural phase, the phonon picture based on the initial phase is no longer meaningful. To see this, the projected phonon intensities in Fig. 4a should be expressed

as amplitudes in units of the lattice constant or bond length, which would then show when the anharmonic regime would be reached.

Author reply: (1) First, we fully agree with the reviewer's opinion on phonon projection. During a phase transition involving significant structural changes, projecting (atomic motion) onto the phonon modes of the initial phase may not rigorously characterize the phonon coupling throughout the entire process. We chose to project onto the phonon eigenvectors of graphite is because this approach provides a continuous picture for analyzing the excitation and evolution behaviors of phonons, intuitively reflects the deviation of phonons from their equilibrium positions, and qualitatively describes the relative excitation stage and extent of different phonon modes. (2) Following the suggestion of the reviewer, we have also calculated the average atomic displacement $\langle \Delta r \rangle$ of the four primarily excited phonon modes at Γ point along the polarization vector direction and presented their time evolution behaviors in Fig. R3. Similar behaviors to that observed in the phonon projection plot have been observed, see Fig. R3.

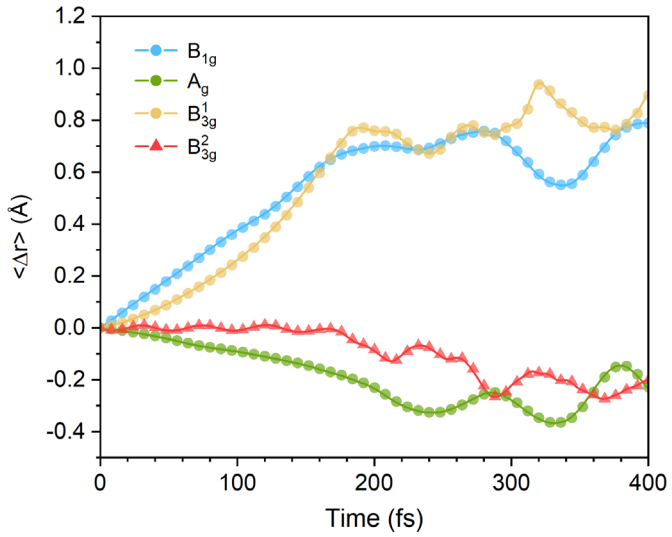

Fig. R3. Time evolution of the four primarily excited phonon motions at Γ point during the graphite phase transition to cubic diamond. $\langle \Delta r \rangle$ represents the average atomic displacement of each phonon mode along the polarization vector direction.

We have added the following discussion in the revised manuscript and Fig. R3 in the SI as Fig. S10:

"The average atomic displacement $\langle \Delta r \rangle$ of the above four primarily excited phonon modes at Γ point is also calculated and presented in Fig. S10, to further demonstrate the lattice dynamics and anharmonicity during the excitation and phase transition process

in real space. Similar behaviors to that observed in the phonon projection plot have been observed, see Fig. S10." (Main text page 10)

6. Also, the authors mention phonon-phonon coupling, but no explicit illustration or analysis is given.

Author reply: We thank the reviewer for pointing out this issue. Quantitative analysis of phonon-phonon coupling would facilitate a deeper understanding of the specific interactions between phonons. We have now calculated the potential energy surfaces (PES) of B_{3g}^2 mode (Fig. R4), under the condition that different B_{3g}^1 mode displacements are present, which effectively reflects the coupling between different phonon modes. The results shows that a small displacement of the B_{3g}^1 mode has negligible effect on the PES of B_{3g}^2, whereas strong mode excitation of B_{3g}^1 lead to significant changes in the PES. As revealed by the dynamic simulations in this work, the B_{3g}^2 mode is not directly excited during the action of light, but rather being gradually activated on a timescale of tens of femtoseconds after the laser irradiation. Consequently, its excitation mechanism neither involves direct coupling with the optical field nor arises directly through electron-phonon couplings. Instead, it is induced through phonon-phonon coupling after certain phonons (*e.g.* B_{3g}^1) have been excited to a specific intensity.

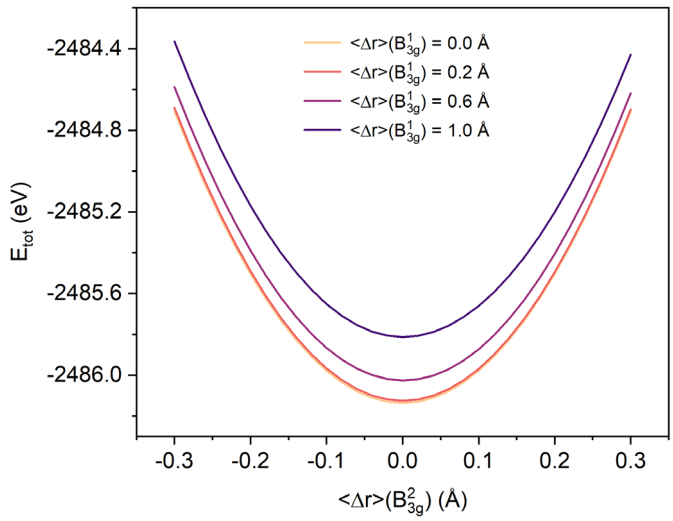

Fig. R4. Potential energy surfaces of B_{3g}^2 mode, corresponding to different displacements $\langle \Delta r \rangle$ of B_{3g}^1 mode. $\langle \Delta r \rangle$ denotes the average displacement of all atoms along a specific phonon mode.

We have added the following discussion in the revised manuscript and Fig. R4 in the SI as Fig. S9:

"More intriguingly, starting from ~160 fs, a fourth phonon mode, namely B_{3g}^2, is gradually excited through phonon-phonon coupling, as indicated by the red triangles in Fig. 4a. This mode represents the out-of-plane non-resonant motions of carbon atoms that lead to the intralayer buckling of graphite. To further explicitly demonstrate the phonon-phonon coupling effects during the phase transition, we calculate the potential energy surfaces (PES) of B_{3g}^2 mode under the condition where the B_{3g}^1 mode exhibits different displacements. The results shown in Fig. S9 indicate that the intense excitation of B_{3g}^1 mode can effectively induce substantial changes in the PES of the B_{3g}^2 mode." (Main text page 9)

7. In the methods section, it is discussed how the time propagation up until 400 fs is done with the TDAP code using ALDA, and after 400 fs the CP2K package is used to do BO molecular dynamics based on the configuration and temperature at 400 fs, and using the BLYP functional. How can the authors be sure that these two methods match? Looking at Fig. 2b: the middle panel shows the buckling height Delta z, which is seen to decrease between 0.3 and 0.4 ps, but when the MD kicks in at 0.4 ps, Delta z suddenly increases. A similar behavior, although less pronounced, is seen in the other two panels of Fig. 2b. Are these artifacts of the computation? How much can the final relaxed state be trusted?

Author reply: For the relaxation of the phase transition structure in BOMD simulations, the atomic positions and velocities of the initial state were extracted from the TDAP trajectory at 400 fs, to ensure the continuity of the atomic dynamics. Since the graphite-to-diamond phase transition has occurred and the structure has evolved into a metastable diamond state at this point, we believe that the impact of minor differences in the electronic state on the final result of structural relaxation can be neglected, despite the slight differences in the software implementation and the exchange-correlation functionals (i.e., the differences are rather small as compared to the drastic changes in structure/energy upon photoexcitation). To verify the reliability of such treatment, we select another configuration at 280 fs from the TDDFT trajectory and proceeded with BOMD simulation for structure relaxation. The overall evolution process is shown in

Fig. R5. Although the relaxation processes initiated with different excited-state configurations exhibit subtle differences in detailed dynamic behaviors, the final diamond structure obtained after the relaxation remains unaffected.

