

Article

Crystal Structures and Mechanical Properties of Ca_2C at High Pressure

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Abstract: Recently, a new high-pressure semiconductor phase of Ca_2C (space group $Pnma$) was successfully synthesized, it has a low-pressure metallic phase (space group $C2/m$). In this paper, a systematic investigation of the pressure-induced phase transition of Ca_2C is studied on the basis of first-principles calculations. The calculated enthalpy reveals that the phase transition which transforms from $C2/m\text{-Ca}_2\text{C}$ to $Pnma\text{-Ca}_2\text{C}$ occurs at 7.8 GPa, and it is a first-order phase transition with a volume drop of 26.7%. The calculated elastic constants show that $C2/m\text{-Ca}_2\text{C}$ is mechanically unstable above 6.4 GPa, indicating that the structural phase transition is due to mechanical instability. Both of the two phases exhibit the elastic anisotropy. The semiconductivity of $Pnma\text{-Ca}_2\text{C}$ and the metallicity of $C2/m\text{-Ca}_2\text{C}$ have been demonstrated by the electronic band structure calculations. The quasi-direct band gap of $Pnma\text{-Ca}_2\text{C}$ at 0 GPa is 0.86 eV. Furthermore, the detailed analysis of the total and partial density of states is performed to show the specific contribution to the Fermi level.

Keywords: pressure-induced phase transition; first-principles calculations; Ca_2C

1. Introduction

Hitherto, the pressure-composition (P - x) phases of binary systems have gained increasing interest and been extensively researched. Among these predicted compounds, some of them have been successfully synthesized [1,2], but the others still need further experiments to confirm their theoretical predictions [3,4]. For the Ca-C system, there are many works that have been done and obtained remarkable achievements [5–16]. Gauzzi et al. [5] found the superconductivity will be enhanced in the intercalated graphite CaC_6 at high pressure. It performs the structural instability and leads to a structural transition with pressure. Nylen et al. [6] studied the structural behavior of CaC_2 at high pressure via the first-principles calculations. Their results suggest an irreversible amorphization, corroborating the structural peculiarities of acetylide carbides, which persists at high pressure conditions. Li et al. analyzed the pressure-induced superconductivity of CaC_2 [7]. They uncovered that it is calcium that contributes to the superconducting behavior, and it is capable of stabilizing carbon sp^2 hybridization at a larger range of pressure. Nourbakhsh et al. [8] investigated the magnetism in CaC ionic compound and observed a perfect Fermi level spin polarization and a half-metallic behavior.

Recently, Li et al. [9] systematically explored all the stable calcium carbides at pressures from 0 to 100 GPa. This resulted in five newly predicted stable stoichiometries (Ca_5C_2 , Ca_2C , Ca_3C_2 , CaC and Ca_2C_3). Using in situ synchrotron powder X-ray diffraction measurements, they successfully synthesized the Ca_2C and Ca_2C_3 . The Ca_2C has two phases: the semiconducting phase $Pnma\text{-Ca}_2\text{C}$ at high pressure and the metallic metastable phase $C2/m\text{-Ca}_2\text{C}$ at low pressure. The $Pnma\text{-Ca}_2\text{C}$ exists in the pressure range of 7.5–100 GPa and possesses the isolated C anions. Carbon atoms polymerize to

isolated dumbbells, occurring a unique metallic metastable $C2/m\text{-Ca}_2\text{C}$ which provides an example of 2D metal. The metal calcium atom of $C2/m\text{-Ca}_2\text{C}$ develops a negative Bader charge, confronting a more electronegative carbon atom. Due to these intriguing properties, in this paper, we will focus on the Ca_2C , presenting its structural, elastic and electronic properties, and systematically investigating the pressure-induced phase transition mechanism. The enthalpy is calculated to reveal the phase transition pressure. In addition, the elastic constants, modulus and anisotropy are calculated to study the elastic properties. Meanwhile, the electronic band structures and the total and partial density of states are analyzed.

2. Results and Discussion

The $2 \times 1 \times 2$ supercell structures of Ca_2C are illustrated in Figure 1. The black and blue spheres represent C and Ca atoms, respectively. At zero pressure, the optimized lattice parameters of $Pnma\text{-Ca}_2\text{C}$ are $a = 6.677 \text{ \AA}$, $b = 4.384 \text{ \AA}$, $c = 7.979 \text{ \AA}$ with two inequivalent Ca atoms occupying 4c (0.0119, 0.2500, 0.8302), 4c (0.1476, 0.2500, 0.4109) and C atoms occupying 4c (0.2521, 0.2500, 0.0918) Wyckoff positions. For $C2/m\text{-Ca}_2\text{C}$, the optimized lattice parameters are $a = 7.166 \text{ \AA}$, $b = 3.775 \text{ \AA}$, $c = 15.490 \text{ \AA}$, and $\beta = 122.9^\circ$. The Wyckoff positions of $C2/m\text{-Ca}_2\text{C}$ are Ca1: 4i (0.2715, 0.0000, -0.1120), Ca2: 4i (-0.2440 , 0.0000, -0.3781) and C: 4i (-1.0479 , 0.0000, -0.9705). For $Pnma\text{-Ca}_2\text{C}$ (see Figure 1a), carbon atoms are isolated anions, whereas the carbon dimers are observed in $C2/m\text{-Ca}_2\text{C}$ (Figure 1b). The interatomic distance of Ca-C for $C2/m\text{-Ca}_2\text{C}$ is $2.44 \text{ \AA}$ in length, and the C-C bond length is $1.29 \text{ \AA}$.

