**Raman spectroscopy and x-ray diffraction of sp³ CaCO₃ at lower mantle pressures**

Sergey S. Lobanov,¹,²,* Xiao Dong,³ Naira S. Martirosyan,¹,² Artem I. Samtsevich,³ Vladan Stevanovic,⁵ Pavel N. Gavryushkin,³,⁶ Konstantin D. Litasov,³,⁶ Eran Greenberg,⁷ Vitali B. Prakapenka,⁷ Artem R. Oganov,⁴,⁸,⁹,¹⁰ and Alexander F. Goncharov¹,¹¹

¹Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, USA
²Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, 3 Prospekt Akademika Koptyuga, Novosibirsk 630090, Russia
³Center for High Pressure Science and Technology Advanced Research, Beijing 100193, China
⁴Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 5 Nobel Street, Moscow 143026, Russia
⁵Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado 80401, USA
⁶Laboratory of Experimental Geochemistry and Petrology of the Earth’s Mantle, Novosibirsk State University, Novosibirsk 630090, Russia
⁷Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60632, USA
⁸Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny City, Moscow Region 141700, Russia
⁹School of Materials Science, Northwestern Polytechnical University, Xi’an 710072, China
¹⁰Department of Geosciences, Center for Materials by Design, Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York 11794, United States
¹¹Key Laboratory of Materials Physics, Institute of Solid State Physics, CAS, Hefei 230031, China

(Received 19 February 2017; revised manuscript received 10 July 2017; published 1 September 2017)

The exceptional ability of carbon to form sp³ and sp² bonding states leads to a great structural and chemical diversity of carbon-bearing phases at nonambient conditions. Here we use laser-heated diamond-anvil cells combined with synchrotron x-ray diffraction, Raman spectroscopy, and first-principles calculations to explore phase transitions in CaCO₃ at P > 40 GPa. We find that postaragonite CaCO₃ transforms to the previously predicted P₂₁/c CaCO₃ with sp³-hybridized carbon at 105 GPa (∼40 GPa higher than the theoretically predicted crossover pressure). The lowest-enthalpy transition path to P₂₁/c CaCO₃ includes reoccurring sp² and sp³ CaCO₃ intermediate phases and transition states, as revealed by our variable-cell nudged-elastic-band simulation. Raman spectra of P₂₁/c CaCO₃ show an intense band at 1025 cm⁻¹, which we assign to the symmetric C-O stretching vibration based on empirical and first-principles calculations. This Raman band has a frequency that is ∼20% lower than the symmetric C-O stretching in sp² CaCO₃ due to the C-O bond length increase across the sp²–sp³ transition and can be used as a fingerprint of tetrahedrally coordinated carbon in other carbonates.

DOI: 10.1103/PhysRevB.96.104101

I. INTRODUCTION

The thermodynamic ground state of carbon at ambient conditions is graphite with a triangular bonding pattern (sp² hybridization). High pressure P, however, favors tetrahedrally bonded (sp³) carbon, and diamond is stable at P > 1.7 GPa (0 K) [1]. The different bonding patterns of graphite and diamond result in very different mechanical, optical, electric, and thermal properties [2], making carbon a truly remarkable element. On top of this, carbon forms very strong directional bonds, leading to high melting temperatures T as well as high activation energies for the solid-state phase transitions [1]. As a result, carbon has a rich variety of metastable phases with mixed sp² and sp³ bonding patterns that may integrate the unique physical properties of both graphite and diamond [3,4]. The synthesis of such novel carbon-based technological materials requires navigating in the carbon energy landscape as well as insights into the trajectories and mechanisms of its phase transitions [5].

Unlike carbon, the thermodynamically stable form of silicon at ambient conditions has the cubic diamond structure. Not surprisingly, nearly all low-pressure silicates incorporate silicon exclusively in the form of sp³-hybridized SiO₃ tetrahedral groups. The electronic structure of SiO₄ tetrahedra is such that each oxygen has a half-occupied p orbital available for polymerization with adjacent groups. The topology of polymerized SiO₄ networks largely governs the physical properties of silicates and serves as the basis for their structural classification [6,7]. On the other hand, sp²-hybridized CO₃ triangular groups have an additional C-O π bond and, as a result, are isolated in the crystal structures of carbonates. This difference in the electronic structures of CO₃ and SiO₄ groups leads to very different physical properties of sp² carbonates and sp³ silicates. At high pressure, however, the electronic structure of carbon in carbonates may change via the C-O π-bond polymerization with adjacent groups. Theoretical computations predict that sp³ carbonates become thermodynamically stable at P ∼ 80–130 GPa [8–12]. Here we investigate the high-P behavior of CaCO₃, one of the most abundant carbonates near the Earth’s surface and a good proxy for carbonate chemical composition in the mantle [13,14].