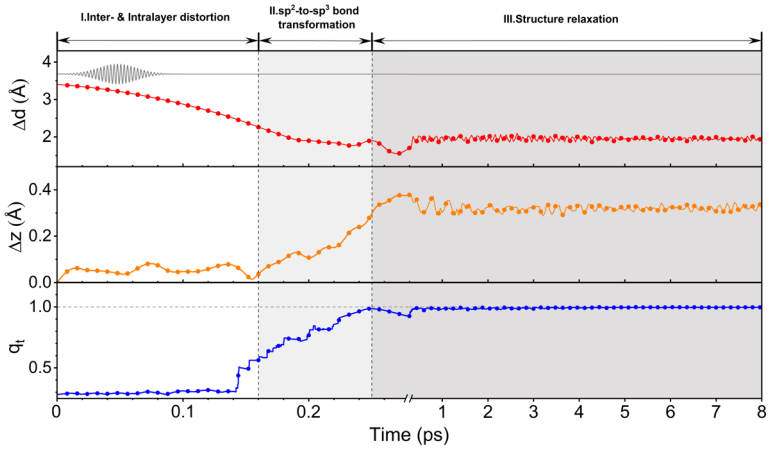

Fig. R5. Time evolution of the interlayer spacing Δd, intralayer buckling height Δz and tetrahedral order parameter q_t of graphite. The annealing process starts with the state obtained at 280 fs in the non-adiabatic simulation and continues up to 8.0 ps.

We have added the following clarification in Methods section in the revised manuscript:

"Initial atomic structure, velocities and temperature for the annealing simulation is obtained from the configuration of non-adiabatic rt-TDDFT simulation at 400 fs." (Main text page 15)

We have added the following discussion in the revised manuscript and Fig. R5 in the SI as Fig. S6:

"To verify the influence of initial state selection on the annealing processes, we extract another configuration from the rt-TDDFT trajectory at 280 fs as the initial state for the thermal relaxation process, as shown in Fig. S6. A comparison of Fig. 2b and Fig. S6 reveals that although the relaxation processes initiated from different excited-state configurations exhibit subtle differences in specific dynamic behaviors, the final phase transition structure remains unaffected." (Main text page 7)

8. Lastly: the calculations are done using a 16-atom supercell. I can imagine that the computational effort that went into this paper was quite substantial. Nevertheless, this

supercell seems quite small, given the massive structural changes that are being simulated here, where the system surely goes through various stages of disorder before reaching again an ordered phase. How can one be sure that the supercell size is adequate to capture this?

Author reply: We adopt the supercell containing 16 carbon atoms in the non-adiabatic dynamic simulations based on the rt-TDDFT, to compromise the heavy computational cost of the state-of-the-art dynamic simulation methods. Following the quest of the reviewer and considering the demanding computational cost of rt-TDDFT simulations, we have repeated our simulations with a larger supercell containing 24 carbon atoms. As indicated in Fig. R6, the process and mechanism of photoinduced structure transformation found in graphite still holds. The dynamics and time scale of phase transition are consistent with the simulation results using smaller supercell (containing 16 atoms). Therefore, the supercell size has no qualitative influence on the process and mechanism of the photoinduced structural transformation in graphite. We agree that the laser-induced phase transition occurring in our simulations is a microscopic short-time non-equilibrium behavior in the local domain, rather than a long-time steady-state macroscopic phenomena. The direct action of the laser pulse on the interior of small lattice supercell may lead to a faster and more sensitive response of graphite, compared to the scenario of the macroscopic object or in the experimental situation.

However, the actual scenario may be more complex. For instance, at mesoscopic or macroscopic scales, lattice defects or even polycrystalline structures may exist, leading to phase transitions that are no longer spatially uniform. In such cases, it becomes necessary to develop methods such as machine learning potential functions incorporating excited-state information to simulate systems comprising thousands of atoms or even larger scales for further investigation. This is a research area of great interest to us, and we have already conducted some preliminary tests in this direction. Clearly, this question cannot be fully addressed within the scope of the present study at the moment.

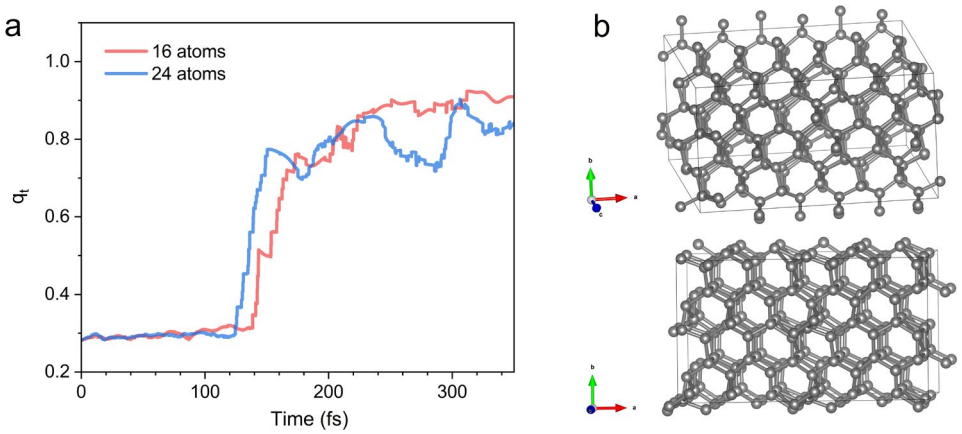

Fig. R6. a Time evolution of the tetrahedral order parameter q_t for two trajectories with different cell size and both forming HD phase. **b** Structures of 16-atom (top) and 24-atom (bottom) trajectories at ~300 fs. The top and bottom figures have undergone 3×2×2 and 2×2×2 supercell expansions, respectively, to ensure the consistent on total number of atoms.

We have added the following discussion in the revised manuscript and Fig. R6 in the SI as Fig. S14:

"To gain further insight into the light-induced graphite-to-diamond phase transition mechanism revealed above, we compared the dynamic behavior of photoinduced structural transformation in graphite across different supercell sizes within the rt-TDDFT non-adiabatic computational framework, and the results show that the phase transition mechanism is essentially consistent (Fig. S14). Compared to large supercells or experimental scenarios, direct interaction of laser pulses with the interior of small supercells is likely to trigger a faster and more sensitive response in phase transition simulations." (Main text page 13)

Reviewer #2 (Remarks to the Author):

This manuscript presents a compelling computational study of ultrafast, laser-induced phase transitions from graphite to diamond, utilizing state-of-the-art non-adiabatic molecular dynamics (NAMD) simulations. The authors propose that light-driven, phonon-specific mechanisms govern the selective formation of either cubic or hexagonal diamond under non-equilibrium conditions. The work is timely and relevant to the fields of laser-matter interaction, phase transformation, and sustainable materials synthesis, with potential implications for energy-efficient diamond production.

The manuscript is generally well-written, and the simulations appear to be thoughtfully designed. However, several points require further clarification and discussion before the manuscript can be recommended for publication.