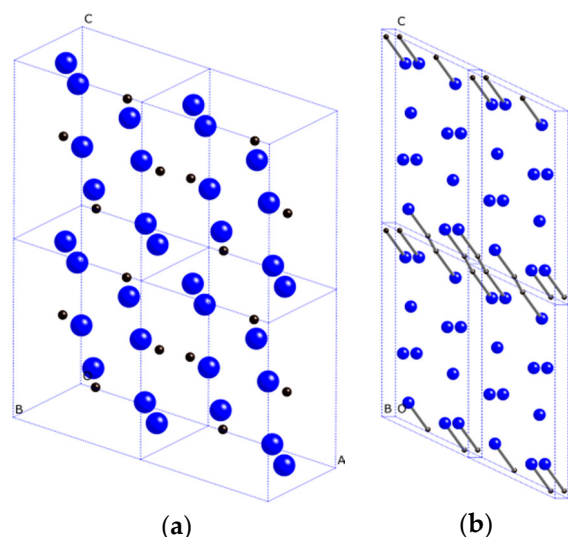


Figure 1. Crystal structures of Ca_2C . (a) $Pnma\text{-Ca}_2\text{C}$; (b) $C2/m\text{-Ca}_2\text{C}$. The black and blue spheres represent C and Ca atoms, respectively.

To determine the phase transition pressure of Ca_2C , the enthalpy differences between two structures are plotted as a function of pressure up to 100 GPa in Figure 2a. There is an intersection between the two enthalpy curves, indicating that the $C2/m\text{-Ca}_2\text{C}$ phase transforms to the $Pnma\text{-Ca}_2\text{C}$ phase at 7.8 GPa and the $Pnma\text{-Ca}_2\text{C}$ is more stable than the $C2/m\text{-Ca}_2\text{C}$ above this pressure point. The known transition pressure data is 7.5 GPa [9], and it is in a good agreement with our result. Meanwhile, the dependence of volume on pressure is presented in Figure 2b. The $C2/m\text{-Ca}_2\text{C}$ is larger than the $Pnma\text{-Ca}_2\text{C}$ in volume. The change of volume at 7.8 GPa shows that the phase transition is first-order with a volume drop of 26.7%. To interpret this large volume collapse, we estimated the ionic radii of the C and Ca within these two structures at 7.8 GPa through Bader charge analysis. The obtained results are listed in Table 1. The calculated charges of the two Ca_2C phase show increasing trends from $C2/m\text{-Ca}_2^{0.928}\text{C}^{-0.928}$ to $Pnma\text{-Ca}_2^{2.348}\text{C}^{-2.348}$ at phase transition pressure point. Compared to $C2/m\text{-Ca}_2\text{C}$ phase ($r_{\text{Ca}} = 1.871 \text{ \AA}$, $r_{\text{C}} = 1.534 \text{ \AA}$), the ionic radius of Ca in the $Pnma\text{-Ca}_2\text{C}$

phase is much shorter (1.485 Å), whereas the ionic radius of C (1.788 Å) in *Pnma*-Ca₂C is relatively longer. Since the contribution from Ca atom is much more than that of C atom to the volume of Ca₂C, the volume collapse from C2/*m* to *Pnma* phase is very large.

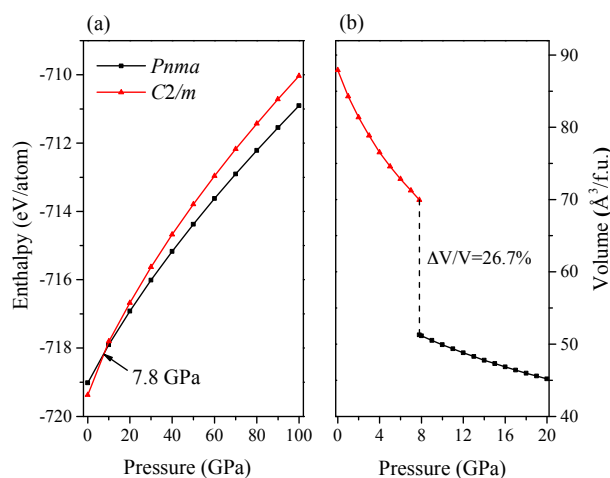


Figure 2. Enthalpy (a) and volume (b) as a function of pressure. The black and red solid lines represent *Pnma*-Ca₂C and C2/*m*-Ca₂C, respectively.

Table 1. Bader charge analysis for C2/*m*- and *Pnma*-Ca₂C at 7.8 GPa.

Phase	Ionic Radius (Å)		Charge Transfers (e)
	C	Ca	Ca → C
C2/ <i>m</i>	1.534	1.871	0.928
<i>Pnma</i>	1.788	1.485	2.348

The lattice parameters of Ca₂C at different pressures are listed in Table 2. In Table 2, an excellent agreement with the previous theoretical and experimental values is shown [9]. The calculated lattice parameters decrease with pressure. To get more details, the variations of lattice parameters X/X_0 of the two Ca₂C phases with pressure are shown in Figure 3. For *Pnma*-Ca₂C (see Figure 3a), along the *b*- and *c*-axis, the degrees of anti-compression along these two directions are almost the same. At low pressure range ($P < 23$ GPa), the incompressibility along *a*-axis is larger than that along *b*- and *c*-axis, which is contrary to the case at high pressure range ($P > 23$ GPa). In Figure 3b, the changes of lattice parameters along the *a*-, *b*- and *c*-axis are similar for C2/*m*-Ca₂C when below 6 GPa, suggesting the same incompressibility along these three directions.

Table 2. Lattice parameters of Ca₂C at various pressures.

Phase	Pressure (GPa)	<i>a</i> (Å)		<i>b</i> (Å)		<i>c</i> (Å)		β (deg)	<i>V</i> (Å ³)	
<i>Pnma</i>	0	6.677	6.689 ^a	4.384	4.389 ^a	7.979	7.981 ^a		233.58	234.32 ^a
	10	6.404	6.415 ^a	4.150	4.154 ^a	7.513	7.518 ^a		199.68	200.35 ^a
			6.449 ^b		4.157 ^b		7.523 ^b			201.7 ^b
	30	5.919	5.929 ^a	3.931	3.933 ^a	7.195	7.204 ^a		167.41	168.04 ^a
C2/ <i>m</i>	0	7.166		3.775		15.490		122.9	351.59	
	5	6.743	6.701 ^a	3.594	3.587 ^a	14.65	14.68 ^a	122.8	298.32	122 ^a
	6.4	6.674		3.554		14.45		122.6	288.87	

^a Calculated data in Ref. [9]; ^b Experimental results in Ref. [9].