Previous high-P studies have revealed a number of pressure-induced transformations in CaCO₃. At P < ∼40 GPa, (meta)stable phases of CaCO₃ include calcite, aragonite, CaCO₃ II, CaCO₃ III, CaCO₃ IVb, and CaCO₃ VI (e.g., [9,15–17]). At P > 40 GPa, CaCO₃ transforms into postaragonite, which has been reported as a stable phase up to 137 GPa [9,18,19]. Importantly, all these structures contain sp²-hybridized carbon forming triangular CO₃ groups.
Pyroxene-like C2221 CaCO3, which has been predicted to be stable at $P > 137$ GPa, has a different bonding pattern, with $sp^3$-hybridized carbon forming polymerized CO2 chains [9]. This prediction gained some experimental support in that the major Bragg peaks of the C2221 CaCO3 were observed in experiment at $P > 140$ GPa [19]. The high synthesis pressure implied that $sp^3$ CaCO3 is not present in the Earth’s mantle (135 GPa is the core-mantle boundary pressure), and further experimental studies of $sp^3$ carbonates were shifted to other compositions. More recently, the $sp^2$-$sp^3$ transition in CaCO3 was revisited by Pickard and Needs [12], who predicted a new $sp^3$ CaCO3 phase ($P2_1/c$) at $P > 76$ GPa, calling for a new synthesis study.

Here we explore phase transitions in CaCO3 at $P > 40$ GPa via synchrotron x-ray diffraction, Raman spectroscopy, and first-principles calculations. We establish the stability field of $sp^3$-bonded $P2_1/c$ CaCO3 and show that this phase has a strong Raman band characteristic of fourfold carbon in its crystal structure. We provide computational insights into the $sp^2$-$sp^3$ phase-transition mechanism, which in CaCO3 appears to be a complex multistage process. Finally, our results support the notion of the effect of $sp^2$-$sp^3$ crossover on the carbonate crystal chemistry in the lower mantle.

II. METHODS

A. Experimental methods

Diamond-anvil cells (DACs) equipped with flat 200–300-μm culets were used to generate high pressure. Rhenium gaskets ($\sim$200-μm thick) were indented to $\sim$30–40 μm by the anvils and laser drilled in the center of the indentation in order to prepare a sample chamber with a diameter of 70–120 μm. The sample chamber was loaded with 99.95% CaCO3 (Alfa Aesar) mixed with Pt powder (20%–30%), which served both as a heating laser absorber and as a pressure standard [20]. No pressure-transmitting medium was used in the experiments.

X-ray diffraction (XRD) measurements and laser heatings were performed on the 13ID-D GeoSoilEnviroCARS beamline (Argonne National Lab, Advanced Photon Source) that allows in situ XRD collections at extreme $P-T$ conditions and a subsequent high-resolution mapping of the sample quenched to ambient temperature [21]. At all pressures a typical heating cycle involved (i) stepwise heating up to $T \sim 2000$ K, while following the diffraction pattern each 100–200 K; (ii) annealing at $T \sim 2000$ K, at which temperature we typically observed the formation of new XRD peaks, while moving the samples by $\sim 10$ μm in horizontal and vertical directions (1-μm step); and (iii) quenching and mapping the heated region in order to find areas with less Pt and more CaCO3. The x-ray energy was 37–42 keV focused to an $\sim 3 \times 4 \times 4$ μm spot. Two-dimensional XRD images were integrated using the DIOPTAS software [22] for online analyses. Selected XRD patterns were analyzed in POWDERCELL 2.4 and Le Bail refined in GSAS/EXPGUI [23,24]. Equation-of-state fitting was performed using EOSFITGUI [25] and VESTA [26] was used for structure visualization.