1. Experimental Validation of Simulation Results (Fig. 2): The manuscript would benefit from a more in-depth discussion of how the simulated light-induced phase transition pathways align with existing experimental observations. Are there published time-resolved studies such as ultrafast electron diffraction, X-ray diffraction, or transient absorption data, that support the key transitions proposed in Fig. 2? Discussing these connections will enhance the credibility and experimental relevance of the simulations.

Author reply: We thank the reviewer for the very constructive comments. Several related experimental papers have reported that graphite can form sp^3-bonded structure under intense femtosecond laser irradiation. For instance, Raman *et al.* clearly captured the process of interlayer compression leading to bond formation using electron diffraction techniques (Phys. Rev. Lett., 2008, 101, 077401). Carbone *et al.* detected signals of interlayer bond formation around ~180 fs after photoexcitation via fs-resolved electron energy loss spectroscopy (Science, 2009, 325, 181-184), which quantitatively aligns with the interlayer bonding forming from ~160 fs, shown in Fig. 2a. Nüske *et al.* observed the formation of nanoscale cubic diamond crystals in the laser-irradiated highly oriented pyrolytic graphite (HOPG) sample using Raman spectroscopy and *X*-ray diffraction (Appl. Phys. Lett. 2012, 100, 043102). Duan *et al.* observed ultrafast formation of a transient two-dimensional diamond-like structure under femtosecond laser irradiation using MeV ultrafast electron diffraction (Phys. Rev. B 2020, 102 155431). Furthermore, several STM-based studies have identified the regions of laser-excited sp^3-bonded domain formation involving interlayer sliding, intralayer buckling, and periodic interlayer bonding (Phys. Rev. Lett., 2009, 102,

087402; Sci. Rep. 2023, 13, 21439). The experimental studies mentioned above probed the photoinduced structural transformation in graphite by various means, demonstrating the formation of sp^3 hybridized structures in graphite is achieved under the action of femtosecond lasers. However, the spatial and temporal resolution of existing experimental studies on the structure transformation process is relatively rough, and there is a lack of exploration into the non-equilibrium electron and phonon dynamics in complete graphite-to-diamond phase transition. One of the key motivations of our work is to stimulate more relevant time-resolved ultrafast experimental measurements.

We have supplemented a thorough discussion of the previous experimental results in Introduction section in the revised manuscript:

"Raman *et al.* clearly captured the process of photoinduced interlayer compression which leads to bond formation using electron diffraction techniques[28]. Carbone *et al.* detected signals of interlayer bond formation around ~180 fs after photoexcitation via fs-resolved electron energy loss spectroscopy[29]. Nüske *et al.* observed the formation of nanoscale cubic diamond crystals in the laser-irradiated highly oriented pyrolytic graphite (HOPG) sample using Raman spectroscopy and X-ray diffraction[7]. Duan *et al.* observed ultrafast formation of a transient two-dimensional diamond-like structure under femtosecond laser irradiation using MeV ultrafast electron diffraction[30]. Furthermore, several STM-based studies have identified the regions of laser-excited sp^3-bonded domain formation involving interlayer sliding, intralayer buckling, and periodic interlayer bonding[31, 32]." (Main text page 2)

We have added a comparison of our simulation results with existing experimental measurement regarding the phenomena of the photo-induced sp^2-*to*-sp^3 phase transition in the revised manuscript:

"Such ultrafast interlayer compression and sliding processes in graphite under light irradiation have been widely observed in previous experiments[7, 28, 30-32], and the time scale for the initial formation of sp^3 bonds is also consistent with the ~180 fs reported in previous experiments[29]." (Main text page 6)

2. Phonon Mode Analysis and Raman Correlation (Fig. 4): The authors emphasize the role of specific phonon modes (e.g., B_3g_1) in driving the transition. It would be useful to discuss whether any ultrafast Raman spectroscopy studies (published or ongoing) support the appearance or evolution of such phonon modes under pulsed laser excitation. Can any characteristic Raman shifts be associated with the phonon activity

simulated in Fig. 4?

Author reply: We thank the reviewer for the very helpful suggestion. To the best of our knowledge, there have been no studies that directly probe and analyze the photo-induced graphite-to-diamond phase transition process using sub-picosecond time-resolved Raman spectroscopy. Femtosecond Raman spectroscopy has been developed to investigate ultrafast photoinduced structural changes of materials. Yoshizawa et al. achieved a temporal resolution on the order of hundreds of femtoseconds (Phys. Rev. A, 1999, 61, 013808), and over the past few years, a temporal resolution as high as tens of femtoseconds has also been successfully realized (JACS, 2021, 143, 9699-9717). Time-resolved Raman scattering technique has been applied to investigate the structure and dynamics of short-lived transients in films (Vib. Spectrosc. 2020, 106, 103011), and used to investigate the non-equilibrium coupling between the E_{1u} and E_{2g} modes of the crystal lattice in bilayer and multilayer graphene (Phys. Rev. B 2023, 108, 075419). We expect that our studies can inspire relevant time-resolved experimental measurements to characterize the phonon coupling and evolution in the ultrafast optically-induced structural phase transition as revealed in our simulation work.

We have added the following discussion in the revised manuscript:

"Femtosecond Raman spectroscopy is expected to provide experimental verification for the mechanism of photoinduced graphite-to-diamond phase transition we proposed. This technique has been developed to investigate ultrafast photoinduced structural changes in materials[54, 55], and has been applied to reveal the nonequilibrium coupling between the E_{1u} and E_{2g} modes of the crystal lattice in bilayer and multilayer graphene[56], as well as the dynamics of short-lived transients in thin films[57]." (Main text page 13)

3. Cubic vs. Hexagonal Diamond Formation Conditions (Fig. 5): Under static HPHT conditions, it is well-known that hexagonal diamond tends to form at lower temperatures than cubic diamond. In Fig. 5, the light-induced phase diagram is intriguing, but lacks clear guidance on which laser parameters (e.g., fluence, pulse duration) favor hexagonal over cubic diamond. For experimentalists, a clearer interpretation of how these regimes are defined and how to tune laser conditions to selectively promote one phase over the other would greatly increase the practical utility of the figure.

Author reply: We thank the reviewer for the constructive suggestion regarding the figure presentation and data interpretation. We have modified the Fig. 5 in the revised

manuscript (as shown in Fig. R7) to emphasize the laser parameter-dependent final structure of the graphite-to-diamond phase transition. At a certain wavelength of pump laser, *e.g.* 800 nm, CD is the primary product of photoinduced phase transformation when the laser fluence falls within the range of ~120-130 mJ/cm². HD tends to form when the fluence is in the ranges of 90–120 and 120-150 mJ/cm². Light-driven conversion of graphite to diamond primarily occurs in regions near the graphite damage threshold. Over a broader wavelength range, longer wavelengths require lower laser power for diamond structure formation (blue shaded area). Laser power is directly correlated with the amount of electron excitation and specific phonon excitation. In Fig. R7b, we use $\langle Q \rangle$ to distinguish between CD and HD structures. It can be observed that within the fluence range where diamond structures are formed, CD structure is more likely to be generated in the middle interval, while the HD structure is more prone to form in the upper and lower regimes.