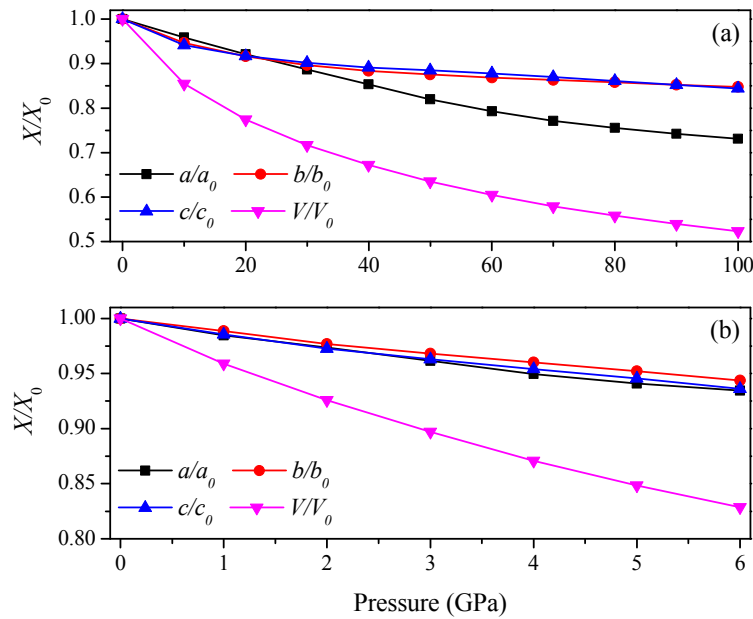


Figure 3. Lattice parameters X/X_0 as a function of pressure. (a) $Pnma$ - Ca_2C ; (b) $C2/m$ - Ca_2C .

The calculated elastic constants and moduli of Ca_2C at 0 GPa and high pressures are shown in Table 3. The strain-stress method was used to calculate the single crystal elastic constants. A small finite strain was applied on the optimized structure and the atomic position was fully optimized. Then, the elastic constants were obtained from the stress of the strained structure. The generalized Born's mechanical stability criteria of orthorhombic phase at 0 GPa are given by [17,18]:

$$C_{ii} > 0, i = 1 \dots 6, \quad (1)$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \quad (2)$$

$$(C_{11} + C_{22} - 2C_{12}) > 0, \quad (3)$$

$$(C_{11} + C_{33} - 2C_{13}) > 0, \quad (4)$$

$$(C_{22} + C_{33} - 2C_{23}) > 0 \quad (5)$$

The stability criteria of monoclinic phase at 0 GPa are given by [17,18]:

$$C_{ii} > 0, i = 1 \dots 6, \quad (6)$$

$$[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, \quad (7)$$

$$(C_{33}C_{55} - C_{35}^2) > 0, \quad (8)$$

$$(C_{44}C_{66} - C_{46}^2) > 0, \quad (9)$$

$$(C_{22} + C_{33} - 2C_{23}) > 0, \quad (10)$$

$$[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0, \quad (11)$$

$$2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] - [C_{15}^2(C_{22}C_{33} - C_{23}^2) + C_{25}^2(C_{11}C_{33} - C_{13}^2) + C_{35}^2(C_{11}C_{22} - C_{12}^2)] + C_{55}g > 0, \quad (12)$$

$$g = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23} \quad (13)$$

Table 3. Calculated elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν , and B/G ratio of Ca_2C at various pressures.

Pressure (GPa)	<i>Pnma</i> - Ca_2C			<i>C2/m</i> - Ca_2C		
	0	50	100	0	6	6.4
C_{11}	92	212	454	32	78	71
C_{22}	87	329	551	62	86	84
C_{33}	67	331	523	56	80	86
C_{44}	40	79	114	8	13	14
C_{55}	26	97	137	19	23	20
C_{66}	38	101	135	13	17	15
C_{12}	23	158	250	11	26	28
C_{13}	35	170	248	16	27	29
C_{23}	27	185	347	7	18	23
C_{15}				−1	0.75	4
C_{25}				−1.4	−0.06	3
C_{35}				0.3	0.44	−1.31
C_{46}				0.04	2.65	2.67
B	46	203	353	24	43	45
G	30	75	122	15	21	19
E	74	200	328	37	54	50
ν	0.23	0.34	0.35	0.24	0.29	0.31
B/G	1.53	2.71	2.89	1.60	2.05	2.37

The mechanical stability in crystals under isotropic pressure is provided by Ref. [19]. This requires the symmetric matrix

$$\hat{G} = \begin{bmatrix} \tilde{C}_{11} & \tilde{C}_{12} & \tilde{C}_{13} & 2C_{14} & 2C_{15} & 2C_{16} \\ \tilde{C}_{21} & \tilde{C}_{22} & \tilde{C}_{23} & 2C_{24} & 2C_{25} & 2C_{26} \\ \tilde{C}_{31} & \tilde{C}_{32} & \tilde{C}_{33} & 2C_{34} & 2C_{35} & 2C_{36} \\ 2C_{41} & 2C_{42} & 2C_{43} & 4\tilde{C}_{44} & 4C_{45} & 4C_{46} \\ 2C_{51} & 2C_{52} & 2C_{53} & 4C_{54} & 4\tilde{C}_{55} & 4C_{56} \\ 2C_{61} & 2C_{62} & 2C_{63} & 4C_{64} & 4C_{65} & 4\tilde{C}_{66} \end{bmatrix} \quad (14)$$

has a positive determinant. In $\hat{G}$ matrix,

$$\begin{aligned} \tilde{C}_{\alpha\alpha} &= C_{\alpha\alpha} - P, \quad \alpha = 1, 2, \dots, 6 \\ \tilde{C}_{12} &= C_{12} + P, \quad \tilde{C}_{13} = C_{13} + P, \quad \tilde{C}_{23} = C_{23} + P \end{aligned} \quad (15)$$

where P is the isotropic pressure.