After the synthesis and XRD measurements, samples with $sp^3$ CaCO3 were characterized by Raman spectroscopy upon decompression at the Geophysical Laboratory using solid-state 488-nm (Spectra-Physics), 532-nm (Laser Quantum GEM), and 660-nm (Laser Quantum Ignis) laser excitations focused to a 3–4 μm spot size in diameter. The use of three excitation wavelengths allows unambiguously identifying bands that are Raman in origin. Backscattered Raman radiation was spatially filtered through a 50-μm pinhole (magnified by 10 using a Mitutoyo 20X NA0.4 long-working-length objective lens) to eliminate spurious signal and was collected by custom Raman spectrometers with CCD array detectors (PIXIS 100, Princeton Instruments) equipped with same-turret 300 and 1200/1500 grooves/mm gratings (HR 460, JOBIN YVON for the 488-nm setup and Acton SP2300/2500 of Princeton Instruments for 532 and 660 nm, respectively). The spectral resolution was $\sim 4$ cm$^{-1}$. The diamond Raman edge stress scale [27] was used to determine pressure on decompression with an uncertainty of $\sim 3$–5 GPa.

B. Theoretical methods

In this study we relied on the previous structural searches [12], but the use of USPEX yields similar results (not presented here). Structural relaxations and Raman intensity calculations were performed based on the density functional theory (DFT) as implemented in the QUANTUM ESPRESSO code [28]. The norm-conserving pseudopotential [29] was used and the electron-electron exchange and correlation was described by the local-density approximation (LDA) exchange-correlation functional of Ceperley and Alder, as parameterized by Perdew and Zunger (CA-PZ) [30]. The plane-wave cutoff energy was 250 Ry, and a $k$-point spacing ($2\pi \times 0.03$ Å$^{-1}$) was used to generate Monkhorst-Pack $k$-point grids for Brillouin zone sampling [31].

III. RESULTS AND DISCUSSION

A. X-ray diffraction

Room-temperature compression to $P > 40$ GPa results in a diffraction pattern with several low-intensity diffuse peaks. Annealing the samples at 40–102 GPa and 1500–2000 K produces new sharp Bragg reflections that can be indexed with the postaragonite (Pmmn) CaCO3 phase [9,18,32]. At 105 GPa, the dominant annealing product is different and forms a new spotty pattern in the XRD images (Fig. 1), but residual broad and diffuse reflections of precursor CaCO3 are also present after the heating. Crystallographic indexing of the new reflections yields monoclinic and orthorhombic solutions with unit cells consistent with the theoretical predictions of C2221 [11] and $P2_1/c$ [12] CaCO3.

Both theoretically proposed models allow indexing the new peaks, yielding almost identical densities at 105 GPa [5.01(2) g/cm$^3$]. Indeed, topological analysis, performed to reveal structural differences between the two $sp^3$ CaCO3 structures, shows a high degree of similarity between the $P2_1/c$ and C2221 structures with an identical atomic coordination (Ca$^{10+}$(CO3)$^{5-}$O$^{15+}$) and arrangement of Ca and C atoms. The only difference between the structures is the orientation of CO3 tetrahedra: all vertex-sharing helices in C2221 CaCO3 are right-handed, while half helices in the $P2_1/c$ CaCO3 are left-handed (Fig. 2). Despite these similarities, the $P2_1/c$ structure has an approximately 0.2 eV/f.u. lower enthalpy than
C22_1 CaCO₃, according to the computation of Pickard and Needs [12], advocating in favor of the monoclinic structure. Here we provide further support for the P2₁/c CaCO₃ as its structural model allows indexing severely split peaks, such as the −112 and 111 Bragg reflections at ~7° and the feature at ~9.2°, 2θ, as well as other minor reflections in the observed XRD pattern [Fig. 1(b)]. Accordingly, Le Bail refinements of the XRD patterns with the P2₁/c structure systematically yield ~5% better fits than that performed with the C22_1 structure. Please note that although we could not perform a full-profile refinement in this work due to the textured XRD pattern, the observed intensities are also consistent with the P2₁/c model [32]. Hence, we confirm the prediction of the P2₁/c CaCO₃, albeit at ~30 GPa higher than the theoretically predicted sp²-sp³ crossover pressure [12]. We note that although P2₁/c and C22_1 models of CaCO₃ have very similar powder XRD patterns, their Raman spectra may bear significant differences and may help to identify the sp³ CaCO₃ phase.