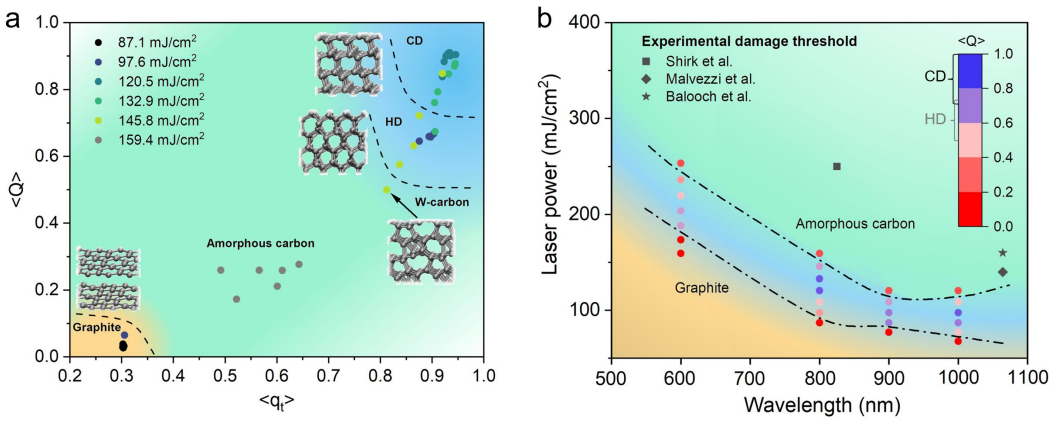

Fig. R7. Phase diagram of light-driven graphite phase transition. a Fluence dependence of laser-induced graphite phase transition under a pump wavelength of 800 nm. Tetrahedral order parameter q_t and bond parameter Q are obtained by averaging from 300 fs to 400 fs in each trajectory. The dashed lines are guides for the eye to distinguish approximate boundaries of different carbon structures. **b** Optical modulation capability of laser on graphite phase transition. The bond parameter Q is used to distinguish CD and HD structures. $\langle Q \rangle$ ~1 stands for a perfect CD structure and $\langle Q \rangle$ ~0.75 indicates a HD structure. Experimental values of graphite damage threshold are shown in black (ref. 36-38). The dashed lines indicate the upper and lower boundaries of the laser fluence required to achieve a stable diamond structure at a given wavelength.

Regarding the influence of pulse duration on the process and products of phase transition, we have conducted new simulations with pulse durations of 64 fs and 120 fs, and compared the results with that of 96 fs, as shown in Fig. R8. It is evident that a

longer pulse exposure increases the electronic excitation level to 5%, resulting in an amorphous final structure of the phase transition. As noted in our paper, the electronic excitation level during the photoexcited phase transition that forms diamond is approximately 3.4% ~ 4.2%. Pulse duration influences the final structure by modulating the total excitation dose.

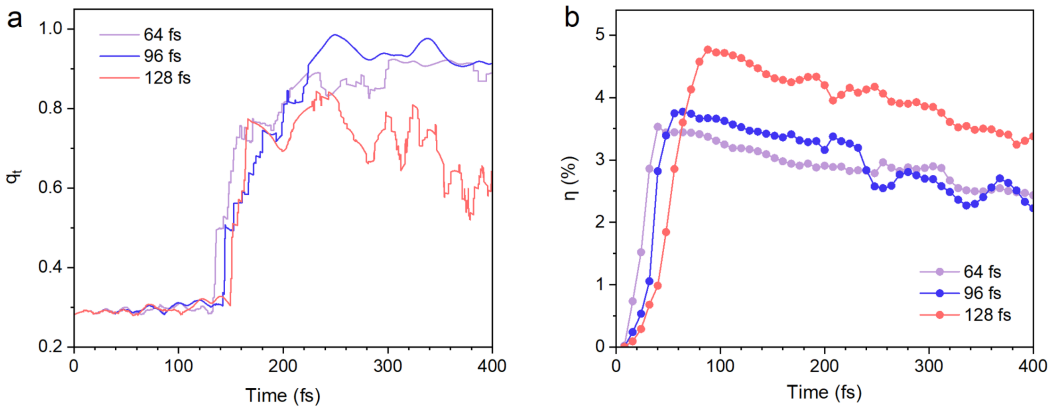

Fig. R8. a Time evolution of the tetrahedral order parameter q_t for different pulse durations (64 fs, 96 fs and 120 fs). **b** Time evolution of the percentage of excited electrons η corresponding to different pulse durations.

We have refined Fig. 5 and added the following discussion in the revised manuscript. Fig. R8 has been added to the SI as Fig. S13b.

"It can also be observed that within the fluence range where diamond structures are formed, CD structure is more likely to be generated in the middle interval, while the HD structure is more prone to form in the upper and lower regimes." (Main text page 12)

"As indicated in Fig. S13, the electronic excitation level in the phase transitions that form CD or HD ranges from ~3.4% to 4.2%." (Main text page 13)

4. Clarification of Fig. S9: In the supplementary Fig. S9, the authors compare cases with Q = 0 and Q = 1. However, the text mentions Q = 0.75, which is not shown in the figure. Please clarify whether this case was simulated and if so, include it in the figure or explain its absence.

Author reply: We apologize for the misunderstanding caused by the lack of clear annotations. The $Q = 0$ and $Q = 1$ shown in original Fig. S9 refer to the bond parameters

for a specific C–C bond, staggered vs. eclipsed (see Fig. R9). For HD structure, the ratio of staggered to eclipsed C–C bonds is 1:3, thus an ideal average value $\langle Q \rangle$ for HD phase should be 0.75.

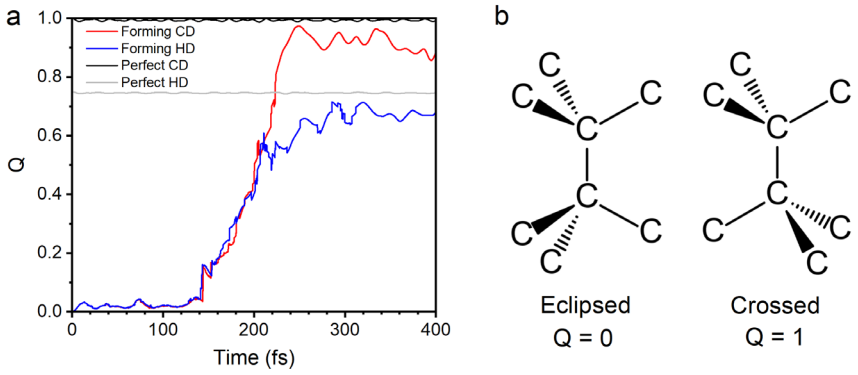

Fig. R9. a Time evolution of bond parameter Q corresponding to trajectories forming CD (red line) and HD (blue line), compared with those corresponding to perfect CD (black line, $\langle Q \rangle \approx 1$) and HD (grey line, $\langle Q \rangle \approx 0.75$) under 300 K. **b** Schematic figure of Q values corresponding to a single C–C bond in either the perfectly eclipsed or crossed conformation.

We have modified the original Fig. S9 (now Fig. S12) in the revised SI and have added better annotations there.

5. Line 39 – Temperature-Dependent CD vs. HD Formation: The sentence referencing the temperature relationship between cubic and hexagonal diamond (CD and HD) formation needs clarification. Please revise for accuracy and consider citing experimental studies that establish this relationship under equilibrium conditions for comparison.