If the elastic constants satisfy these stability criteria, it means the structure is mechanically stable. From Table 3, one can see that orthorhombic *Pnma*- Ca_2C is mechanical stable up to at least 100 GPa. For monoclinic *C2/m*- Ca_2C , the criteria $\tilde{C}_{44}\tilde{C}_{66} - C_{46}^2 > 0$, which is similar to the Equation (9), is obeyed only up to 6.4 GPa, as seen in Figure 4, showing that it has mechanical stability below 6.4 GPa. Furthermore, the phonon spectra are presented in Figure 5 to ensure the dynamical stability. As observed, there is no imaginary frequency in the whole Brillouin zone, indicating that *Pnma*- Ca_2C is dynamically stable up to at least 100 GPa and that the *C2/m*- Ca_2C is dynamically stable below 6.4 GPa. The elastic constants as a function of pressure are displayed in Figure 6 with an approximately upward tendency. We noticed that, for *Pnma*- Ca_2C , C_{11} is larger than C_{22} or C_{33} at 0 GPa, whereas it is less than C_{22} or C_{33} at high pressures, which is in consistent with our previous analyses on the incompressibility along the *a*-, *b*-, and *c*-axis.

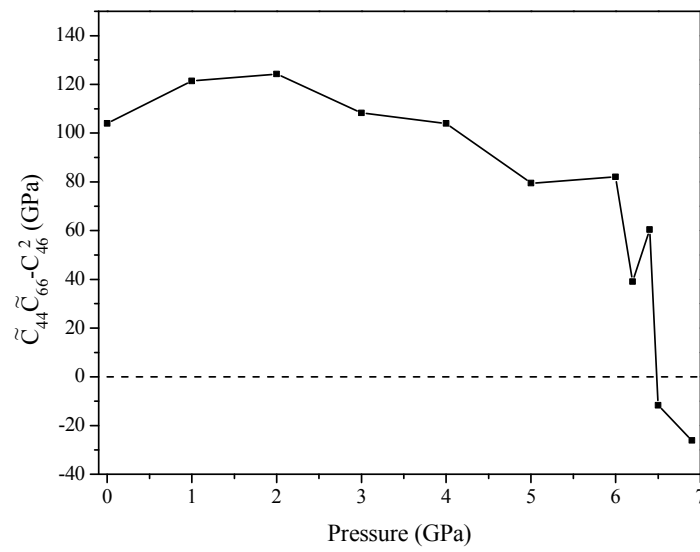


Figure 4. Calculated $\tilde{C}_{44}\tilde{C}_{66} - C_{46}^2$ of C2/*m*-Ca₂C under different pressures.

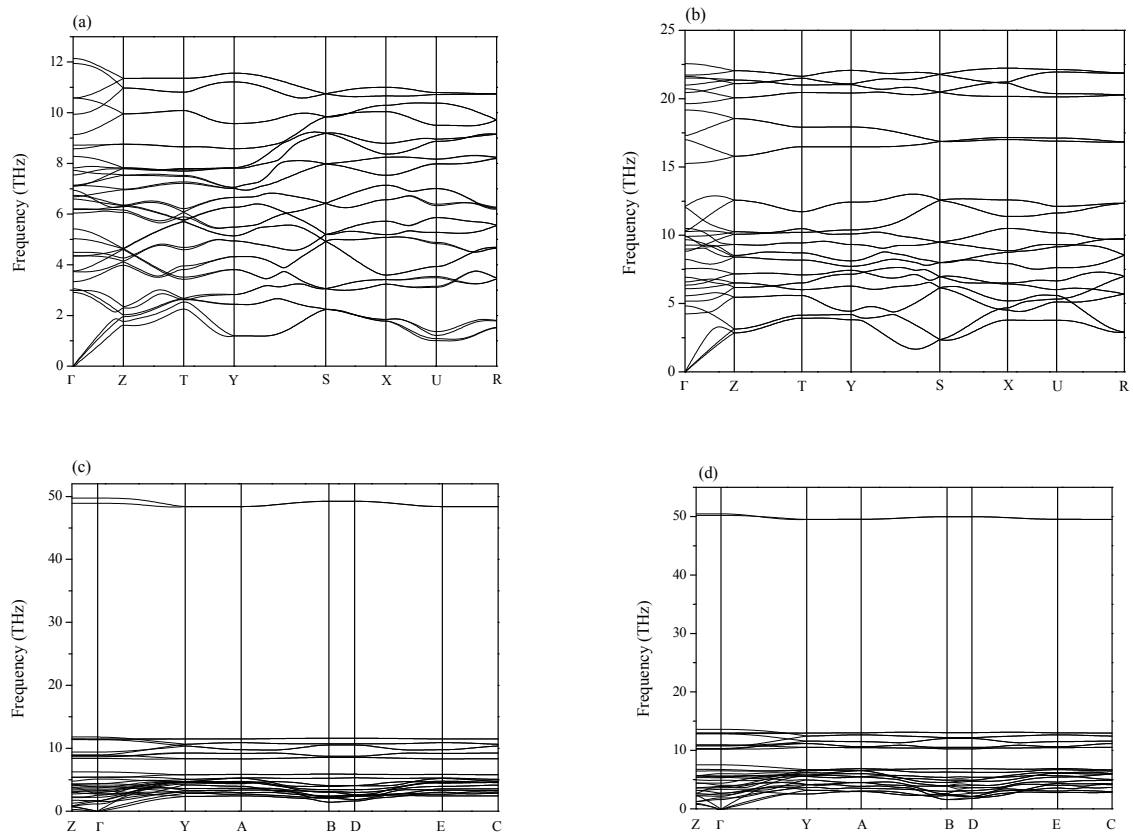


Figure 5. Phonon spectra for (a) *Pnma*-Ca₂C at 0 GPa; (b) *Pnma*-Ca₂C at 100 GPa; (c) C2/*m*-Ca₂C at 0 GPa; (d) C2/*m*-Ca₂C at 6.4 GPa.

