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The Catenation of Carbon in LaC₂ Predicted under High Pressure.

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Abstract

Carbon has the capability of forming various bonding states to affect the structures and properties of transition metal carbides. In this work, structural search was performed to explore the structural diversity of LaC₂ at pressures of 0.0-30.0 GPa. Five stable structures of LaC₂ reveal a variety of carbon structural units ranging from dimer to bent C₃, zigzag C₄ and armchair polymer chains. A series of pressure-induced structural transformations are predicted, as *I4/mmm* (i.e. experimental α phase) \rightarrow *C2/c* \rightarrow *Pnma* \rightarrow *Pmma*, which involves catenations of carbon from dimer to zigzag C₄ units and further to armchair polymer chains. The bent C₃ unit appears in a novel *Immm* structure. This structure is the theoretical ground state of LaC₂ at ambient conditions, but is kinetically inaccessible from experimental α phase. LaC₂ becomes thermodynamically metastable relative to La₂C₃ + diamond above 17.1 GPa, and eventually decomposes into constituent elements above 35.6 GPa. The presented results indicate that a catenation of carbon can be realized even in simple inorganic compounds at nonambient conditions.

1. Introduction

Transition metal carbides (TMCs) are produced by incorporating carbon atoms into the interstitial sites of their parent metals, which typically include all 3d elements and 4d/5d elements of groups 3-6 early transition metals.¹ At ambient condition, the interstitial sites in TMCs is usually separated by a long distance preventing a strong interaction between carbon atoms. Therefore, although long carbon chains of interconnecting C–C bonds have been predicted in some group I and II metal carbides such as Li₂C₂², CaC₂³ and CaC⁴ at high pressure, a catenation of carbon in the transition metal matrix is very unusual and, to the best of our knowledge, has not been reported in the literature.

Pressure is a versatile and controllable thermodynamic variable that can be used to alter the bonding patterns of materials. Compression might provide a means to study the catenation of carbon in the metal lattice. TMCs with a metal:carbon ratio of 1:2, such as LaC₂, YC₂ and CeC₂ are formed by a insertion of carbon dimer into the metal lattice.⁵

These dicarbides have several advantages over monocarbides in exploring the catenation of carbon in the metal matrix under pressure. Firstly, the metallic lattice of the former expand much more than the latter providing more vacant spaces for the dimers to approach each other. Secondly, the metals have weaker interaction with carbon dimers than with carbon atoms facilitating the occurrence of phase transitions. Thirdly, a higher carbon:metal ratio offers more chance to form new C–C bonds.

Here we report the first theoretical evidence for the catenation of carbon in TMCs under high pressure. As a typical transition metal dicarbide, LaC_2 crystallizes in a tetragonal $I4/mmm$ structure (i.e. α phase) consisting of carbon dimer at ambient pressure.^{5–8} By combining an unbiased structure searching method coupled with first-principles density functional calculations, we found that LaC_2 favors a novel monoclinic $C2/c$ structure at high pressure. The phase transition from the experimental $I4/mmm$ structure to the predicted $C2/c$ structure involves a catenation of the carbon dimers to form C_4 units. At higher pressures, LaC_2 transforms into orthorhombic $Pnma$ and $Pmma$ structures, with the C_4 units catenate into one-dimensional armchair carbon chains. LaC_2 is thermodynamically metastable relative to La_2C_3 + diamond, and eventually decomposes into constituent elements above 35.6 GPa.

2. Method

We searched for LaC_2 ground-state structures through CALYPSO methodology as implemented in CALYPSO code.^{9,10} This method has been proved to be reliable by the successful predictions of high pressure structures for various systems.^{11–15} Our structure searches using the CALYPSO code with system sizes that ranging from 2 to 4 formula per simulation cell were performed at pressures of 0.0, 10.0, 20.0 and 30.0 GPa. The total energy calculations and local structural relaxations were carried out using the density functional theory as implemented in the VASP code.¹⁶ The van der Waals interactions may exist between the dimers or carbon chains of structures. So, we used the optimized exchange van der Waals functional B86b of Becke (optB86b vdW) functional to estimate the effect of van der Waals interactions.¹⁷ The projector augmented wave (PAW) potentials^{18,19} with $5s^25p^65d^16s^2$ and $2s^22p^2$ electrons as valence were adopted for La and C, respectively. The cutoff energy (800 eV) for the expansion of the wave function into plane waves and Monkhorst-Pack k point meshes with a grid of 0.025 \AA^{-1} were chosen to ensure that enthalpy calculations were well converged to better than 1 meV/atom. To determine the dynamical stability of the studied structures, we performed phonon calculations by using a supercell approach²⁰ as implemented in the phonopy code²¹. To deal with the effects of changing temperature on the Helmholtz free energy, we adopted harmonic approximation to incorporate the effects of thermal vibrations (phonons).²²

3. Results and discussions

LaC_2 has been synthesized by several groups *via* heating lanthanum and graphite to

high temperature.^{6,8,23} The X-Ray and neutron diffraction studies reveal that this phase crystallize in the tetragonal CaC_2 -type structure (i.e. α phase) at ambient condition. The α phase (2 f.u./cell) is situated in a distorted NaCl lattice in which La cations and C_2 anions form two interpenetrating face centered cubic (*fcc*) sublattices, with the octahedral voids of one type filled by the other type of ions (Fig. 1a). The calculated lattice vectors of the *fcc* sublattice are 5.54 Å, 5.54 Å and 6.56 Å, respectively, clearly representing a tetragonal distortion. The distortion of the unit cell breaks down the ideal octahedral environment in α phase and reduces the coordination number from 6 to 4+2. In Table 1, we listed the optimized structural parameters of α phase, and made a comparison with previously reported experimental data,⁸ which yields a good agreement. These results also indicate that the optB86b vdW functional¹⁷ is suitable for LaC_2 system.