Depending on the probed sample area, we observed a coexistence of the postaragonite phase with P2₁/c CaCO₃ at 103–105 GPa, which indicates that this pressure is close to the phase transition pressure. At 105 GPa and 300 K, the unit-cell parameters of postaragonite CaCO₃ are a = 3.9360(6) Å, b = 4.4372(3) Å, and c = 3.9049(4) Å [ρ = 4.87(2) g/cm³], while those of P2₁/c CaCO₃ are a = 4.5288(13) Å, b = 3.3345(3) Å, c = 9.0927(24) Å, and β = 105.37(9)° [ρ = 5.01(2) g/cm³] [32]. The structure of sp³ CaCO₃ is ~3% denser than that of its sp²-bonded counterpart at 105 GPa (Fig. 3), which is larger than the previously reported density contrasts of 0.5% [19] and 1.25% [9] across the sp²-sp³ transition. Importantly, the average carbon-oxygen bond length increases across the phase transition from 1.228 to 1.315 Å (by ~7%) as a result of the increased carbon coordination. Note that in order to determine the change in C-O bond length over the sp²-sp³ transition in CaCO₃ we used the experimentally refined lattice parameters of the coexisting CaCO₃ phases at 105 GPa and theoretically computed atomic positions [12].
in combination with its yet unidentified phase, or minor nonmolecular CO\textsubscript{2} formed upon CaCO\textsubscript{3} thermal decomposition on Pt chunks. (b) Experimental spectrum of Gray areas are guides to compare the computed spectra with experiment.

Although we did not refine the atomic positions based on the experimental XRD, the observed intensities are consistent with the theoretically proposed \( P2_1/c \) CaCO\textsubscript{3} model\cite{32}. Because of the increase in C-O bond length, one would expect an abrupt decrease in the frequency of the carbon-oxygen stretching vibration across the \( sp^2 \)-\( sp^3 \) transition.

B. Raman spectroscopy

Group theory for \( P2_1/c \) CaCO\textsubscript{3} allows 30 Raman active vibrations (15\( A_g \) + 15\( B_g \)). Raman spectra collected from the laser-heated area consistently show at least eight new peaks, all of which appear to be characteristic of the vibrational normal modes in the new carbonate as the frequency and relative intensity of these bands are independent of the excitation wavelength (Fig. 4). Particularly important is the new intense band at 1025 cm\textsuperscript{-1}. Considering the increased C-O bond length across the \( sp^2 \)-\( sp^3 \) transition, it is reasonable to suppose that this high-frequency band corresponds to the C-O stretching vibration in the CO\textsubscript{4} unit. We have a rough check on this assignment by assuming a harmonic oscillator and an empirically established relation of the force constant and bond length for CX compounds \cite{33}: \( f = a(r - 0.61)^{-3} \), where \( X \) is a second-period element, \( a \) is a constant, and \( r \) is the C-X equilibrium bond length. Accepting the change in C-O bond length across the \( sp^2 \)-\( sp^3 \) transition as well as the frequency of C-O symmetric stretching vibration in \( sp^2 \) CaCO\textsubscript{3} at 105 GPa (1290 cm\textsuperscript{-1}), we obtain a frequency of 1059 cm\textsuperscript{-1} for this vibration in \( sp^3 \) CaCO\textsubscript{3}. This is within 5\% of the observed frequency of 1025 cm\textsuperscript{-1}, in support of its assignment to the C-O symmetric stretching in tetrahedral-coordinated carbon. A similar comparison for the graphite-diamond C-C stretch modes yields a frequency of 1273 cm\textsuperscript{-1} for the diamond \( T_{2g} \) band at 1 atm, which is again <5\% off its actual value (1333 cm\textsuperscript{-1}).