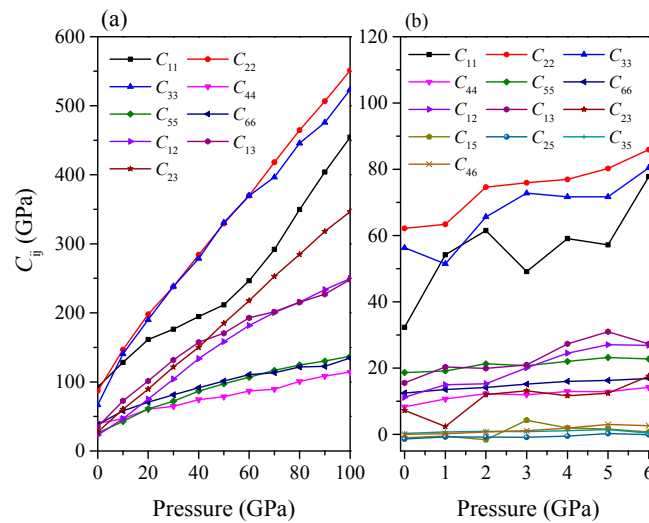


Figure 6. Elastic constants as a function of pressure. (a) *Pnma*-Ca₂C; (b) *C2/m*-Ca₂C.

In Table 3, the bulk modulus B and shear modulus G are calculated by Voigt-Reuss-Hill approximations [20–22]. The Young's modulus E and Poisson's ratio, ν are given by the following equations [22]:

$$E = \frac{9BG}{3B + G}, \nu = \frac{3B - 2G}{2(3B + G)} \quad (16)$$

The *Pnma*-Ca₂C is larger than *C2/m*-Ca₂C in bulk modulus, shear modulus and Young's modulus at 0 GPa, as listed in Table 3. All the elastic modulus increase with pressure for *Pnma*-Ca₂C. According to Pugh [23], the brittle material has a small B/G ratio ($B/G < 1.75$), whereas, the ductile material has a larger ratio ($B/G > 1.75$). It is interesting that *Pnma*-Ca₂C and *C2/m*-Ca₂C show the brittle manner at 0 GPa and transform to ductile manner at 9.3 GPa and 2.0 GPa, respectively.

Calculating the elastic anisotropy of crystal is of great importance to further study the physical and chemical properties. The calculated universal elastic anisotropy index (A^U), shear anisotropic factors (A_1 , A_2 and A_3) and percentage of anisotropy in compressibility and shear (A_B and A_G) are listed in Table 4. For arbitrary symmetry, the universal elastic anisotropy index A^U is obtained by [24,25]:

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \quad (17)$$

Table 4. Calculated universal elastic anisotropy index A^U , shear anisotropic factors A_1 , A_2 and A_3 , and percentage of anisotropy in compressibility and shear A_B and A_G (in %) of Ca₂C.

Phase	Pressure (GPa)	A^U	A_1	A_2	A_3	A_B	A_G
<i>Pnma</i>	0	0.37	1.79	1.06	1.14	0.6	3.5
	50	0.62	1.56	1.34	1.81	3.8	5.1
	100	0.15	0.95	1.44	1.06	1.3	1.2
<i>C2/m</i>	0	0.95	0.58	0.72	0.69	2.7	8.2
	6	0.54	0.53	0.70	0.62	0.06	5.1

When A^U is 0, it means the solid is isotropic, otherwise the solid is anisotropic. The results of *Pnma*-Ca₂C are 0.37 at 0 GPa, 0.62 at 50 GPa and 0.15 at 100 GPa, respectively. And the results of *C2/m*-Ca₂C are 0.95 at 0 GPa and 0.54 at 6 GPa, respectively. All of them are larger than 0, indicating an elastic anisotropy. The shear anisotropic factors provide a measure of the degree of anisotropy in

the bonding between atoms in different planes. The shear anisotropic factor for the {100} shear plane between the <011> and <010> directions is [26,27]:

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (18)$$

For the {010} shear plane between the <101> and <001> directions, it is:

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \quad (19)$$

For the {001} shear plane between the <110> and <010> directions, it is:

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \quad (20)$$

The factors A_1 , A_2 and A_3 are 1.0 for any isotropic crystals. As observed in Table 3, all the calculated shear anisotropic factors are not 1.0, presenting the elastic anisotropy. The percentage anisotropy in compressibility and shear are defined as [26]:

$$A_B = \frac{B_V - B_R}{B_V + B_R}, \quad (21)$$

$$A_G = \frac{G_V - G_R}{G_V + G_R}, \quad (22)$$

where B and G are the bulk and shear modulus, and the subscripts V and R represent the Voigt and Reuss bounds. The values of isotropic crystal are 0.0. In Table 3, the values of A_B and A_G suggest that these two structures of Ca_2C are anisotropic in compressibility and shear.

To intuitively illustrate the elastic anisotropy, the directional dependence of elastic anisotropy was calculated by the ELAM code [28], which shows the 2D figures of the differences in each direction. The calculated Young's modulus along different directions as well as the projections in different planes are demonstrated in Figure 7. The ratios of $E_{\max}/E_{\min}$ are 1.76 (1.19) and 2.32 (1.85) for $Pnma\text{-Ca}_2\text{C}$ at 0 (100) GPa and $C2/m\text{-Ca}_2\text{C}$ at 0 (6.0) GPa, respectively, which means $C2/m\text{-Ca}_2\text{C}$ has greater anisotropy. The anisotropy in yz plane is the greatest for $Pnma\text{-Ca}_2\text{C}$ at both 0 and 100 GPa (see Figure 7a,b). In Figure 7c,d, the $C2/m\text{-Ca}_2\text{C}$ also has the largest anisotropy in yz plane at both 0 and 6 GPa. The 2D representations of Poisson's ratio are revealed in Figure 8. All of them show the elastic anisotropy. From Figure 8a,b, it can be found that the $Pnma\text{-Ca}_2\text{C}$ has the greatest anisotropy in yz plane at 0 GPa and in xz plane at 100 GPa. However, the greatest anisotropy of $C2/m\text{-Ca}_2\text{C}$ is in yz plane at both 0 and 6 GPa (see Figure 8c,d). The $C2/m\text{-Ca}_2\text{C}$ is more anisotropic than the $Pnma\text{-Ca}_2\text{C}$ in Poisson's ratio. As far as the 2D projections of shear modulus in xy , yz , and xz planes shown in Figure 9, both $C2/m\text{-Ca}_2\text{C}$ and $Pnma\text{-Ca}_2\text{C}$ exhibit the obvious elastic anisotropy. From Figure 9a,b, it is seen that the 2D projections of shear modulus in xz plane at 0 GPa and in yz plane at 100 GPa are almost a perfect circle, showing a slight anisotropy character in these two cases. The anisotropy of $Pnma\text{-Ca}_2\text{C}$ at high pressure is smaller than that at 0 GPa. The same case occurred for $C2/m\text{-Ca}_2\text{C}$, as seen in Figure 9c,d. Similar to the anisotropy of Poisson's ratio, the shear modulus of $Pnma\text{-Ca}_2\text{C}$ has the greatest anisotropy in yz plane at 0 GPa and in xz plane at 100 GPa, and that of $C2/m\text{-Ca}_2\text{C}$ is the most anisotropic in yz plane at both 0 and 6 GPa.