At atmosphere pressure, our *ab initio* structural search have successfully uncovered the experimental α phase and, moreover, predicted two low-energy structures with *Immm* and *C2/c* symmetry. As shown in Fig. 2, the experimental α phase has an energy of 16 and 34 meV/atom higher than the theoretical *C2/c* and *Immm* structure, respectively. To account for the discrepancy between experiment and theory, we compared the Helmholtz free energy of the two theoretical structures with experimental α phase, considering that α phase was synthesized at high temperature. As shown in Table 2, α phase regains the advantage in energy at temperatures above 1240 K, in agreement with the experimental temperature (1300 K) of synthesis.⁸ At low temperatures, the low energy clearly indicates that the *Immm* structure (hereafter, α' phase) is the thermodynamic ground state of LaC_2 , and therefore, the high-temperature α phase is metastable at ambient pressure.

A significant structural feature, which separates the α' phase (6 f.u./cell) from α phase, is that carbon atoms form bent C_3 units in the former but dimers in the latter (Fig. 1b). At ambient pressure, the theoretical cell parameters of the orthorhombic α' phase are $a = 3.843$ Å, $b = 11.177$ Å and $c = 6.758$ Å. The C-C bond length is 1.34 Å and the C-C-C bond angle is 165°. The coordination number of the bent C_3 unit can be viewed as 2+6, i.e. two 'side-on' positions and six 'end-on' positions. The $\alpha\text{-Mg}_2\text{C}_3$ represents the first example of a metal carbide consisting of C_3 units. However, these C_3 units are linear and has C-C bond length of 1.33 Å. The $\alpha\text{-Mg}_2\text{C}_3$ can be synthesized by reaction of magnesium with n-pentane vapor,²⁴ but which is thermodynamically metastable with a formation energy(ΔE) of +0.824 eV/f.u. (+79.5 kJ/mol).^{25,26} Our calculations reveal that the $\alpha'\text{-LaC}_2$ is thermodynamically stable with respect to its formation elements with ΔE of -0.523 eV/f.u. (-50.4 kJ/mol). Inspired by the experimental method to synthesize the $\alpha\text{-Mg}_2\text{C}_3$, we speculate that it's possible to synthesize the $\alpha'\text{-LaC}_2$ with similar procedure. But we suggest to use propane vapor instead of n-pentane vapor, as which already has the bent C_3 unit necessary for $\alpha'\text{-LaC}_2$. Possibly, the $\alpha'\text{-LaC}_2$ structure can also be synthesized in other systems such as CeC_2 , PrC_2 and NdC_2 , because the cations of these system have similar chemical properties with La.

With the increasing of pressure to 3.3 GPa, the $C2/c$ structure becomes energetically more favorable than the α' phase. To check the stability of the $C2/c$ structure at high pressure, we performed additional structural search at 10.0 GPa, which indicates that the $C2/c$ structure is exactly the equilibrium state of LaC_2 at this pressure. As shown in Fig. 1c, the $C2/c$ structure (8 f.u./cell) is close to a distorted tetragonal structure with the theoretical cell parameters of $a = 5.303 \text{ \AA}$, $b = 5.289 \text{ \AA}$, $c = 12.081 \text{ \AA}$ and $\beta = 98.795^\circ$. A distinct structural feature of the $C2/c$ structure is that carbon atoms exist as zigzag C_4 unit. To the best of our knowledge, the formation of C_4 unit in transitional metal carbides is reported here for the first time. The nearest La-La distance, 3.47 \AA , is $\sim 7\%$ shorter than the next nearest La-La distance of 3.74 \AA and comparable to the double of the covalent radius of La (1.69 \AA). Considering the two nearest La atoms as a pair, we find some similarities between α phase and $C2/c$ structure: The $C2/c$ structure is also situated in a distorted NaCl lattice, but the two interpenetrating fcc sublattices in which are formed by La_2 'pair' and C_4 unit, respectively; The coordination number can also be viewed as $4+2$, i.e. four 'side-on' positions and two 'end-on' positions. Both of the La_2 pairs and the C_4 units are almost aligned along the c axis (Fig. 1c).

The above total energy calculations reveal that the thermodynamically most stable structure of LaC_2 is the α' phase at ambient condition, the α phase at high temperature ($> 1240 \text{ K}$) and ambient pressure, and the $C2/c$ structure at 0 K and high pressure ($> 3.3 \text{ GPa}$), respectively. At ambient condition, LaC_2 should have the ground state structure (α' phase) if which is kinetically accessible. However, in experiments, the high temperature α phase has been successfully quenched to ambient condition, indicating that a large energy barrier exists between the valleys of the α and α' phase and blocks the phase transition between them. A question to ask is that what the origin of the barrier is. We note that LaC_2 reveals rich carbon species, e.g. C_2 unit in the α phase and C_3 unit in the α' phase. The $\alpha \leftrightarrow \alpha'$ phase transition must involve the dissociation of carbon-carbon bonds. We suspect that the large carbon-carbon bond energy, usually at a level of several eV, is an obstacle for the $\alpha \leftrightarrow \alpha'$ phase transition. To get a 'feel' of the energy barrier, we simulated an ideal transformation from C_2 units to linear C_3 units. Calculation shows that this transformation has to go through a large barrier (see Fig. 3). Thus, our suspicion is proved to be right.