Author reply: Following the reviewers' suggestions, we carefully verified the cited literature and experimental data involved, confirming that the synthesis of CD reported by Bundy et al. in 1955 was achieved under a pressure of >100,000 kg·m/cm² and a temperature of >2300 K, while the HD synthesis reported in their 1966 work was carried out at a pressure of 130 kbar and a temperature of >1000°C.

We have revised the following discussion in the text:

"Over half a century ago, Bundy *et al.* reported the successful synthesis of man-made cubic diamond (CD)[9] and hexagonal diamond (HD)[13] under high-pressure, high-

temperature (HPHT) conditions, with synthesis temperatures exceeding 2000 ℃ and 1000 ℃, respectively. Recently, the breakthrough in successfully synthesizing nano-sized, high-purity HD from graphite under HPHT conditions has further advanced the research progress in engineering the desirable features of carbon allotropes[3, 20].” (Main text page 2)

Reviewer #3 (Remarks to the Author):

This is a great work, very impressive and opening the doors to the future where diamond and other materials could be synthesized using lasers. The paper should be accepted. However, I have several questions that I hope can be addressed:

We would like to express our gratitude to the reviewer for the comments and recognition of our work.

1. What does 4% electronic excitation mean? 4 percent of 4 valence electrons per atom are excited?

Author reply: "Approximately 4% electronic excitation" means 4% of the total valence electrons in the system are excited to the conduction band above the Fermi energy level under laser irradiation.

2. Simulations are done for a single crystal of graphite with a particular orientation of the polarization plane of the laser with respect to the crystal. How do the results translate to a polycrystal of graphite? Will more fluency be needed?

Author reply: We appreciate the insightful questions raised by the reviewer. The phase transition process presented in the main text is induced by light polarized along the *y*-axis within the graphite plane. To investigate the relevant scenario in polycrystalline graphite, we first applied also lasers polarized along the *x*-axis (lying within the graphite plane) and the *z*-axis (perpendicular to the graphite plane), respectively, as shown in the Fig. R10. When light is polarized within the graphite plane (*x*-*y* plane), a relatively consistent photoinduced phase transition process is observed. In contrast, when light is polarized perpendicular to the *x*-*y* plane, it fails to induce a phase transition in graphite due to the inability to generate enough excited electrons. This indicates that in polycrystalline samples, graphite layers aligned parallel to the light polarization direction exhibit preferential phase transitions, while those oriented perpendicular to the polarization show no significant response. Second, our simulations on single-crystal graphite with defects also suggest that grain boundaries and high defect concentrations in polycrystalline graphite may hinder the transformation of graphite phases into diamond phases.

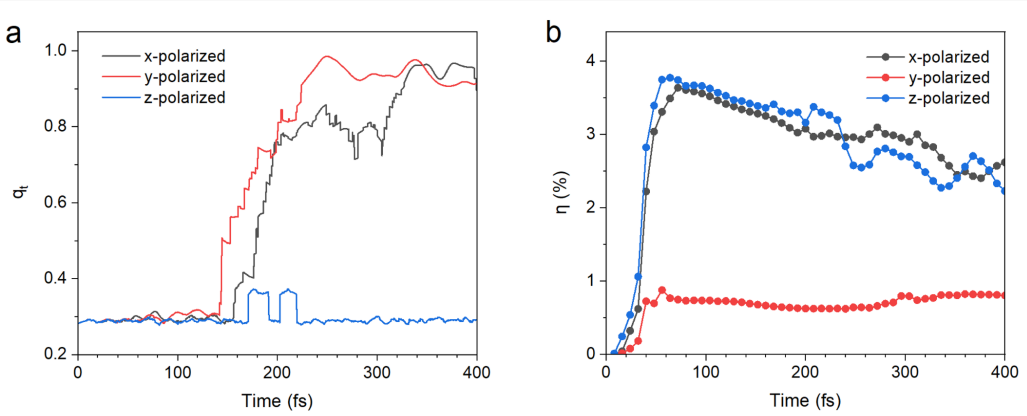

Fig. R10. Time evolution of **(a)** the tetrahedral order parameter q_t and **(b)** the percentage of excited electrons η, corresponding to different light polarization directions.

We have added the following discussion in the revised manuscript and Fig. R10 in the SI as Fig. S15:

"Furthermore, investigations into the effects of laser polarization direction (Fig. S15) and graphite defects indicate that laser irradiation polarized perpendicular to the graphite plane barely generates sufficient excited electrons to induce phase transitions, while defects would also hinder the order-to-order phase transition process. These results suggest that for polycrystalline graphite, the presence of grain boundaries and high defect concentrations may substantially reduce the efficiency of the photoinduced graphite-to-diamond phase transition." (Main text page 13)

3. Simulations are done in a small 16-atom cell. Can the authors estimate size effects? For once, diamond formation may be hindered by the interfacial energy. Other allotropes might appear too.

Author reply: We adopt the supercell containing 16 carbon atoms in the non-adiabatic dynamic simulations due to the demanding computational cost of the state-of-the-art methods. Regarding size effects, we have further conducted comparative simulations using 24-atom supercells. As demonstrated in Fig. R6, the process and mechanism of photoinduced structure transformation found in graphite are essentially consistent for both unit cell sizes. At the same time, we acknowledge that the laser-induced phase transition occurring in our simulations is a microscopic, short-time non-equilibrium behavior in the local domain, rather than along-time steady-state macroscopic phenomena. The direct action of the laser pulse on the interior of small lattice supercell may lead to a faster and more sensitive response of graphite, compared to the scenario

of large supercell or in the experimental situation. Owing to the computational cost of first-principles non-adiabatic molecular dynamics simulations, current research cannot encompass physical behaviors at mesoscopic or beyond—such as phenomena involving defects, interfaces and grain boundaries. The development of machine learning potential function methods incorporating excited-state information may enable computational exploration to extend to larger scales and more complex scenarios. Regarding the formation of other allotropes, we provide a detailed explanation in the next question.

We have added the following discussion in the revised manuscript and Fig. R6 in the SI as Fig. S14:

"To gain further insight into the light-induced graphite-to-diamond phase transition mechanism revealed above, we compared the dynamic behavior of photoinduced structural transformation in graphite across different supercell sizes within the rt-TDDFT non-adiabatic computational framework, and the results show that the phase transition mechanism is essentially consistent (Fig. S14). Compared to large supercells or experimental scenarios, direct interaction of laser pulses with the interior of small supercells is likely to trigger a faster and more sensitive response in phase transition simulations." (Main text page 13)

4. For cold compression of graphite, the easiest allotrope to form is M-carbon (Li 2009; Boulfelfel 2012). Other candidates included carbon, bct4 carbon and dozens of other hypothetical forms (see paper by Haiyang Niu). Can the authors comment on their possibility to occur as a result of laser irradiation?

Author reply: In our laser-induced graphite-to-diamond phase transition simulations, we indeed observed the formation of the allotrope W-carbon, when the laser fluence is relatively high but below the intensity required to form an amorphous structure. The combined effects of electron–phonon coupling and phonon–phonon interactions lead to excitation of specific phonon modes, resulting in the formation of different carbon allotropes (as shown in Fig. 4 in the main text). Achieving different carbon allotropes may require varying laser intensities and other parameters. In summary, while laser irradiation may indeed produce a broader range of carbon network structures, including those mentioned by the reviewer, with a certain probability, the formation of these structures is likely uncontrollable and random unless their specific microscopic mechanisms and transformation pathways can be clearly identified.