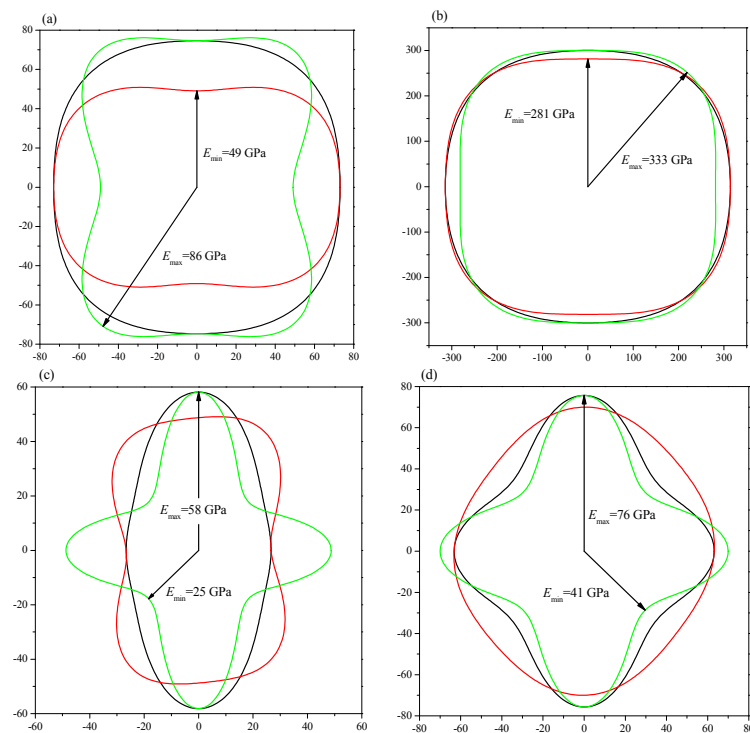


Figure 7. 2D representations of the Young's modulus. (a) *Pnma*-Ca₂C at 0 GPa; (b) *Pnma*-Ca₂C at 100 GPa; (c) *C2/m*-Ca₂C at 0 and 6 GPa; (d) *C2/m*-Ca₂C at 6 GPa. The black, red and green lines represent the *xy*, *xz* and *yz* planes, respectively.

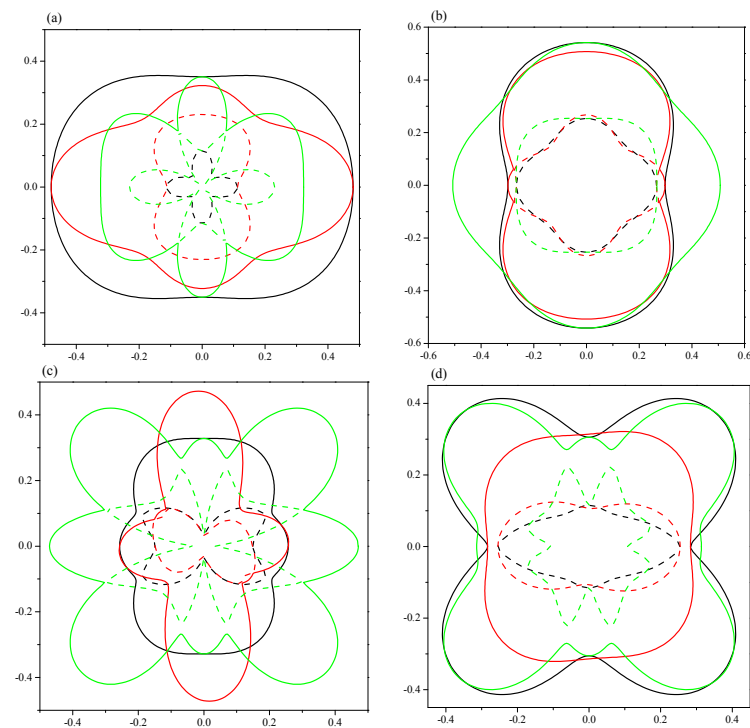


Figure 8. 2D representations of Poisson's ratio. (a) *Pnma*-Ca₂C at 0 GPa; (b) *Pnma*-Ca₂C at 100 GPa; (c) *C2/m*-Ca₂C at 0 GPa; (d) *C2/m*-Ca₂C at 6 GPa. The solid and dash lines represent the maximal and minimal positive values, respectively. The black, red and green lines represent the *xy*, *xz* and *yz* planes, respectively.