The above analysis shows that the energy barriers play an important role in the dynamics of LaC_2 . Notably, the large barrier in breaking the carbon-carbon bonds might block not only the $\alpha \leftrightarrow \alpha'$ phase transition at high temperature but also the $\alpha' \leftrightarrow C2/c$ phase transition at high pressure. The equilibrium volume of α phase ($16.780 \text{ \AA}^3/\text{atom}$) is about 2% and 10% larger than that of the α' phase and the $C2/c$ structure, respectively, at ambient condition. It is no doubt that LaC_2 should transform to a denser polymorph under compression. We suspect that the experimental α phase would transform to the predicted high pressure $C2/c$ structure directly at high pressure, as the $\alpha \rightarrow \alpha'$ transitions pathway is blocked by large energy barriers. In view of that the volume of the $C2/c$ structure is smaller than the α phase by 9% at 10.0 GPa, and no large barrier has been found in the transformation of C_2 dimers to linear C_4 unit (Fig. 3), we argue that a

catenation of C₂ dimers to form zigzag C₄ units in the $\alpha \rightarrow C2/c$ phase transition would happen at pressures below 10.0 GPa.

During the structure search at 10.0 GPa, we also found several metastable structures. There is one inviting structure with enthalpies falling into the range between the most stable *C2/c* structure and the metastable α' phase: an orthorhombic *Pnma* structure. This structure has a volume of ~3% smaller than the *C2/c* structure, indicating that which might become energetically more favorable at higher pressures. We thus performed additional structure searches to explore the structural evolutions. The orthorhombic *Pnma* structure (4 f.u./cell) and another orthorhombic *Pmma* structure (2 f.u./cell) are predicted to be the most stable structures of LaC₂ at 20.0 and 30.0 GPa, respectively. The phase transition pressures of *C2/c* \rightarrow *Pnma* and *Pnma* \rightarrow *Pmma* are 19.1 and 21.9 GPa, respectively (see Fig. 2). The narrow stable pressure regime of the *Pnma* structure indicates that which is likely to be an intermediate phase between the *C2/c* and *Pmma* structure. At 20.0 GPa, the C-C distance along the chains falls in a range of 1.45-1.46 Å in the *Pnma* structure, whereas is 1.46-1.50 Å in the *Pmma* structure. The two orthorhombic structures share a main structural feature: the formation of 1D armchair carbon chains (as shown in Fig. 1e for the *Pmma* structure).

In order to check the dynamical stability of the various predicted structures of LaC₂, we performed phonon calculations for α phase, α' phase, *C2/c* structure, *Pnma* structure and *Pmma* structure. No imaginary frequency was found in the phonon dispersion curves of these structures (Fig. S1-S5 in ESI†), indicating that they are dynamically stable. We compared the enthalpy of LaC₂ at various pressures with that of the high-pressure phases of Carbon²⁷ + La₂C₃²⁸ and Carbon²⁷ + Lanthanum²⁹. As shown in Fig. 2, LaC₂ is metastable relative to diamond + β -La₂C₃²⁸ above 17.1 GPa, which seems to bring a challenge to synthesize the polymeric carbon chains from C₄ units in LaC₂. However, we note that the β -La₂C₃ consists of hexagonal C₆ rings and the diamond has a pure *sp*³ C-C bonding network. The decomposition of LaC₂ into β -La₂C₃ + diamond will inevitably involve the dissociation of C-C bonds and the rehybridization of the C-C bonds from *sp*² to *sp*³, and therefore, the decomposition pressure is very likely to be significantly increased by the large energy barrier involved. In contrast, in the *C2/c* \rightarrow *Pnma* transition of LaC₂, the formation of 1D carbon chains from C₄ units is unlikely to involve a large energy barrier as which can be easily accomplished by connecting the C₄ units. Therefore, although the decomposition pressure of LaC₂ (17.1 GPa) is a little bit lower than the *C2/c* \rightarrow *Pnma* transition pressure (19.1 GPa), it is hard to say which transition will appear first when taking into account the kinetic effects. Moreover, LaC₂ becomes thermodynamically metastable relative to La and C above 35.6 GPa (Fig. 2), indicating that this compound will eventually decompose into the elements under enough compression.

To study the nature of the chemical bonding in the modifications of LaC₂, we performed the electronic structure simulation in terms of the electron localization function (ELF)³⁰ and Bader charge analysis³¹. At atmosphere pressure, the calculated ELF for α phase

shows that two C atoms bond together to form a C₂ dimer (Fig. 4a). The bond distance is 1.30 Å, to be compared with the free carbon dimer bond length of 1.27 Å. Therefore, the C-C bond length stretches by 0.03 Å in the presence of La metals. From Bader charge analysis, we find that the La atoms are positively charged with +1.75e, while all the C atoms are negatively charged. In the α' phase, the calculated ELF (Fig. 4b) shows that three C atoms in the C₃ units bond together by two C-C bonds. The shape of the C₃ units looks like bean pod. The C-C bond length is 1.34 Å, the same with C-C double bond length. Bader charge analysis shows that the La atoms are positively charged with +1.56e or +1.69e, meanwhile all the C₃ units are negatively charged. Thus, the charge transfer from La to C is evident in α phase and α' phase.