We have incorporated the above discussion into the revised manuscript:

"Although we only observed the formation of the W-carbon under the laser conditions employed, different carbon allotropes[48-50] may also form when specific phonon modes are excited through the combined effects of electron–phonon coupling and phonon–phonon interactions." (Main text page 10)

5. I'm surprised that laser fluence monotonically decreases with wavelength. Surely this trend must break at some wavelength, otherwise very weak radiowaves would make diamond from graphite:

Author reply: As shown in Figure 5b in the main text, the laser fluence required for inducing graphite-to-diamond phase transition gradually decreases with increasing wavelength and tends to converge in the range of 900–1000 nm, suggesting the existence of a minimum intensity threshold. Furthermore, as shown in Fig. R11, this trend is established under the premise of achieving a certain level of excitation. In regions with very low photon energy, such as microwave fields, it is difficult to reach the ~3–4% electronic excitation threshold, thus it challenging to drive strong phonon excitation to achieve the sp^2-to-sp^3 structural phase transition.

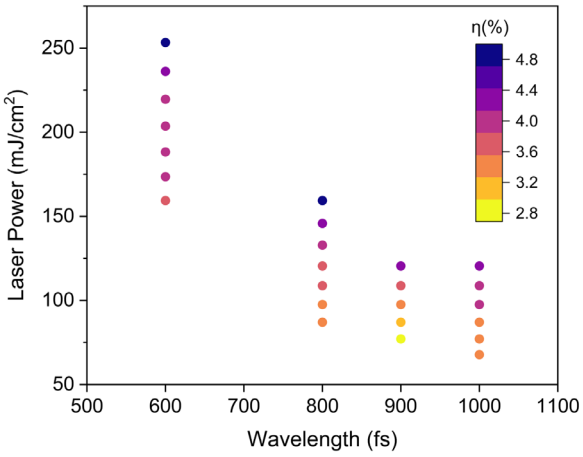

Fig. R11. Maximum percentage η of excited electrons in graphite under different laser parameters.

We have added the following discussion and Fig. R11 as Fig. S13 to the revised SI:

"As shown in Fig. 5b and Fig. S13a, although the laser fluence required to induce graphite-to-diamond phase transformation gradually decreases with increasing wavelength, it tends to saturate in range of 900–1000 nm, indicating the existence of a

minimum intensity threshold. This trend is established under the premise of achieving a specific excitation level. In regions with low photon energy (*e.g.*, the microwave field), it is difficult to reach the approximately 3–4% electron excitation threshold required to drive strong phonon excitation for the sp^2-*to*-sp^3 structural phase transition." (Supplementary Information page 16)

6. After electrons are excited to 2-4 eV above Fermi level, they should eventually relax back to the ground state, releasing energy as either light or more likely heat. So one will have very hot diamond at ambient pressure. Won't it revert back to graphite? This is what hot diamond usually does at ambient pressure.

Artem R. Oganov

Author reply:

As noted by the reviewer, electrons excited into the conduction band undergo electron-hole recombination due to electron-electron and electron-phonon scattering, leading to a reduction in the number of carriers, as shown in Fig. S8 in the revised SI. During this ultrafast process, excited electrons introduce sliding and compressive phonon vibration modes via electron-phonon coupling. Subsequently, specific phonon modes induced by phonon-phonon coupling determine the formation of interlayer bonds, which corresponds to the second stage emphasized in the manuscript. In this ultrafast process, the dissipation of the system with the external environment is not considered, which may lead to an overestimation of the evolution rate and extent of the system. Subsequently, we employed a BOMD thermal bath to partially address dissipation between the system and environment, reducing the ionic temperature of the system to room temperature. We observe that the metastable diamond structure evolves toward the more stable diamond phase. For instance, a metastable CD structure generated by an ultrafast laser pulse with a photon energy of 1.55 eV and a fluence of 120 mJ/cm^2 undergoes relaxation to the ground state upon system annealing. The band gap expands from 3.27 eV to 3.63 eV, and the interlayer bond length also tends to stabilize, as reported in Fig 2b. Overall, once the laser field provides sufficient energy to drive graphite over the reaction energy barrier and form a transient diamond-like structure, further energy dissipation coupled with the environment tends to drive the structures toward a more stable ground state.

Reviewer #4 (Remarks to the Author):

This work has identified and is focusing on a timely and interesting topic. The authors use cutting-edge simulation techniques to compute electron dynamics and coupling of electron and phonons. In principle this work has the potential to be of interest to the audience of this journal, however, the current manuscript does not meet this standard. The work is exclusively computational and, while that itself is not a problem, the work does not rigorously address this scientific question.

First, I suggest the authors start by a schematic and quantitative figures that captures the relevant processes. This should estimate energies and time scales for the crucial steps that are relevant here. Are the initial and final states, as well as the pathways that connect both, quantitatively reasonable? At the same time, routes towards computational or experimental validation of the provided results are necessary.

Author reply: We appreciate the reviewer's valuable suggestions. We have made detailed revisions to the schematic diagram of light-driven graphite-to-diamond phase transition pathway in Fig. 1 of the main text, and added a description of the time scale to the figure caption. Our results indicate that the degree of electron excitation is the key factor determining the phase transition pathway, therefore, we have adjusted the vertical axis from a vague energy definition to defining a specific amount of excitation, as shown in Fig. R12. By manipulating the electronic excitation, optical control over the transition pathways between the initial graphite structure and the final reaction products can be achieved on ultrafast timescales.

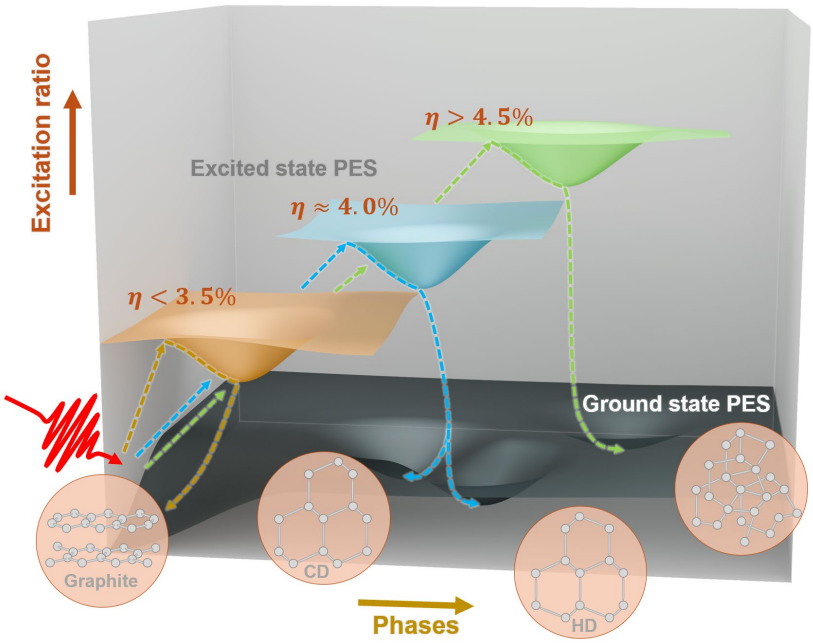

Fig. R12. Schematic diagram of light driven graphite-to-diamond phase transition. Optical control over the transition pathways between the initial graphite structure and the final reaction products can be achieved on ultrafast timescales (hundreds of femtoseconds) by manipulating the electronic excitation amount η. The three excited-state potential energy surfaces with different election excitation ratios are depicted in orange, blue, and green, respectively, corresponding to different phase transition pathways and products.