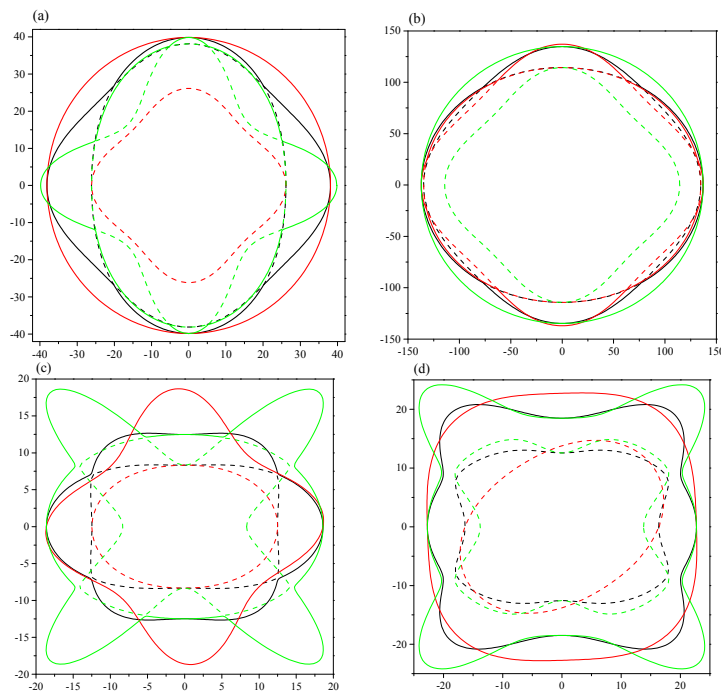


Figure 9. 2D representations of shear modulus. (a) *Pnma*-Ca₂C at 0 GPa; (b) *Pnma*-Ca₂C at 100 GPa; (c) *C2/m*-Ca₂C at 0 GPa; (d) *C2/m*-Ca₂C at 6 GPa. The solid and dash lines represent the maximal and minimal positive values, respectively. The black, red and green lines represent the *xy*, *xz* and *yz* planes, respectively.

As shown in Figure 10, a research of the electronic band structure and density of state (DOS) of Ca₂C at 0 GPa was also made. The dashed line represents the Fermi level (E_F). From Figure 10a, one can see that *Pnma*-Ca₂C is a semiconductor characterized by a quasi-direct band gap of 0.86 eV (the direct band gap at Γ point is 0.87 eV). The conduction band minimum (CBM) is just at Γ point, and the valence band maximum (VBM) locates at (0, 0, 0.378) along the Γ -Z direction. The calculated band gap of *Pnma*-Ca₂C at 14 GPa is direct band gap with 0.65 eV, which is close to the previous value of 0.64 eV [9]. It is known that the calculated band gap with DFT is usually underestimated by 30%–50%, so the ideal band gap is larger than this calculated result. The DOS of *Pnma*-Ca₂C near Fermi level is mainly originated from the contributions of C-*p* orbital electrons. In Figure 10b, the calculated electronic band structure crosses the Fermi level along many directions in the Brillouin zone, showing the metallic character. And the DOS near Fermi level is mainly characterized by the Ca-*d* orbital electrons.

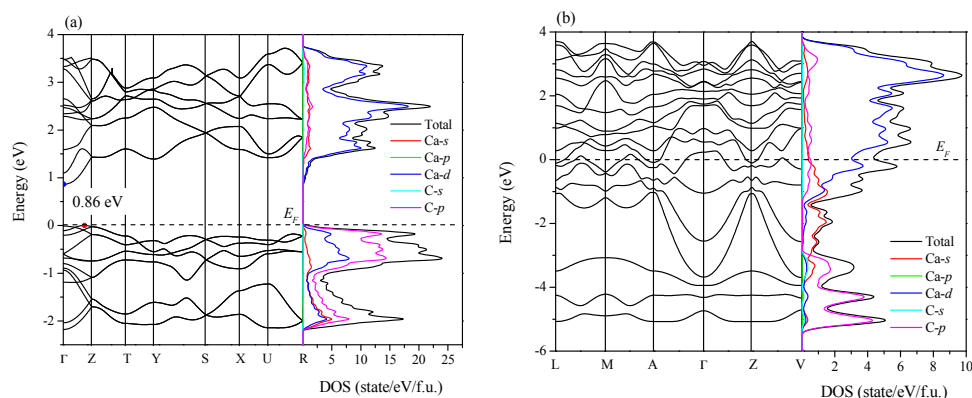


Figure 10. Electronic band structure and density of state of *Pnma*-Ca₂C (a) and *C2/m*-Ca₂C (b) at 0 GPa.

3. Computational Methods

Our calculations are performed via the generalized gradient approximation (GGA) parameterized by Perdew-Burke-Eruzerhof (PBE) [29] in the Cambridge Serial Total Energy Package (CASTEP) code [30], which is based on the density functional theory (DFT) [31,32]. For the two Ca_2C phases, the ultrasoft pseudo-potential [33] which describes the interactions between the ionic core and valence electrons is used with the cutoff energy of 420 eV. The k-points of $Pnma\text{-Ca}_2\text{C}$ ($7 \times 11 \times 6$) and $C2/m\text{-Ca}_2\text{C}$ ($6 \times 9 \times 3$) in the first irreducible Brillouin zone are generated using Monkhorst-Pack mesh scheme [34]. Furthermore, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [35] is used in geometry optimization. The convergence is within 1 meV/atom in the total energy convergence tests for all calculation parameters. The self-consistent convergence of the total energy is 5×10^{-6} eV/atom, the maximum force on the atom is 0.01 eV/Å, the maximum stress is 0.02 GPa and the maximum ionic displacement is 5×10^{-4} Å.

4. Conclusions

A systematic analysis of the pressure-induced phase transition of Ca_2C is made by first-principles calculations. The enthalpy and dependence of volume on pressure of Ca_2C are performed. We found that there is a phase transition which occurs at 7.8 GPa transforming from $C2/m\text{-Ca}_2\text{C}$ to $Pnma\text{-Ca}_2\text{C}$ with a volume drop of 26.7%. The $Pnma\text{-Ca}_2\text{C}$ is larger than $C2/m\text{-Ca}_2\text{C}$ in the calculated bulk modulus, shear modulus, Young's modulus and Poisson's ratio at 0 GPa. Both of them exhibit the elastic anisotropy. The low-pressure phase $C2/m\text{-Ca}_2\text{C}$, which is mechanically stable up to 6.4 GPa, has the greater anisotropy over the $Pnma\text{-Ca}_2\text{C}$. The electronic band structures reveal the semiconductivity of $Pnma\text{-Ca}_2\text{C}$ and the metallicity of $C2/m\text{-Ca}_2\text{C}$. The quasi-direct band gap of $Pnma\text{-Ca}_2\text{C}$ at 0 GPa is 0.86 eV. Furthermore, the total and partial density of states is provided to study the specific contribution to Fermi level.