In the *C2/c* structure, the calculated ELF at 10.0 GPa (Fig. 4c) shows that four C atoms in the C₄ units bond together by three C-C bonds, indicating that C₄ units is not the formal dimer of two C₂ dimers. Fig. 4c and Fig. S6 (ESI†) show that the central carbon atoms of the C₄ unit each has three domains of electron localization (three valence basins). Two of the domains are C-C bonds (disynaptic valence basins), and one of the domains is a lone pair of electrons (monosynaptic valence basin).³²⁻³⁴ This is a clear *sp*² C-C bonding character.^{28,35} The C-C-C angle of 151 ° is significantly deviate from the ideal (120 °) *sp*² bonding. The high values of ELF on two ends of C₄ units indicate the strong localization of carbon valence electrons (Fig. 4c), revealing an unsaturated nature of this C₄ unit. Bader charge analysis shows that the La atoms are positively charged with +1.54e, and C atoms are negatively charged. Note that the two nearest neighbors of La are very close to each other and, seem like a 'pair'. The La₂ 'pair' provide a help in grasping the structural character of La sublattice from *C2/c* structure, however, as a matter of fact that the negligibly small ELF along the connecting line does manifest a very weak interaction between the two atoms.

The *Pmma* structure is consisted of La atoms and the armchair carbon chains. The ELF at 30.0 GPa (Fig. 4d and Fig. S7 in ESI†) shows that the bonding character of the carbon atoms in the armchair chain is very similar with that of the central carbon atoms in the C₄ units. In the *Pmma* structure, each carbon atom has three valence basins: two disynaptic valence basins (C-C bonds) and one monosynaptic valence basin (a lone pair of electrons).³²⁻³⁴ This allows us to identify the *sp*²-like nature of the C-C bonding in *Pmma* structure.^{28,35} This is in agreement with the fact that the C-C bond length in the chain falls in a range of 1.45-1.49 Å lying between the length of C-C double and single bond. The carbon chains has a C-C-C bond angle of 137 °, which is higher than the ideal value of 120 ° for *sp*² hybridized carbon bonds. The monosynaptic valence basins (lone pairs of electrons) of the armchair carbon chains (see Fig. 4d and Fig. S7 in ESI†) reveals an unsaturated nature of the carbon chains. Bader charge analysis reveals that each La atom losses 1.37e, and the carbon chains are negatively charged. Notably, the *sp*² bonding character is much significant in the carbon chains than in the C₄ units (Fig. 4c), which is in accordance with the fact that the C-C-C bond angle of the former (137 °) is much smaller than the latter (151 °). The carbon bonding behavior of the *Pnma* structure is similar to the *Pmma* structure, and Bader charge analysis shows La atom is

positively charged with +1.47e at 30.0 GPa.

The α -LaC₂ has been shown to be a weak-coupling BCS-type superconductor with T_c of ~ 1.8 K.⁸ It is interesting to compare the electronic density of states (DOS) of the predicted structures and α phase to make a guess of the superconductivity of them. As shown in Fig. 5, all the four structures are metallic by the evidence of the electron population at the Fermi level. Around the Fermi level one obtains La d -bands with carbon p -character mixed in. The predicted structures reveal a DOS at the Fermi level ranging from 1.13 states/eV/f.u. in α' phase (at 0.0 GPa) to 0.33 states/eV/f.u. in $C2/c$ structure (at 10.0 GPa), which is not much more than 1.05 states/eV/f.u. in α phase (at 0.0 GPa). According to the BCS theory, T_c is governed by three parameters: the typical phonon energy, the pairing potential arising from the electron-phonon interaction and the electronic density of states at the Fermi level.³⁶ It seems that the small DOS at the Fermi level would not help the predicted structures to access T_c much higher than that of α phase.

4. Conclusions

In the present study, we report the first theoretical evidence for the catenation of carbon in TMCs under high pressure. By combining an unbiased structure search and first-principles density functional calculations on LaC₂, we found the experimental α phase transforms into a metallic $C2/c$ structure under compression. This phase transition involves a catenation of the carbon dimers to form C₄ units. At higher pressures (above ~ 19 GPa), LaC₂ theoretically transforms into orthorhombic $Pnma$ and $Pmma$ structures, with the C₄ units catenate into one-dimensional armchair carbon chains. LaC₂ becomes thermodynamically metastable relative to La₂C₃ + diamond above 17.1 GPa, and eventually decomposes into constituent elements above 35.6 GPa. Moreover, a novel α' phase consisting of C₃ units is predicted to be the ground state structure at ambient conditions, but which is kinetically inaccessible from the experimental α phase. Our findings indicate that a catenation of carbon can be realized even in simple inorganic compounds at nonambient conditions and, call for further experiments to investigate the evolution of carbon bonds in TMCs under pressure.

Acknowledgments

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References

- 1 H. H. Hwu and J. G. Chen, *Chem. Rev.*, 2005, **105**, 185–212.