We have refined Fig.1 and its caption in the revised manuscript and added further explanation.

"The phase transition pathway and final structure are closely correlated with the proportion of photoexcited electrons. Excessive excitation leads to the formation of an amorphous state, while insufficient excitation fails to drive the graphite structure to overcome the reaction energy barrier and complete phase transition. An appropriate amount of electron excitation is crucial for the formation of the diamond structure." (Main text page 3)

Second, the simulation techniques and involved approximations come with error bars that are absent in this work. This needs to be explained and quantified, to better understand what is relevant and what is the accuracy in this work. The physics present and absent in these simulations, due to the used approximations, need to be explained.

It also is necessary to connect these error bars to possible experimental validation of these simulations. The chosen pulse parameters in this work should be connected to experimentally achievable pulse parameters and discussed explicitly in the paper.

Author reply: Regarding the reviewer's concerns about the impact of inherent approximations in the computational methods on the results and the explicit comparison with actual experimental parameters, we provide the following analysis and explanations:

(1) Our findings are not based on a single non-equilibrium molecular dynamics trajectory, but rather on physical properties and behaviors obtained from multiple trajectories with a certain statistical average. The error bars in Fig. 2a represent the statistical standard deviation of the instantaneous energy across different trajectories.

(2) The rt-TDDFT dynamic simulations reported in this study, while inevitably relying on the single-particle approximations and mean-field approximations, remains one of the most effective tools currently available for describing the dynamic behavior of real materials under strong field excitation. It has been applied to the investigation of various photoexcited phase transition phenomena (*e.g.* Comput. Mater. Today, 2024, 2, 100012).

(3) Due to the high computational cost associated with rt-TDDFT dynamic calculations, a relatively small supercell, containing 16 atoms, was adopted in our study. By comparing results of a supercell containing 24 carbon atoms, graphite supercells of different sizes exhibit essentially consistent photoinduced structural transformation processes and mechanisms, as shown in Fig. R6. The direct action of the laser pulse on the interior of small supercell may lead to a faster and more sensitive response of graphite, compared to that in experiment.

(4) Laser parameters we explored include (i) wavelength, ranging from 600 nm to 1000 nm. Wavelengths of 532 nm, 800 nm, and 1064 nm are most widely used in the experiments. (ii) Energy density, reaching the order of magnitude of 10^2 mJ/cm^2 — a level achievable in many experiments (Carbon 39, 2001, 1183-1193; Appl. Phys. A, 2005, 81, 729-735). (iii) High fluence rate, meaning the aforementioned energy density is delivered within a short time (~100 fs), corresponding to a power density of 10^{12} W/cm^2 (Phys. Rew. Lett. 2012, 109, 195005; Laser & Photonics Rev. 2023, 17, 2100705).

We have added the following discussion in the revised manuscript:

"We propose a wavelength-fluence phase diagram for the graphite-to-diamond

transition in Fig. 5b, where the laser wavelength ranging from 600 nm to 1000 nm and the light fluence reaching the order of magnitude of 10^2 mJ/cm^2 are all experimentally achievable[36, 51-53].” (Main text page 12)

Third, I am wondering what technique is used to model electron-phonon coupling and how do the authors deal with the large difference in time scales between electrons and phonons.

Author reply: The non-adiabatic molecular dynamic (NAMD) simulations performed here are within the framework of real-time time-dependent density functional theory (rt-TDDFT) and Ehrenfest dynamics. To solve the time-dependent Schrödinger equation,

$$\hat{H}_{mol}\Psi(\boldsymbol{r},\boldsymbol{R},t) = i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},\boldsymbol{R},t),$$

the Hamiltonian is written as

$$\hat{H}_{mol}(\boldsymbol{r},\boldsymbol{R}) = -\sum_{\gamma}\frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2 - \sum_{i}\frac{\hbar^2}{2}\nabla_i^2 + \sum_{i<j}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|} - \sum_{\gamma,i}\frac{Z_\gamma}{|\boldsymbol{R}_\gamma-\boldsymbol{r}_i|} + \sum_{\gamma<\zeta}\frac{Z_\gamma Z_\zeta}{|\boldsymbol{R}_\gamma-\boldsymbol{R}_\zeta|}.$$

Within the theoretical framework of Ehrenfest dynamics that we have adopted, the total wave function is expressed in the following form,

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) = \Phi(\boldsymbol{r},t)\Omega(\boldsymbol{R},t)exp\left[\frac{i}{\hbar}\int_{t_0}^{t}dt'E_{el}(t')\right],$$

$$E_{el}(t) = \iint d\boldsymbol{r}d\boldsymbol{R}\Phi^*(\boldsymbol{r},t)\Omega^*(\boldsymbol{R},t)\hat{\mathcal{H}}_{el}(\boldsymbol{r},\boldsymbol{R})\Phi(\boldsymbol{r},t)\Omega(\boldsymbol{R},t).$$

Based on this, the respective evolution equations for the electronic and ionic subsystems can be derived as

$$i\hbar\frac{\partial\Phi(\boldsymbol{r},t)}{\partial t} = -\frac{\hbar^2}{2}\sum_i\nabla_i^2\Phi(\boldsymbol{r},t) + \left[\int d\boldsymbol{R}\,\Omega^*(\boldsymbol{R},t)\hat{V}(\boldsymbol{r},\boldsymbol{R})\Omega(\boldsymbol{R},t)\right]\Phi(\boldsymbol{r},t),$$

$$i\hbar\frac{\partial\Omega(\boldsymbol{R},t)}{\partial t} = -\frac{\hbar^2}{2}\sum_\gamma M_\gamma^{-1}\nabla_\gamma^2\Omega(\boldsymbol{R},t) + \left[\int d\boldsymbol{r}\,\Phi^*(\boldsymbol{r},t)\hat{\mathcal{H}}_{el}(\boldsymbol{r},\boldsymbol{R})\Phi(\boldsymbol{r},t)\right]\Omega(\boldsymbol{R},t).$$

Indeed, both the electronic and ionic subsystems evolve within mean fields determined by each other's real-time states. Consequently, the electron–phonon coupling also evolves in real time. This treatment represents a notable advantage of the real-time time-dependent density functional theory (rt-TDDFT) dynamics approach we have adopted, as it constitutes a first-principles methodology.

Unlike the excitation of IR-active modes that are directly coupled to the optical field, under intense light excitation, coherent phonons can exhibit significant excitation within tens of femtoseconds, as demonstrated in Fig. 4a. Therefore, the rt-TDDFT method we employ is capable of capturing such phonon excitation signals. For both electronic and ionic subsystems, our simulations use a time step of only 0.04 fs, which is sufficient to resolve electronic excitations as well as coherent phonon responses despite the longer simulation time is used for the latter.

We have added a new section (Supplementary Note 1: Electron–phonon coupling calculation in real-time TDDFT molecular dynamics) into the Supplementary Information to elaborate on the nonadiabatic dynamics simulation method we developed (Supplementary Information page 2).

