Investigation of exotic stable calcium carbides using theory and experiment

Yan-Ling Li¹, Sheng-Nan Wang², Artem R. Oganov²,³,⁴,⁵, Huiyang Gou⁶, Jesse S. Smith⁷ & Timothy A. Strobel⁶

It is well known that pressure causes profound changes in the properties of atoms and chemical bonding, leading to the formation of many unusual materials. Here we systematically explore all stable calcium carbides at pressures from ambient to 100 GPa using variable-composition evolutionary structure predictions using the USPEX code. We find that Ca₅C₂, Ca₂C, Ca₃C₂, CaC, Ca₂C₃ and CaC₂ have stability fields on the phase diagram. Among these, Ca₂C and Ca₂C₃ are successfully synthesized for the first time via high-pressure experiments with excellent structural correspondence to theoretical predictions. Of particular significance is the base-centred monoclinic phase (space group C₂/m) of Ca₂C, a quasi-two-dimensional metal with layers of negatively charged calcium atoms, and the primitive monoclinic phase (space group P2₁/c) of CaC with zigzag C₄ groups. Interestingly, strong interstitial charge localization is found in the structure of R-3m-Ca₅C₂ with semi-metallic behaviour.
Unexpected chemical reactions can happen under extreme conditions, with emergence of rich phase diagrams and materials possessing intriguing properties. Recently, by combining variable-composition structure prediction methods with first-principles total energy calculations, pressure-composition (P-x) phase diagrams were predicted for such binary systems as Mg-O (ref 2) and Na-Cl (ref 3). In both cases, the predicted unexpected compounds have been successfully synthesized. Elemental carbon and calcium both exhibit rich diversity of stable and metastable phases under pressure. Compressed calcium shows unique structural and electronic properties and exhibits the highest recorded superconducting critical temperature among pure elements. For carbon, only graphite and diamond are experimentally known as thermodynamically stable solids (graphite is thermodynamically stable at ambient condition and diamond under high pressure), although numerous metastable phases are known. For example, by applying pressure to graphite at low temperatures, a new superhard carbon allotrope was found, and its properties match those of one of the theoretically predicted structures (M-carbon). The well-known Ca carbides include CaC2 and CaC3, whose high-pressure behaviours have been studied experimentally and by ab initio calculations.

An interesting structural evolution has been uncovered under pressure: carbon atoms polymerize from dumbbells to one-dimensional (1D) chains to ribbons to two-dimensional (2D) graphene sheets in compressed CaC2 (ref 16) and from graphite sheets to a mixed sp2–sp3 structure in CaC6 (ref 20). In addition, superconductivity was predicted in metallic high-pressure phases of CaC2 with critical temperatures comparable to those observed in CaC6 (ref 16).

Here, using variable-composition structure prediction code USPEX, the pressure-composition phase diagram of the Ca-C system was explored in order to fully understand the structural diversity and evolution of the C-C bonding types under high pressure. This resulted in five newly predicted stable stoichiometries (CaC2, CaC, Ca3C2, CaC and CaC3) with diverse carbon arrangements: isolated atoms in CaC2, hitherto unknown zigzag tetramers in CaC, and ribbons consisting of five-membered rings in CaC. Two phases (CaC and Ca3C2) were confirmed experimentally via in situ synchrotron powder X-ray diffraction (PXRD) measurements. Most surprising is that the low-pressure phase (monoclinic C2/m structure) of CaC exhibits quasi-2D metallic behaviour and contains negatively charged calcium atoms. In addition, strong interstitial electron localization was found in the newly predicted R-3m phase of CaC2, just as in compressed elements Li (ref 22), Na (ref 23) and Ca (ref 6), as well as in the compound Mg2O2 (ref 2).