- 2 X.-Q. Chen, C. L. Fu and C. Franchini, *J. Phys. Condens. Matter*, 2010, **22**, 292201.
- 3 Y.-L. Li, W. Luo, Z. Zeng, H.-Q. Lin, H. Mao and R. Ahuja, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 9289–94.
- 4 Y.-L. Li, S.-N. Wang, A. R. Oganov, H. Gou, J. S. Smith and T. a Strobel, *Nat. Commun.*, 2015, **6**, 6974.
- 5 M. Atoji, *J. Chem. Phys.*, 1961, **35**, 1950.
- 6 M. Atoji, K. Gschneidner, A. H. Daane, R. E. Rundle and F. H. Spedding, *J. Am. Chem. Soc.*, 1958, **80**, 1804–1808.
- 7 X. Wang, I. Loa, K. Syassen, R. Kremer, a. Simon, M. Hanfland and K. Ahn, *Phys. Rev. B*, 2005, **72**, 064520.
- 8 V. Babizhetskyy, O. Jepsen, R. K. Kremer, A. Simon, B. Ouladdiaf and A. Stolovits, *J. Phys. Condens. Matter*, 2014, **26**, 025701.
- 9 Y. Wang, J. Lv, L. Zhu and Y. Ma, *Phys. Rev. B*, 2010, **82**, 094116.
- 10 Y. Wang, J. Lv, L. Zhu and Y. Ma, *Comput. Phys. Commun.*, 2012, **183**, 2063–2070.
- 11 J. Lv, Y. Wang, L. Zhu and Y. Ma, *Phys. Rev. Lett.*, 2011, **106**, 015503.
- 12 L. Zhu, H. Wang, Y. Wang, J. Lv, Y. Ma, Q. Cui, Y. Ma and G. Zou, *Phys. Rev. Lett.*, 2011, **106**, 145501.
- 13 L. Zhu, Z. Wang, Y. Wang, G. Zou, H. Mao and Y. Ma, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 751–3.
- 14 Q. Li, D. Zhou, W. Zheng, Y. Ma and C. Chen, *Phys. Rev. Lett.*, 2013, **110**, 136403.
- 15 D. Nishio-Hamane, M. Zhang, T. Yagi and Y. Ma, *Am. Mineral.*, 2012, **97**, 568–572.
- 16 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- 17 J. Klimeš, D. R. Bowler and A. Michaelides, *Phys. Rev. B*, 2011, **83**, 195131.
- 18 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- 19 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.

- 20 K. Parlinski, Z. Li and Y. Kawazoe, *Phys. Rev. Lett.*, 1997, **78**, 4063–4066.
- 21 A. Togo, F. Oba and I. Tanaka, *Phys. Rev. B*, 2008, **78**, 134106.
- 22 A. Togo and I. Tanaka, *Scr. Mater.*, 2015, **108**, 1–5.
- 23 R. W. Green, E. O. Thorland, J. Croat and S. Legvold, *J. Appl. Phys.*, 1969, **40**, 3161.
- 24 H. Fjellvåg and P. Karen, *Inorg. Chem.*, 1992, **31**, 3260–3263.
- 25 M. Chase, *J. Phys. Chem. Ref. Data*, 1998, 1952.
- 26 T. A. Strobel, O. O. Kurakevych, D. Y. Kim, Y. Le Godec, W. Crichton, J. Guignard, N. Guignot, G. D. Cody and A. R. Oganov, *Inorg. Chem.*, 2014, **53**, 7020–7.
- 27 M. E. Straumanis and E. Z. Aka, *J. Am. Chem. Soc.*, 1951, **73**, 5643–5646.
- 28 X. Zhong, Y. Wang, F. Peng, H. Liu, H. Wang and Y. Ma, *Chem. Sci.*, 2014, **5**, 3936.
- 29 G. J. Piermarini and C. E. Weir, *Science*, 1964, **144**, 69–71.
- 30 A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.*, 1990, **92**, 5397.
- 31 G. Henkelman, A. Arnaldsson and H. Jónsson, *Comput. Mater. Sci.*, 2006, **36**, 354–360.
- 32 B. Silvi, *J. Mol. Struct.*, 2002, **614**, 3–10.
- 33 F. Kraus, T. Hanauer and N. Korber, *Angew. Chemie Int. Ed.*, 2005, **44**, 7200–7204.
- 34 V. Polo, P. Gonzalez-Navarrete, B. Silvi and J. Andres, *Theor. Chem. Acc.*, 2008, **120**, 341–349.
- 35 F. Peng, M. Miao, H. Wang, Q. Li and Y. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 18599–605.
- 36 W. L. McMillan, *Phys. Rev.*, 1968, **167**, 331–344.

Table 1 The structural parameters of α phase obtained from experiment⁸ and DFT calculation, respectively. The symbol z_C and d_{C-C} represent the carbon atomic positional parameter and C-C distance, respectively.

α phase		a (Å)	c (Å)	V_{cell} (Å ³)	z_C	d_{C-C} (Å)
	Exp.		3.927	6.575	101.383	0.403
Theory		3.918	6.557	100.679	0.401	1.297

Table 2 The calculated Helmholtz free energy at different temperature for α phase, $Immm$ structure and $C2/c$ structure.

T (K)	F (eV/atom)		
	α	$Immm$	$C2/c$
0	-7.461	-7.486	-7.472
580	-7.589	-7.606	-7.589
1240	-7.916	-7.916	-7.897
1400	-8.011	-8.006	-7.987