Furthermore, we reproduced the frequencies and intensities of all experimentally observed new Raman bands in our LDA-DFT computations of the Raman spectrum of \( P2_1/c \) CaCO\textsubscript{3} at 105 GPa\cite{32}. Please note that our computations systematically yielded ~1.5\% lower frequencies for all corresponding Raman bands observed in experiment, but when corrected for that, they show remarkable agreement with the experimental spectrum (Fig. 4). Such a correction is justified because LDA-DFT

![FIG. 4. (a) Raman spectra of CaCO\textsubscript{3} at 105 GPa collected with 488-, 532-, and 660-nm excitations. The gray curve is the spectrum of postaragonite CaCO\textsubscript{3} collected outside of the heated region. Black vertical bars are computed Raman modes of \( P2_1/c \) CaCO\textsubscript{3} (bottom) and postaragonite CaCO\textsubscript{3} (top) corrected upwards in frequency by 1.5\% and 0.5\%, respectively. The height of the bars is proportional to the band intensity. The peak indicated by the question mark deviates significantly from the \( P2_1/c \) CaCO\textsubscript{3} model and may be due to the unheated CaCO\textsubscript{3}, its yet unidentified phase, or minor nonmolecular CO\textsubscript{2} formed upon CaCO\textsubscript{3} thermal decomposition on Pt chunks. (b) Experimental spectrum of CaCO\textsubscript{3} laser heated at 105 GPa in comparison with the theoretical spectra of \( P2_1/c \) and \( C2\overline{2}2 \) CaCO\textsubscript{3} at 105 GPa as computed by LDA-DFT. Gray areas are guides to compare the computed spectra with experiment.](https://doi.org/10.1103/PhysRevB.96.104101)
yields an equilibrium volume that deviates from experimental observations by up to a few percent (e.g., [34]). In addition, we computed a Raman spectrum of CaCO3 at 105 GPa [32], which, expectedly, shows a C-O vibron frequency (996 cm\(^{-1}\)) that is very close to that in P2\(_1\)/c CaCO3 (1011 cm\(^{-1}\)). Despite this similarity, Raman bands in the 600–850 cm\(^{-1}\) spectral range show subtle, yet important, differences between the C22\(_1\) and P2\(_1\)/c structures. This difference is likely due to the contrasting packing of the CO\(_4\) chains in the structures, which results in slightly different frequencies of deformation modes in CO\(_4\) units. As is clear from Fig. 4(b), the P2\(_1\)/c model has better agreement with the experiment than the C22\(_1\) structure, providing strong spectroscopic evidence for P2\(_1\)/c CaCO3 at 105 GPa.

Upon decompression, we could follow the major Raman bands of sp\(^2\)-bonded CaCO\(_3\) down to 57 GPa (Fig. 5). The pressure-frequency dependence of these bands appears to be consistent with that computed for P2\(_1\)/c CaCO\(_3\), in support of the band assignment and product identification. Below 57 GPa, however, we could not observe any Raman bands that can be reliably assigned to P2\(_1\)/c CaCO\(_3\). Evidently, this indicates a full transformation to an sp\(^3\)-bonded CaCO\(_3\) phase below 57 GPa, as is also recorded in the intensification of the band at \(\sim1200\) cm\(^{-1}\), which is representative of CO\(_3\) groups (symmetric stretch). Identification of this phase was outside the scope of this work. We note, however, that the CaCO\(_3\) system is rich in metastable phases (e.g., [16]), and it is possible that the CaCO\(_3\) phase formed on unloading to 45 GPa is different from postaragonite.