Results

Convex hull. We have used the ab initio evolutionary algorithm USPEX, which can simultaneously find stable stoichiometries and the corresponding structures in multicomponent systems, to explore stable Ca-C compounds and their structures. In these calculations, all stoichiometries were allowed (with the constraint that the total number of atoms in the unit cell be below 16 atoms), and calculations were performed at 10, 20, 40, 80 and 100 GPa. The pressure-composition phase diagram of the Ca-C system is given in Fig. 1a, in which the convex hull was obtained from the calculated enthalpies of the most stable structures for each composition at a given pressure. Thermodynamically, the convex hull at a given pressure connects the phases that are stable against decomposition into other binaries or the elements.
In order to analyse these predicted structures, we recall that the C–C bond length depends on the bond order, and at 1 atm these lengths are 1.20 Å for the triple C–C bond, 1.33 Å for double bond and 1.54 Å for single C–C bond. The carbon patterns predicted for calcium carbides, on the basis of calculations presented in this work, are plotted in Fig. 3. The carbon patterns together with their pressure range of existence in calcium carbides are summarized in Fig. 4 and in Supplementary Table 2. Combining this knowledge with the results of Bader analysis (see Supplementary Table 1), we unravel very diverse chemistry. From the results of the Bader analysis, one can clearly see the correlation between the charge and volume: negatively charged calcium atoms occupy significantly greater volume. In addition, we observe the decrease in C–C bond order from triple to double to single bonds as pressure increases. Note, however, that at pressures up to 100 GPa, the carbon-richest stable compound is CaC₂. Below we consider the predicted phases in order of increasing carbon content.

\[ \text{Ca}_5 \text{C}_2 \]  

The stable structure of Ca₅C₂ has a \( R-3m \) symmetry. It is a semi-metal (see Supplementary Fig. 8) and is thermodynamically stable at pressures ranging from 58 GPa to at least 100 GPa (see Fig. 4). This phase has novel structural features: it can be described as consisting of alternating CaC₂ layers (where Ca is octahedrally coordinated by C atoms) and layers with

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**Figure 2 | The predicted crystal structures of stable Ca-C compounds.** (a) Thermodynamically stable \( \overline{P}nma \) structure of \( \text{Ca}_2 \text{C} \). (b) The metastable low pressure \( P4/mbm \) structure of \( \text{Ca}_3 \text{C}_2 \). (c) Thermodynamically stable high pressure \( C2/c \) structure of \( \text{Ca}_3 \text{C}_2 \). (d) Thermodynamically stable \( P2/c \) structure of \( \text{Ca}_3 \text{C}_2 \). (e) Thermodynamically stable high pressure \( \overline{I}m\overline{m}a \) structure of \( \text{CaC} \). (f) \( \text{Ca}_2 \text{C}_3 \) crystallizes in \( C2/m \) structure at pressures up to 28 GPa. (g) Thermodynamically metastable \( C2/c \) structure of \( \text{Ca}_3 \text{C}_2 \). (h) Thermodynamically metastable \( \overline{P}2 \overline{1}c \) structure of \( \text{Ca}_3 \text{C}_2 \). (i) Thermodynamically metastable \( \overline{I}m\overline{m}a \) of \( \text{Ca}_3 \text{C}_2 \). (j) Thermodynamically stable \( \overline{P}1 \) structure of \( \text{Ca}_3 \text{C}_2 \). (k) Thermodynamically stable \( \overline{I}m\overline{m}m \) structure of \( \text{CaC}_2 \). The blue and brown spheres represent calcium and carbon atoms, respectively.
composition Ca. The electron localization function distribution in Ca$_2$C$_2$ shows strong charge transfer from Ca to C. Non-nuclear charge density maxima are located in the Ca$_4$ layer as plotted in Fig. 5 (electron localization function = 0.75 at 60 GPa). Bader charges are $+1.039$ for Ca$_1$, $+0.823$ for Ca$_2$, $+0.973$ for Ca$_3$, and $-0.459$ for the interstitial electron density maximum.