Fourth, what is not clear to me is, is to which extent this work just presents a possible mechanism and what are other possible mechanisms. In real samples, many other effects contribute (defects, substrate, temperature, ...) and it is not clear to me, to what extent the idealized simulations here are providing a realistic picture that can be demonstrated in a real sample.

As it stands, I view the provided results as a proposal for a reaction mechanism, but that alone is not sufficient for the high standards of this journal.

Author reply: We sincerely appreciate the reviewer's insightful questions, which have helped us to identify the scope of applicability of our research findings. We, based on first-principles non-adiabatic dynamics methods, have explored the photoinduced phase transition process in periodic graphite single crystals. (1) The phase transition mechanism we propose holds for both single-crystal graphite or locally uniform phases within polycrystalline graphite. A necessary condition for the phase transition to occur is that the polarization direction of the excitation light field is approximately parallel to the graphite plane, as illustrated in Fig. R10. (2) Our simulations on single-crystal graphite containing defects indicate that the defects and grain boundaries in

polycrystalline graphite significantly impede the phase transition from graphite to diamond. (3) The photoinduced phase transition mechanism we proposed exhibits minimal correlation with the environmental temperature. In our study, the environment acts as an energy dissipation channel, enabling the relaxation of a metastable hot configuration after intense excitation to a stable ground-state structure.

Experimentally, Carbone et al. detected signals of interlayer bond formation around ~180 fs after photoexcitation via enhanced bulk plasmon signals (Science, 2009, 325, 181-184), which is quantitatively in agreement with the interlayer bonding phenomenon shown in Fig. 2a, beginning to form at around 160 fs. We anticipate that the complete process and mechanism of the photoinduced graphite-to-diamond phase transition proposed by in this study can be verified in high-quality single-crystal graphite through ultrafast laser excitation combined with time-resolved characterization measurements. This is highly challenging, but is very promising to be achieved.

We have added a comparison of our simulation results with existing experimental measurement regarding the phenomena of the photo-induced sp^2-*to*-sp^3 phase transition in the revised manuscript:

"Such ultrafast interlayer compression and sliding processes in graphite under light irradiation have been widely observed in previous experiments[7, 28, 30-32], and the time scale for the initial formation of sp^3 bonds is also consistent with the ~180 fs reported in previous experiments[29]." (Main text page 6)

We have added two new paragraphs at the end of the Results section in the revised manuscript, to discuss potential factors that may affect the scenario we described and suggest relevant experiments that may verify our proposed mechanism:

"To gain further insight into the light-induced graphite-to-diamond phase transition mechanism revealed above, we compare the dynamic behavior of photoinduced structural transformation in graphite across different supercell sizes within the rt-TDDFT non-adiabatic computational framework, and the results show that the phase transition mechanism is essentially consistent (Fig. S14). Compared to large supercells or experimental scenarios, direct interaction of laser pulses with the interior of small supercells is likely to trigger a faster and more sensitive response in phase transition simulations. Furthermore, investigations into the effects of laser polarization direction (Fig. S15) and graphite defects indicate that laser irradiation polarized perpendicular to the graphite plane barely generates sufficient excited electrons to induce phase

transitions, while defects also significantly hinder the transition process. These results suggest that for polycrystalline graphite, the presence of grain boundaries and high defect concentrations may substantially diminish the efficiency of the photoinduced graphite-to-diamond phase transition.

Femtosecond Raman spectroscopy is expected to provide experimental verification for the mechanism of photoinduced graphite-to-diamond phase transition we proposed. This technique has been developed to investigate ultrafast photoinduced structural changes in materials[54, 55], and has been applied to reveal the nonequilibrium coupling between the E_{1u} and E_{2g} modes of the crystal lattice in bilayer and multilayer graphene[56], as well as the dynamics of short-lived transients in thin films[57].” (Main text page 13)

RESPONSES TO THE REVIEWER COMMENTS (2nd Round)

First of all, we would like to express our gratitude to all reviewers for valuable comments during the previous round of review. These suggestions are very helpful for us to further improve the quality of the manuscript. We also thanks the reviewers for their recognition of the scientific merit of our work. The latest round of review comments are listed below, along with our responses and revisions made in the revised manuscript.

Reviewer #1 (Remarks to the Author):

The authors have substantially revised their manuscript in response to four referee reports. I believe that the paper has been much improved, and I am overall satisfied with the response of the authors to my own questions and comments. I think the authors also did a good job with the other three referee reports.

One point remains, namely the issue of the ALDA's inability to properly describe the Auger effect. In the paper the authors just add the single short sentence "Since adiabatic TDDFT tends to underestimate the carrier-carrier interaction and the scattering rates in real systems to some extent[42], the real electron-electron scattering effects may be more pronounced than indicated by the present simulation results."

In their rebuttal, the authors have made a convincing case that their approach at least includes electron-electron scattering to some degree, for instance due to their use of a supercell, and mediation via lattice distortions. Also, they found evidence by tracking orbital occupations. I would like to suggest to the authors to include a couple of brief additional sentences in the paper where these arguments are explicitly discussed, to justify that the Auger mechanism can be invoked here in spite of using ALDA.

Apart from this, the paper is now ready to be accepted.

Author reply: We greatly appreciate the reviewer's further valuable suggestions as well as the support and recognition for our work. Following the reviewer's suggestion, we have incorporated further discussions on this point in the revised manuscript:

"It is worth noting that although the Hamiltonian used in our non-adiabatic calculations does not explicitly include electron-electron scattering terms[42], the incorporation of multiple k-points and the presence of lattice distortions (or virtual phonons) allow electron scattering to be included to a certain extent. This enables us to capture key

Auger process and carrier transport. Since adiabatic TDDFT tends to underestimate the carrier-carrier interaction and the scattering rates in real systems to some extent, the real electron-electron scattering effects may be more pronounced than indicated by the present simulation results." (Main text page 8)

Reviewer #3 (Remarks to the Author):

I am satisfied with the responses of the authors and their revision.
The paper can be accepted now.

Artem R. Oganov

Author reply: We sincerely appreciate the reviewer for the support and recognition of our work. Their valuable suggestions have been of great help to us in improving the manuscript.

Reviewer #4 (Remarks to the Author):

The authors provided thoughtful answers to all reviewer questions. These answers, in particular those that connect the computational simulations and experiment, maintain my concern that the paper studies an interesting mechanism, but does not provide strong enough evidence that the simulations indeed study the previously reported situations. The conditions studied in this work are, in my opinion, far from experimentally achievable situations. The excitation of 4% seems huge, compared to what can be expected in experiment, without vaporizing the sample, if it can be achieved over significant volume (or surface) of the sample. Again, I think this is a very interesting model study, but it does not strongly enough connect experiment and theory and, thus, should be reported in a more specialized journal.

Author reply: First and foremost, we sincerely appreciate the valuable time you have dedicated during the two rounds of review and the insightful questions you raised. These have inspired us to further enhance our technical capabilities in excited-state dynamics to better address the needs of practical research. It must be acknowledged that theoretical computation has its limitations, while current simulation methods are insufficient to fully replicate the complexity of real-world systems, and some degree of approximation is inevitable. However, we believe we have sufficiently recognized the limitations of these approximations and have strived to interpret our observations as objectively as possible, so as to avoid exaggerating or distorting the facts, and to prevent any potential misinterpretation by readers.