IV. MECHANISM OF THE sp\(^2\)-sp\(^3\) TRANSITION IN CaCO\(_3\)

To reveal the mechanism of the Pmmn CaCO\(_3\) \(\rightarrow\) P2\(_1\)/c CaCO\(_3\) structural phase transition we performed variable-cell nudged-elastic-band (VCNEB) [35] simulations at 100 GPa, as implemented in the USPEX code [36,37]. First, we obtained an initial trajectory between the two phases using an algorithm developed by Stevanovic et al. [38] (in preparation) to map crystal structures onto each other. The mapping algorithm relies on criteria of minimizing the total Euclidian distance between the corresponding atoms in the end structures and minimizing the change in their coordination along the map (pathway). The initial pathway was subsequently refined by the VCNEB method for the minimum-energy pathway. Both Pmmn \(\rightarrow\) P2\(_1\)/c and P2\(_1\)/c \(\rightarrow\) Pmmn paths were prepared (in general, this algorithm may find different paths for forward and backward transitions), and then optimized with VCNEB. The lowest-enthalpy path is presented in detail here. VCNEB calculations required forces and stresses, which were computed by VASP [39] at the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) level of theory [40]. Our VCNEB calculations started with 10 intermediate images, and this number automatically increased whenever the path became longer. The climbing image – descending image technique [41] was used to precisely locate transition states (TSs) and intermediate minima [corresponding to potential metastable intermediate phases (IPs)]. Spring constants varied from 3 to 6 eV/Å\(^2\). VCNEB calculations were run for 1000 steps, enabling accurate and well-converging results. At a pressure of 100 GPa, the P2\(_1\)/c CaCO\(_3\) phase is more stable by 0.02 eV/atom than postaragonite. The barrier height is quite large, 0.14 eV/atom (or 0.70 eV/f.u.), implying that this transition is kinetically feasible only at high temperatures, in agreement with the experimental results of this work.

One important distinction between the crystal structures of sp\(^2\) and sp\(^3\) CaCO\(_3\) is that CO\(_3\) groups in postaragonite are isolated, while CO\(_2\) groups in P2\(_1\)/c CaCO\(_3\) are corner linked into pyroxenelike chains. Accordingly, the transformation mechanism is quite complex and can be divided into four stages (Fig. 6): each stage corresponds to an energy minimum, and boundaries between them correspond to TSs. In the first stage of the transformation, the postaragonite structure distorts gradually, with all CO\(_3\)-triangles becoming nonplanar. This distortion becomes critical at transition state 1 (TS1), triggering the second stage of the transition with all carbon atoms forming...
FIG. 6. Mechanism of the Pmmn (postaragonite) → $P_{21}/c$ transition of CaCO$_3$ at 100 GPa. Structures of initial postaragonite phase; transition states TS$_1$, TS$_2$, and TS$_3$; intermediate phases IP$_1$ and IP$_2$; and final $P_{21}/c$ of CaCO$_3$ are shown (for clarity, we highlighted CO$_4$ tetrahedra). The evolution of the five shortest C-O distances is shown across the proposed transition path.

additional bonds with oxygen atoms of the next layer, stitching isolated CO$_3$ groups into infinite chains of CO$_4$ tetrahedra. This topology corresponds to a local enthalpy minimum and has a $P_{21}$ symmetry (intermediate phase 1, IP$_1$). However, the enthalpy minimum of IP$_1$ is very shallow (Fig. 6). Towards transition state TS$_2$, one of the C-O bonds of the original CO$_3$ triangle gradually elongates and eventually breaks. In the third stage, between transition states TS$_2$ and TS$_3$, yet another metastable structure with a $P_{21}$ symmetry appears, featuring flat and noncoplanar CO$_3$ triangles and a shallow enthalpy minimum. As this structure distorts towards transition state TS$_3$, carbonate triangles reorient, nearby oxygens displace towards them, and eventually, one obtains infinite chains of CO$_4$ tetrahedra in the same topology as in the $P_{21}/c$ structure. The final fourth stage of the transformation is just a relaxation towards the theoretically predicted $P_{21}/c$ CaCO$_3$ structure [12].

Transition states define the crossover between different topologies, i.e., the point at which chemical bonds are formed or broken. It is very tempting to think of some maximum bond lengths characteristic of a given pair of atoms (e.g., C-O), beyond which bonds break. However, our results show this not to be the case as the values of
critical C-O bond lengths vary for different transitions. This suggests that the phase transitions are driven not just by the nearest-neighbor interactions but also by longer-range interactions and cooperative effects are important.