Ca$_2$C. Known alkali earth methanides include well-known Be$_2$C ($Fm-3m$, $Z = 4$) and Mg$_2$C (antifluorite) recently synthesized by Kurakevych et al. However, no theoretical or experimental information has been reported on the methanide Ca$_2$C (ref. 26). According to our calculations, Ca$_2$C is thermodynamically stable above 15 GPa (space group $Pnma$ ($Z = 4$)). For $Pnma$-Ca$_2$C, we observe the largest negative charge of carbon atoms among all these phases: $-2.321$. In this semiconducting phase with band gap of 0.64 eV at 14 GPa (see Supplementary Fig. 9), C atoms are isolated and one can represent this compound as a carbide with an idealized charge transfer scheme (Ca$^{2+}$)$_2$C$_4$ adhering to the Zintl concept. Metallic metastable C$_2$m-Ca$_2$C has a unique structure, consisting of alternating layers of stoichiometry Ca$_2$(C$_2$) and Ca$_2$ (two kinds of calcium atoms play distinctly different roles, see Fig. 6 a), and these layers have net charges of $+0.582$ and $-0.582$, respectively (see Supplementary Table 1). What is unusual is that the Ca layer is negatively charged, that is, it is a reservoir of electrons. To further analyse this phenomenon, it is instructive to look first at the Ca$_2$(C$_2$) layer. This C$_2$ group...
can be represented as having a triple C–C bond and its ideal charge is $-2$ (Bader charge is $-1.892$), and if each Ca had the ideal charge of $+2$, the total charge of the Ca$_2$(C$_2$) layer would be $+2$, and two electrons would be transferred to the Ca$_2$ layer (see Supplementary Table 1). In reality, the C–C bond here has a somewhat lower order (C–C distance is 1.28 Å at 5 GPa) and therefore takes more electrons from Ca atoms, leaving less for the Ca$_2$ layer, but not changing the picture qualitatively. To our knowledge, this is the first example of negatively charged metal atoms in a compound with more electronegative atoms. Note the enormous difference of Bader volumes of the positively and negatively charged Ca atoms (16.570 versus 41.901 Å$^3$). One can expect that the electrons in the Ca layer are very loosely bound, and the work function of this compound can be expected to be extremely low. The density of states of the metastable C2/m phase of CaC reveals a remarkable step-like feature near the bottom of the valence band, followed by a nearly constant density of states (see Fig. 6b), presenting an example of a quasi-2D electronic structure as observed in Li–Be alloys$^{27}$. The calculated Fermi surface of C2/m-CaC at 3 GPa has a hollow square cylinder-like Fermi shape along the Γ–V direction (that is, reciprocal lattice basis vector $b_1$ direction) in the Brillouin zone (BZ), signalling quasi-2D electronic properties (see Fig. 6c).

Ca$_3$C$_2$. For Ca$_3$C$_2$, no thermodynamically stable phase exists below 50 GPa. A metastable P4/mmbm ($Z = 2$) phase, favoured in the pressure range from 5 to 30 GPa, transforms into a C2/c ($Z = 4$) structure at 30 GPa, which is thermodynamically stable above 50 GPa. The structure of P4/mmbm-Ca$_3$C$_2$ contains doubly bonded C$_2$ groups (C–C distance 1.39 Å at 20 GPa), with an ideal charge $-4$, that is, accepting four electrons from calcium atoms, leaving two electrons per formula to form Ca–Ca bonds in this metallic compound. Metallic C2/c-Ca$_3$C$_2$ with a pseudogap at the Fermi level (see Supplementary Fig. 10) has singly bonded C$_2$ groups (C–C bond length 1.51 Å at 38.7 GPa), which have ideal charge $-6$, exactly balanced by three Ca atoms in the formula.