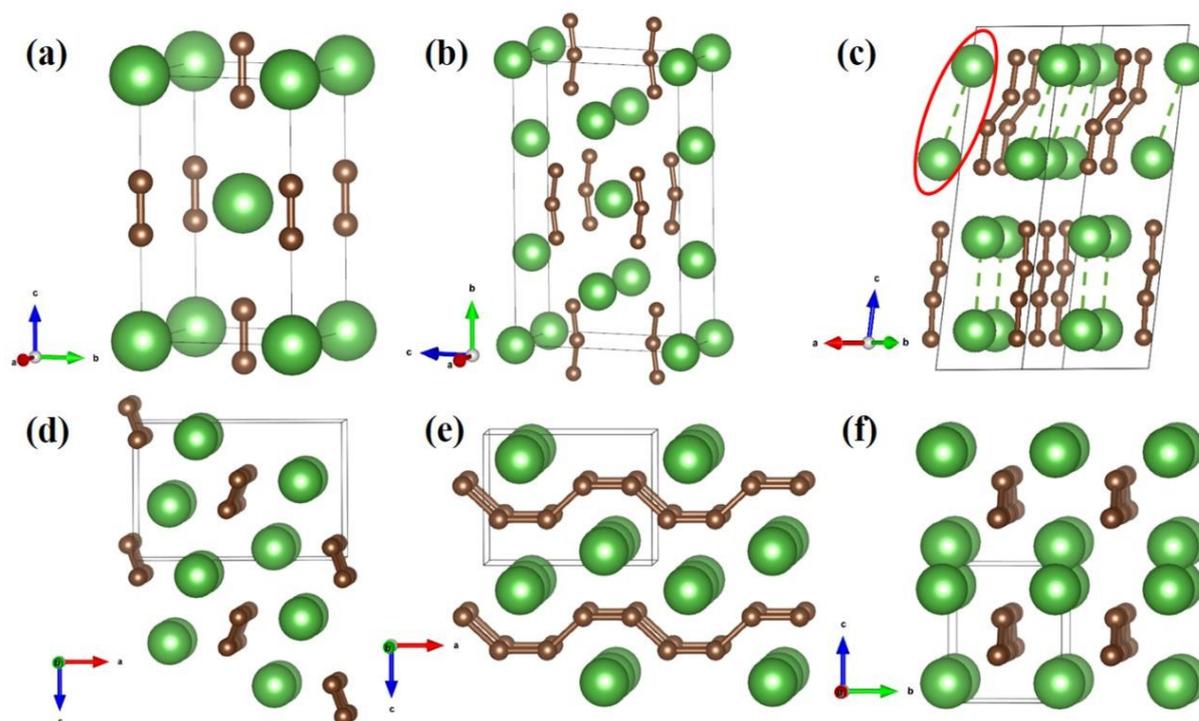


Fig. 1 Predicted structures of LaC_2 at ambient and high pressure. The large and small spheres represent La and C atoms, respectively. (a) α phase. (b) α' phase. (c) $C2/c$ structure. (d) $Pnma$ structure. (e) and (f) $Pmma$ structure. Detailed structural parameters can be found in the ESI.†

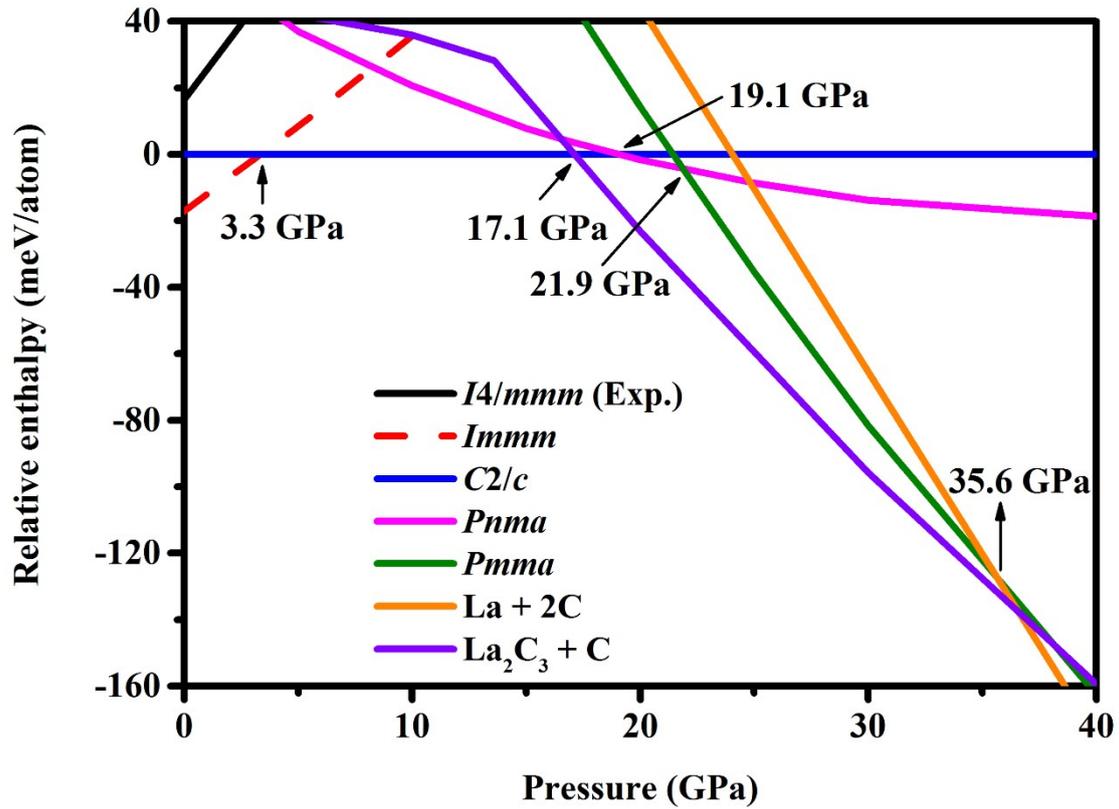


Fig. 2 Enthalpy curves (with respect to the $\text{C}2/c$ structure) as a function of pressure for various predicted structures, $\text{La} + 2\text{C}$, and $\text{La}_2\text{C}_3 + \text{C}$.