Three fundamental comments are necessary regarding the mechanism of this phase transition. First, the intermediate minima (IP1 and IP2) in this case are so shallow that they are unlikely to be quenched in the experiment: these minima are not strongly kinetically protected and will rapidly decay into postaragonite and $P2_1/c$, respectively. The role of these intermediate minima is to be “stepping-stones” on the transition pathway, lowering the overall barrier. This is in contrast to the case of BH, a newly predicted compound, where the phase transition involves a very deep and most likely experimentally obtainable, intermediate phase [42]. Second, the transition mechanism discussed here is the best mechanism that we could find (i.e., with the lowest activation enthalpy). However, as we did not perform an exhaustive search over transition paths, we cannot rule out the possibility of other mechanisms. At the moment, there is no algorithm for predicting the globally optimal transition pathway, even within the mean-field picture. Third, the mechanism we just presented is based on the mean-field approach accesses crude but crystallographically and intuitively tractable models. Full exploration of nucleation and growth phenomena requires very large systems (with $10^2–10^4$ atoms) and advanced sampling techniques, such as transition-path sampling (e.g., [43]); we refer the reader to our recent works employing this methodology (also implemented in the USPEX code) [44,45] and note that such simulations require an accurate force field and, at the $ab\ initio$ level of theory, are computationally unaffordable at the moment.

### V. EXPERIMENTAL EVIDENCE FOR $sp^3$-BONDED CARBONATES

Identification of $sp^3$-bonded carbonates based solely on XRD is problematic as it requires precise structure determination, which is often challenging at high pressure. Most previous reports on $sp^3$ carbonates in MgCO$_3$ and FeCO$_3$ systems relied on Le Bail–type fits of theoretically predicted structures to experimentally observed powder-like XRD patterns. For example, Ref. [46] has reported $sp^3$ MgCO$_3$ at $P \sim 80$ GPa and $T \sim 2000$ K based on the match of XRD to the theoretical prediction of Ref. [11]. One notable exception is the report of Mg$_2$Fe$_2$CO$_3$O$_9$ with tetrahedrally coordinated carbon at 135 GPa [47] with single-crystal-structure solution methods applied to a multigrain sample synthesized in the (Mg,Fe)CO$_3$ system. We summarize previous experimental reports on $sp^3$ carbonates in the Table I.

Unlike XRD, vibrational spectroscopy provides bonding fingerprints of the material and is particularly sensitive to the carbon hybridization and chemical environment (e.g., [50]). As such, Raman spectroscopy and/or infrared spectroscopy provide independent evidence for tetrahedrally coordinated carbon and must be used together with crystallographic probes for reliable identification of $sp^3$ carbonates in high-pressure experiments. Realizing weaknesses of XRD probes in identifying the bond character, Boulard et al. [49] reported on synchrotron infrared absorption experiments in (Mg$_{0.5}$Fe$_{0.5}$)CO$_3$ at 80 GPa, noting a new band that is characteristic of the C-O asymmetric stretching vibration in CO$_4$ groups. The band assignment relied on first-principles calculations of the infrared spectrum of $sp^3$ MgCO$_3$ ($P2_1/a$ space group). However, other theoretically predicted bands were not fully assigned in the experiment [49].

In contrast to previous studies, here we provided strong spectroscopic evidence of $sp^3$ carbonates. Specifically, the intense Raman band at $\sim 1025$ cm$^{-1}$ (at 105 GPa) and its pressure dependence ($\sim 1.8$ cm$^{-1}$/GPa) in $P2_1/c$ CaCO$_3$ are characteristic of the symmetrical stretching vibration in its CO$_4$ groups. In principle, these spectroscopic features can be used in future studies of $sp^3$ carbonates at high pressure to confirm fourfold carbon coordination.

Our results are also important to validate density functionals used in crystal-structure predictions. Pickard and Needs [12] noted that PBE-GGA and LDA yield essentially similar transition pressures and thus the predicted value is reliable. Here we identified the $sp^3$ CaCO$_3$ phase and the $sp^2$-$sp^3$ crossover pressure (105 GPa), which appears to be $\sim 30$ GPa higher than the theoretically predicted transition pressure of 76 GPa (at 0 K), suggesting that the entropy term in the free energy is substantial. We showed that high temperature is required to overcome the kinetic barriers associated with the $sp^2$-$sp^3$ transition, indicating that complex energy landscapes are typical not only of pure carbon but also of carbonates. As a result, a variety of metastable $sp^3$ CaCO$_3$ polymorphs have been observed at $P < 40$ GPa [16]. If $sp^3$-CaCO$_3$ also exhibits rich polymorphism, then the Raman signature of $sp^3$ carbonates may come in useful for their identification.