CaC. Metallic CaC has two thermodynamically stable phases below 100 GPa. At 14 GPa, the metastable orthorhombic Immm structure transforms into a monoclinic P2$_1$/c structure (stable thermodynamically above 26 GPa, favoured over a wide pressure range of 14–57.5 GPa), followed by a thermodynamically stable Imma structure. P2$_1$/c-CaC is very interesting because its structural formula Ca$_4$(C$^3_4$) contains a unique and hitherto unknown zigzag C$_4$ group, with C–C distances between 1.48 and 1.50 Å at 14 GPa, indicating bond orders between 1 and 2 and ideal charges of about $-2.5$ for the end C atoms (Bader charge $-1.447$) and about $-1$ for the central C atoms (Bader charge $-0.905$).

Imma-CaC has infinite zigzag chains of C atoms (C–C bond length of 1.55 Å at 57.5 GPa, indicating a weakened single bond) in the y axis direction. The structural formula of metastable Immm-CaC is Ca$_3$(C$_2$), and with a doubly bonded C$_2$ group (C–C distance 1.33 Å at 7.1 GPa) that has an ideal charge of $-4$ (Bader charge $-2.340$), it exactly balances the ideal charge of two Ca atoms. All three phases of CaC beautifully conform to the trend of increasing polymerization of the C sublattice with increasing pressure.

Ca$_3$C$_4$. The structure of Mg$_2$C$_3$ (space group Pnma, $Z = 2$), the only known alkaline-earth metal allylenide with C$_3^-$ anions$^{26}$,
was considered when searching for stable phases of CaC$_2$. Total energy calculations exclude the possibility of the ambient-pressure MgC$_2$-type structure. The semiconducting C$_2$m structure (band gap of 1.06 eV at 10 GPa, see Supplementary Fig. 11) is instead the most stable one below 34.5 GPa (thermodynamically stable from 0 to 28 GPa), followed by metastable C$_2$c structure. By fitting energy versus volume data to the third-order Birch–Murnaghan equation of state$^{28}$, the calculated bulk modulus $B_0$ of C$_2$m-CaC$_2$ is $\sim$ 89 GPa, which is higher than that of CaC$_2$ (50 GPa). At $\sim$ 40 GPa, the metallic C$_2$c structure transforms into a metastable P-1 structure (metal), which dominates the pressure range between 40 and 65 GPa. At higher pressures, a metallic metastable Imma structure is stable and contains zigzag carbon chains (Figs 3 and 4). We searched at much higher pressures for 3D-polymeric carbon frameworks in Ca$_2$C$_3$, but found none at pressures up to at least 300 GPa. For comparison, in CaC$_2$, we have found that graphene sheets predicted in the high-pressure phase can be stable up to at least 1TPa (ref. 16).

For Ca$_2$C$_3$, the carbon arrangement changes from isolated C$_3$ to carbon chains to ribbons (Fig. 3). The structure of C$_2$m-Ca$_2$C$_3$ can be described as Ca$_2$ layers linked together by nearly linear symmetric C$_2$ groups with double C–C bonds (C–C distances 1.32 Å at 18.1 GPa). With this configuration, the total charge of the C$_3$ group should be $-4$ (Bader charge $-2.692$), exactly compensating the charge of two Ca atoms in the formula (see Supplementary Table 1). Central carbon atoms in the C$_3$ group in this valence scheme should be neutral, and yet turn out to have a large negative Bader charge of $-0.738$, whereas the end atoms, whose idealized charge is $-2$, develop a lower Bader charge ($-0.977$). This discrepancy is explained by the effects of Ca atoms, which form significant bonds with the central carbon atom in the C$_3$ group and transfer some electronic charge to them. Most recently, some of us reported the prediction and synthesis of $\beta$-Mg$_2$C$_3$ (ref. 29), which is isostructural with our C$_2$m-Ca$_2$C$_3$ reported here. The structure of C$_2$c-Ca$_2$C$_3$ (C–C distances 1.43–1.47 Å at 34.5 GPa) has an idealized charge transfer scheme $\text{Ca}_4^{+}:\text{C}_2^{2-}$. In this metallic phase, C atoms are polymerized into infinite chains with nearly closed six-member rings running through channels of Ca host lattice. P-1-Ca$_2$C$_3$ features a complicated extended 1D ribbon of carbon atoms with nearly single C–C bonds (lengths 1.47–1.50 Å at 40 GPa).