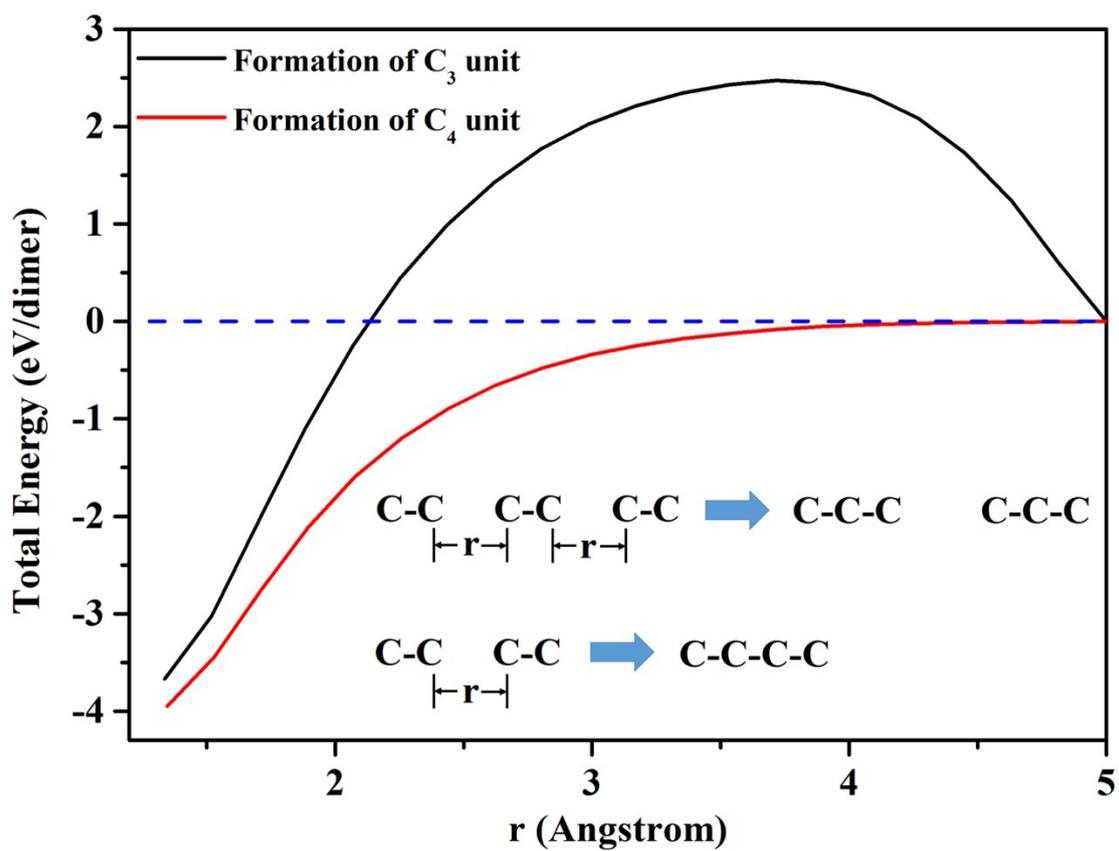


Fig. 3 Energy curves for the formation of C_3 and C_4 unit, respectively.