### VI. GEOCHEMICAL AND GEOPHYSICAL IMPLICATIONS OF $sp^3$ CARBONATES IN THE LOWERMOST MANTLE

The equilibrium composition of mantle carbonates is governed by the chemical reactions with surrounding minerals [13,14,51] and the thermodynamic stability of corresponding...
carbonate phases. Due to the chemical interaction with pyroxene or bridgmanite in the mantle, CaCO$_3$ transforms to Fe-bearing magnesite (up to 10% Fe) at 2–80 GPa [53–56] despite several phase transitions in $sp^2$ CaCO$_3$ which can modify the chemical equilibrium in this pressure range [9,12]. Also, the spin transition in Fe-bearing MgCO$_3$ at $P \sim 45$ GPa may promote iron solubility in the carbonate phase due to crystal-field effects [57] and the ionic size similarity of low-spin Fe$^{2+}$ to Mg$^{2+}$ [58], but this has never been quantitatively addressed in experiment. The $sp^2$-$sp^3$ transition in MgCO$_3$ at $P \sim 80$ GPa further uplifts the Mg-rich carbonate composition, as revealed by a computation of enthalpies in the reaction MgCO$_3$ + CaSiO$_3$ = CaCO$_3$ + MgSiO$_3$ as a function of pressure and accounting for phase transitions [11,12]. The theoretically predicted $sp^2$-$sp^3$ transition in CaCO$_3$ at 76 GPa eventually stabilizes CaCO$_3$ against MgCO$_3$ at $P > \sim 100$ GPa [12]. Here we have synthesized the predicted $P_{21}/c$ CaCO$_3$ at $P \sim 105$ GPa and $T \sim 3000$ K, about 30 GPa higher than the theoretically predicted $sp^2$-$sp^3$ transition pressure at 0 K. Taking into account this 30 GPa difference, we propose that the crossover to Ca carbonates in Earth (i.e., at high temperature) may be expected at $P \sim 135$ GPa, which corresponds to the pressure at the core-mantle boundary. This inference can be tested via high-pressure studies of chemical reactions in mechanical mixtures of MgCO$_3$ with CaSiO$_3$ or CaCO$_3$ with MgSiO$_3$ at high pressure and temperature.

**VII. CONCLUSIONS**

In summary, we located the $sp^2$-$sp^3$ transition in CaCO$_3$ and identified the $P_{21}/c$ CaCO$_3$ at $P > \sim 105$ GPa using x-ray diffraction and Raman spectroscopy. Using first-principles methods, we showed that the mechanism of the $sp^2$-$sp^3$ crossover in CaCO$_3$ involves several intermediate phases with $sp^2$ and $sp^3$ bonding motifs. Finally, our results support the idea of the crossover in the carbonate crystal chemistry that leads to Ca-rich carbonates at the base of the mantle.

**ACKNOWLEDGMENTS**

This work was supported by the National Science Foundation, Grants No. NSF EAR/IF 1531583, No. NSF EAR-1520648, and No. NSF EAR/IF-1128867, No. NSF EAR-1723160; the Army Research Office (56122-CH-H); the Carnegie Institution of Washington; and the Deep Carbon Observatory. S.S.L. was partly supported by State Assignment Project No. 0330-2014-0013. Portions of this work were performed at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation Division of Earth Sciences (Grant No. EAR-1128799) and Department of Energy Geosciences (Grant No. DE-FG02-94ER14466). This research used resources of the Advanced Photon Source, a US Department of Energy (DOE), Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The calculation was performed on the TianheII supercomputer at Chinese National Supercomputer Center in Guangzhou. We thank Dr. E. V. Alexandrov for his assistance in topological analysis. P.N.G. was supported by the Ministry of Education and Science of the Russian Federation (Grants No. 14.B25.31.0032 and No. MK-3417.2017.5). A.F.G. was partly supported by the Chinese Academy of Sciences visiting professorship for senior international scientists (Grant No. 2011T2J20), the Recruitment Program of Foreign Expert, the National Natural Science Foundation of China (Grants No. 21473211 and No. 11674330), and the Chinese Academy of Sciences (Grant Bi, YZ201524). A.R.O. was supported by the Russian Science Foundation (Grant No. 16-13-10459).