Imma-Ca$_2$C$_3$ has a very interesting structure with extended 1D ribbons of carbon atoms cut from the graphene layer. Bond lengths in this ribbon are 1.50–1.52 Å at 70 GPa, slightly longer than in graphene and indicating predominantly single bonds. Electronic structure calculations show that both P-1 and Imma phases of Ca$_2$C$_3$ are metals. On the basis of Allen and Dynes modified equation$^{30}$, we have checked for superconductivity in these phases at 34 and 65 GPa, respectively, and found none.

CaC$_2$. CaC$_2$ is thermodynamically stable above 21 GPa (see Fig. 1a). The lower-pressure phases C$_2$m and Cmcn reported previously$^{16}$ are metastable, which could be unrecognizable by calculating enthalpy of formation ($\Delta H_f$) at lower pressure. Considering that graphite is the ground state of carbon at zero pressure, we performed additional calculations where the van der Waals interaction is accounted for by using the optPBE-van der Waals functional$^{23}$. At zero pressure, the calculated $\Delta H_f$ ($-0.17$ eV per atom) of CaC$_2$ is close to the experimental standard $\Delta H_f$ ($-0.21$ eV per atom at 298 K and 1 atm (ref. 32)) but higher than that of CaC$_3$, confirming the thermodynamic metastability of CaC$_2$ under ambient conditions (see Fig. 1a). It is very unexpected, but the above numbers fully confirm this conclusion, that the well-known and industrially produced compound CaC$_2$ is metastable under ambient conditions, while the so far never seen compound Ca$_2$C$_3$ is actually stable. This could be either due to kinetics, or due to high-temperature conditions of synthesis. In addition to our previous result$^{16}$, we found a new phase with the P-1 symmetry, which contains infinite carbon chains with five-membered rings (C–C distance is between 1.442 and 1.507 Å at 20 GPa (see Fig. 3i), signalling single or double bonds), and is the lowest enthalpy structure over a wide pressure range from 7.5 to 37 GPa (thermodynamically stable from 21 to 37 GPa, see Fig. 4 and Supplementary Fig. 12). With further application of pressure, metallic P-1-CaC$_2$ transforms into metallic Immm-CaC$_2$ (ref. 16), in which carbon atoms are polymerized to form quasi-1D ribbons (see Figs 2–3).

**Experiments.** In order to confirm theoretical structure predictions, we performed synthesis under high-pressure/high-temperature conditions. Diamond anvil cells were loaded with both calcium- and carbon-rich Ca + C mixtures, compressed to pressures up to 25 GPa, heated to temperatures up to $\sim$ 2,000 K and probed in situ using synchrotron PXRD. Under these pressure conditions, the formation of Immm-CaC$_2$, C$_2$m-Ca$_2$C$_3$ and Pnnma-Ca$_2$C may be expected on the basis of thermodynamic stabilities, as these phases are the only stable ones that appear on the convex hull up to 25 GPa (see Fig. 1); indeed, two of these three structures were observed experimentally.

When samples were compressed above $\sim$ 10 GPa and heated to $\sim$ 2,000 K, mixtures of elemental glassy carbon and face-centred cubic (fcc) Ca transformed into a new low-symmetry phase. After comparison with density functional theory (DFT) structure predictions, PXRD reflections originating from this phase were readily indexed to the monoclinic C$_2$m/Ca$_2$C$_3$ structure with excellent agreement between experiment and theory (see Supplementary Table 3). Figure 7 shows experimental PXRD data obtained at 17 GPa with $a = 5.169(4)\ \text{Å}, \ b = 4.994(3)\ \text{Å}, \ c = 6.322(3)\ \text{Å} \text{ and } \beta = 128.53(3)^\circ$, which compares with $a = 5.151\ \text{Å}, \ b = 4.962\ \text{Å}, \ c = 6.306\ \text{Å} \text{ and } \beta = 128.81^\circ$ for the theoretical structure relaxed at 18 GPa. This sample was decompressed in steps of $\sim 2$ GPa to obtain lattice parameters as a function of pressure (see Fig. 8). Theoretical lattice parameters show excellent agreement with experimental data in the high-pressure range for both C$_2$m/Ca$_2$C$_3$ phases, and the Ca$_2$C$_3$ metastable phase was recoverable to ambient pressure. This confirms the thermodynamic stability of CaC$_2$ at pressures up to 25 GPa, in good agreement with theoretical predictions (89 GPa).