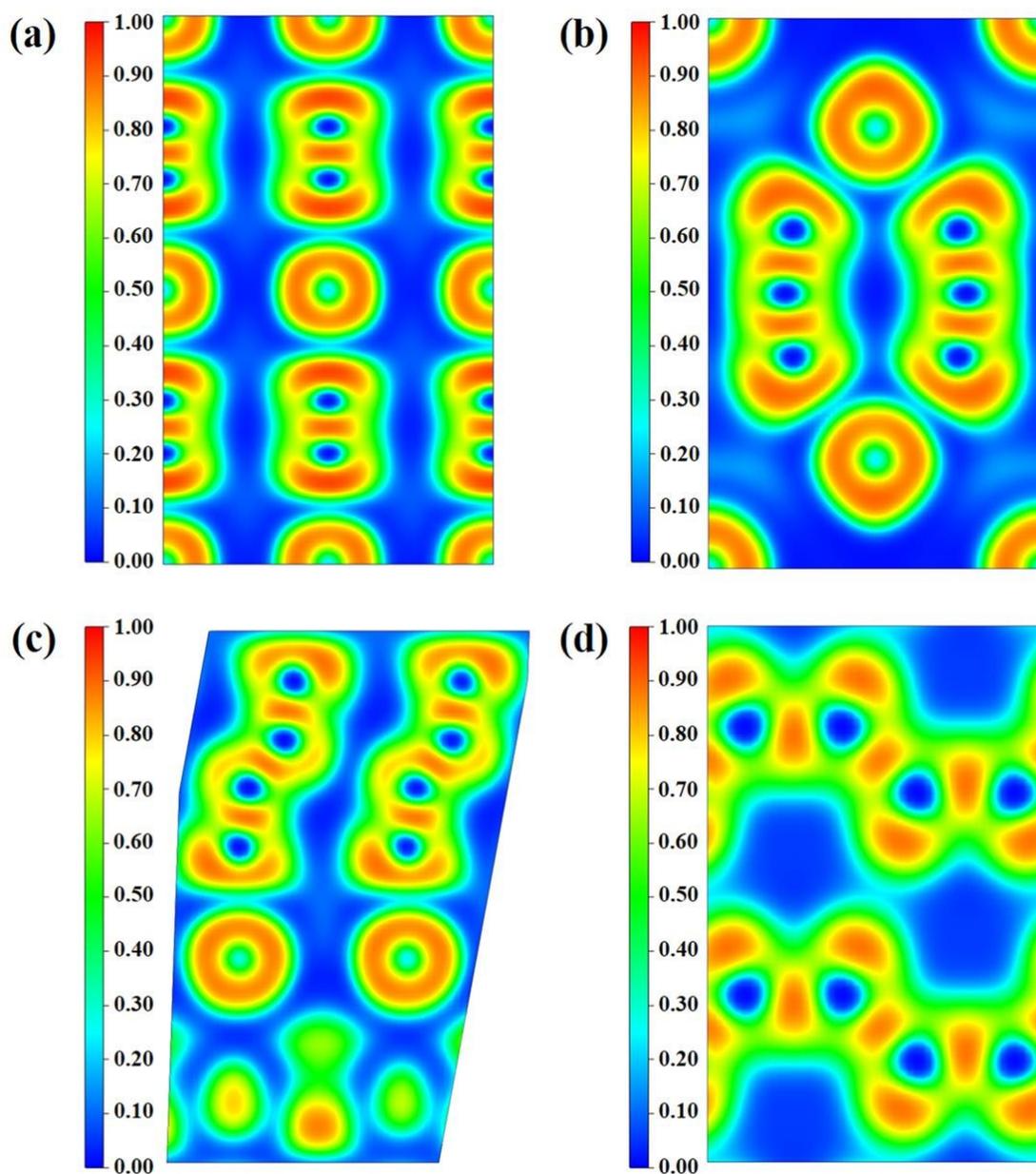


Fig. 4 ELF maps of the planes which the C_2 dimers, C_3 units, C_4 units and one-dimensional armchair carbon chains lie for (a) α phase (0.0 GPa), (b) α' phase (0.0 GPa), (c) $C2/c$ structure (10.0 GPa) and (d) $Pmma$ structure (30.0 GPa), respectively.

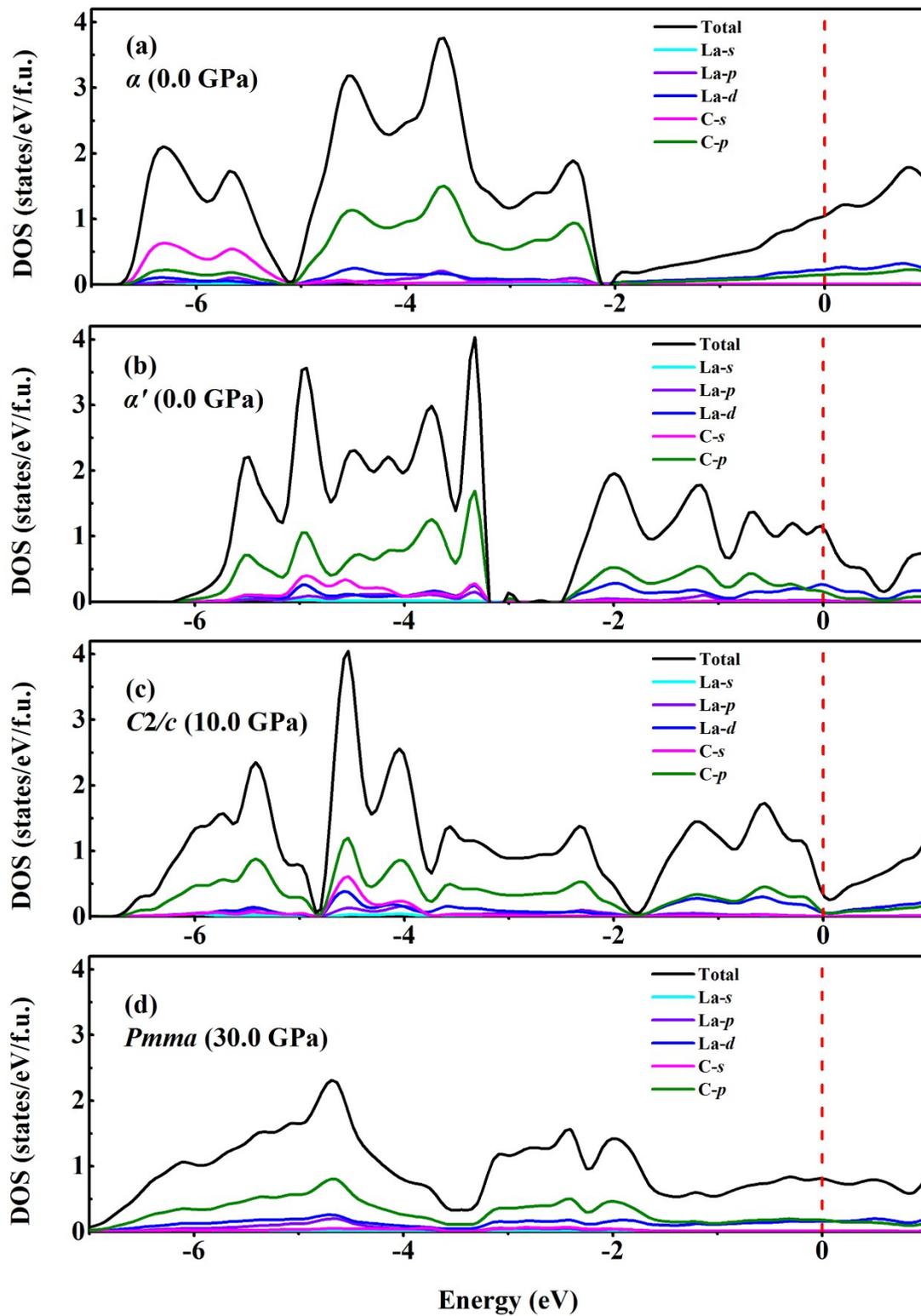


Fig. 5 The calculated densities of states for (a) α phase, (b) α' phase, (c) C2/c structure and (d) Pmma structure, respectively.