At pressures above $\sim 22$ GPa, a second carbide phase (Pnnma-Ca$_2$C$_3$) was synthesized upon laser heating. This phase has reproducibly formed both from elemental Ca + C mixtures and from samples containing C$_2$m-Ca$_2$C$_3$, indicating disproportionation of CaC$_3$ into a more stable carbide phase when pressure is raised above $\sim 22$ GPa, i.e. above its predicted stability field. Figure 7 shows experimental PXRD data at 24 GPa with $a = 6.122(1)\ \text{Å}, \ b = 4.004(1)\ \text{Å}, \ c = 7.223(1)\ \text{Å} \text{, which compares with } a = 6.044\ \text{Å}, \ b = 3.977\ \text{Å}, \ c = 7.265\ \text{Å} \text{ for DFT calculations at the same pressure (see Supplementary Table 4). Calculated lattice parameters show an average absolute deviation of 0.5% from experimental values between 25 and 5 GPa (see Fig. 8), which was the lowest pressure obtained due to failure of a diamond anvil. Fitting the P–V data to a second-order Birch–Murnaghan equation of state yields $B_0 = 84(2)$ GPa, in good agreement with theoretical predictions (89 GPa).

**Discussion**

We find that the carbon sublattice within all predicted carbide phases has close correlation with the Ca:C ratio (see Fig. 2). With increasing carbon content, isolated carbon atoms are
polymersized, in turn, into C₂ dumbbells, C₃ and C₄ groups, chains, ribbons and graphene sheets (see Fig. 4 and Supplementary Table 2). The polymeric carbon structures reveal an expected trend when comparing with the structural chemistry of the heavier congeners of group IV elements in Zintl phases (alkali or alkaline-earth silicides, germanides and stannides)\(^{17,33}\). Yet in spite of certain similarities to silicides, calcium carbides differ from them because of distinct bonding features. Combining present analysis and our previous results\(^{16,17,20}\), one can conclude that for the Ca-C system, one can cover \(sp\) to \(sp^2\) to \(sp^2 + sp^3\) hybridizations of carbon as pressure increases. This pressure-induced structural evolution of carbon was also found in other alkali metal or alkaline-earth metal carbides\(^{17,20,24}\). Together with our previous results for CaC\(_2\) (ref. 16) and CaC\(_6\) (ref. 20), it is clear that a 3D network of carbon in CaC\(_x\) can be formed when \(x\) is greater than 2 (from sheets to 3D frameworks to Ca-C phase separation with slabs of diamond at high C content), consistent also with the behaviour of the metastable CaC\(_x\) compound found in our structural searches. On the other hand, the structural features of carbon-rich compounds\(^{20}\) can be extended to alkali-metal or alkaline-earth metal congeners of the group-IV elements, which allows one to fabricate a variety of the 3D framework structures of the group-IV elements by removing metal sublattices. The unexpected mechanical\(^{20,34}\) or electronic characteristics\(^{35}\) uncovered in these 3D framework structures pave the way to novel materials.

**Methods**

**Structure search and theoretical calculations.** Searches for stable structures of the Ca-C system under compression were carried out using the evolutionary algorithm USPEX in combination with the VASP code\(^{36}\) on the basis of DFT within the generalized gradient approximation with the exchange-correlation functional of Perdew, Burke and Ernzerhof\(^{37}\), employing the projector-augmented wave\(^{38}\) method [He] and [Ne] cores for C and Ca atoms, respectively. For carbon, a ’hard’ PAW potential was used in search for stable structures. For the crystal structure searches, we used a plane-wave basis set cutoff of 700 eV and performed the BZ integrations using uniform Gamma-centred k-point meshes. The most
interesting structures were further relaxed at a higher level of accuracy with a basis set cutoff of 1,000 eV and a k-point grid of spacing \( 2\pi \times 0.018\ \text{Å}^{-1} \). Iterative relaxation of atomic positions was stopped when all forces were smaller than 0.001 eV/\text{Å}. For compounds predicted via variable-composition searches, we re- 
searched their stable structures using fixed-composition calculations, with two, three and four formula units per unit cell. For \( \text{CaC}_2 \), some evolutionary calculations were also performed under the pressure of 30, 50, 80, 120, 160, 240 and 300 GPa with two or four chemical formula units per unit cell so as to discern the possibility of 3D network carbon.

The enthalpy of formation per atom of \( \text{CaC}_2 \) is defined as

\[
\Delta H(\text{CaC}_2) = -H(\text{CaC}_2) - nh(Ca) - n\text{H}(\text{C})/(n + m),
\]

where all enthalpies \( H \) are given at the same pressure and zero temperature. At a given pressure, the calcium carbides located on the convex hull are thermodynamically stable against decomposition to any other binaries or the elements, while the compounds above the convex hull are meta-stable.

The Bader analysis was performed for exploring chemical bonding and local electrons. To get a converged charge density, the wave plane kinetic energy cutoff of 1,000 eV and Monkhorst-Pack k-point meshes with the reciprocal space resolution of \( \pi \times 0.02\ \text{Å}^{-1} \) were used for all the structures. A series of FFT grids to accurately reproduce the correct total core charge were tested by increasing parameters NG(X,Y,Z)F to 1.5, 2 and 2.5 times the default one.

The lattice dynamics and superconducting properties of \( \text{CaC}_2 \) were calculated by the Quantum ESPRESSO package using\(^4\) the electron-phonon coupling was convergent with a finer grid of \( 48 \times 48 \times 48 \) k points and a Gaussian smearing of 0.01 Ry. For other compounds, phonon calculations were performed using the Phonopy code.\(^4\) The Fermi surface of \( \text{C}_2\text{H}_2\text{C}_2 \) at 3 GPa was calculated using Quantum ESPRESSO and \( 16 \times 16 \times 8 \) of Monkhorst-Pack k-point mesh.

**Experiment.** Reagents for experimental studies consisted of commercial calcium metal (Sigma-Aldrich, dendritic pieces, 99.99%) and glassy carbon (Sigma-Aldrich, 2–12 μm, 99.95%). The carbon powder was degassed for 12 h at ~200 °C in a vacuum oven and then sealed under Ar. Diamond anvil cell syntheses were performed at pressures up to 25 GPa and 2,000 K with \( \text{in situ} \) PXRD) were performed at High Pressure Collaborative Access Team (HPCAT), sector 16, of the Advanced photon Source. A small amount of carbon powder and Ca metal shavings were pressed in thin layers between a rhenium gasket in a diamond anvil cell equipped with 400-μm cuvettes. The electron–phonon coupling was convergent with a finer grid of \( 48 \times 48 \times 48 \) k points and a Gaussian smearing of 0.01 Ry. For other compounds, phonon calculations were performed using the Phonopy code.\(^4\) The Fermi surface of \( \text{C}_2\text{H}_2\text{C}_2 \) at 3 GPa was calculated using Quantum ESPRESSO and \( 16 \times 16 \times 8 \) of Monkhorst-Pack k-point mesh.

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Author contributions

Y.-L.L. and A.R.O. designed the research. T.A.S. designed the experiments. Y.-L.L., A.R.O. and S.-N.W. performed calculations. H.G., J.S.S. and T.A.S. performed the experimental studies. All authors analysed the data and contributed to write the paper.

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