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References

1. Zhang, W.; Oganov, A.R.; Goncharov, A.F.; Zhu, Q.; Boulfelfel, S.E.; Lyakhov, A.O.; Stavrou, E.; Somayazulu, M.; Prakapenka, V.B.; Konôpková, Z. Unexpected stable stoichiometries of Sodium Chlorides. *Science* **2013**, *342*, 1502–1505. [[CrossRef](#)] [[PubMed](#)]
2. Kurakevych, O.O.; Strobel, T.A.; Kim, D.Y.; Cody, G.D. Synthesis of Mg_2C : A Magnesium Methanide. *Angew. Chem. Int. Ed.* **2013**, *52*, 8930–8933. [[CrossRef](#)] [[PubMed](#)]
3. Fan, Q.; Chai, C.; Wei, Q.; Yang, Y.; Yang, Q.; Chen, P.; Xing, M.; Zhang, J.; Yao, R. Prediction of novel phase of silicon and Si-Ge alloys. *J. Solid State Chem.* **2016**, *233*, 471–483. [[CrossRef](#)]
4. Wei, Q.; Yan, H.; Zhu, X.; Lin, Z.; Yao, R. Theoretical investigations on the elastic and thermodynamic properties of Rhenium Phosphide. *Z. Naturforsch. A* **2016**, *71*, 1–8. [[CrossRef](#)]
5. Gauzzi, A.; Takashima, S.; Takeshita, N.; Terakura, C.; Takagi, H.; Emery, N.; Hérold, C.; Lagrange, P.; Loupiaz, G. Enhancement of superconductivity and evidence of structural instability in intercalated Graphite CaC_6 under high pressure. *Phys. Rev. Lett.* **2007**, *98*, 067002. [[CrossRef](#)] [[PubMed](#)]
6. Nylén, J.; Konar, S.; Lazor, P.; Benson, D.; Häussermann, U. Structural behavior of the acetylide carbides Li_2C_2 and CaC_2 at high pressure. *J. Chem. Phys.* **2012**, *137*, 224507. [[CrossRef](#)] [[PubMed](#)]

7. Li, Y.L.; Luo, W.; Zeng, Z.; Lin, H.Q.; Mao, H.K.; Ahuja, R. Pressure-induced superconductivity in CaC₂. *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 9289–9294. [[CrossRef](#)] [[PubMed](#)]
8. Nourbakhsh, Z.; Hashemifar, S.J.; Akbarzadeh, H. First-principles insights into *p* magnetism in CaC and CaN ionic compounds. *J. Magn. Magn. Mater.* **2013**, *341*, 56–59. [[CrossRef](#)]
9. Li, Y.L.; Wang, S.N.; Oganov, A.R.; Gou, H.; Smith, J.S.; Strobel, T.A. Investigation of exotic stable calcium carbides using theory and experiment. *Nat. Commun.* **2015**, *6*, 6974. [[CrossRef](#)] [[PubMed](#)]
10. Dong, S.; Ding, H.; Zhou, B.; Duan, C.; Wu, P.; Zhao, H. First-principles and Monte Carlo studies on the magnetic stability of half-metallic zinc-blende CaC and similar compounds. *J. Magn. Magn. Mater.* **2015**, *378*, 469–477. [[CrossRef](#)]
11. Debessai, M.; Hamlin, J.J.; Schilling, J.S.; Rosenmann, D.; Hinks, D.G.; Claus, H. Superconductivity for CaC₆ to 32 GPa hydrostatic pressure. *Phys. Rev. B* **2010**, *82*, 132502. [[CrossRef](#)]
12. Mazin, I.I.; Boeri, L.; Dolgov, O.V.; Golubov, A.A.; Bachelet, G.B.; Giantomassi, M.; Andersen, O.K. Unresolved problems in superconductivity of CaC₆. *Physics C* **2007**, *460–462*, 116–120. [[CrossRef](#)]
13. Zhang, L.; Xie, Y.; Cui, T.; Li, Y.; He, Z.; Ma, Y.; Zou, G. Pressure-induced enhancement of electron-phonon coupling in superconducting CaC₆ from first principles. *Phys. Rev. B* **2006**, *74*, 184519. [[CrossRef](#)]
14. Moradi, M.; Mohammadi, A.; Afshari, M.; Soltani, Z. The half-metallicity of zinc-blende CaC/GaAs (001) heterojunction: A density functional theory study. *J. Magn. Magn. Mater.* **2013**, *332*, 81–84. [[CrossRef](#)]
15. Nourbakhsh, Z.; Hashemifar, S.J.; Akbarzadeh, H. Ab initio study of different structures of CaC: Magnetism, bonding, and lattice dynamics. *J. Alloys Compd.* **2013**, *579*, 360–364. [[CrossRef](#)]
16. Gao, G.Y.; Yao, K. Surface *sp* half-metallicity of zinc-blende calcium monocarbide. *J. Appl. Phys.* **2009**, *106*, 053703. [[CrossRef](#)]
17. Wu, Z.-J.; Zhao, E.-J.; Xiang, H.-P.; Hao, X.-F.; Liu, X.-J.; Meng, J. Crystal structures and elastic properties of superhard IrN₂ and IrN₃ from first principles. *Phys. Rev. B* **2007**, *76*, 054115. [[CrossRef](#)]
18. Fan, Q.Y.; Wei, Q.; Yan, H.Y.; Zhang, M.G.; Zhang, D.Y.; Zhang, J.Q. A New Potential Superhard Phase of OsN₂. *Acta Phys. Pol. A* **2014**, *126*, 740–746. [[CrossRef](#)]
19. Sin'Ko, G.V.; Smirnov, N.A. Ab initio calculations of elastic constants and thermodynamic properties of bcc, fcc, and hcp Al crystals under pressure. *J. Phys. Condens. Matter* **2002**, *14*, 6989–7005.
20. Voigt, W. *Lehrbuch der Kristallphysik*; Teubner: Leipzig, Germany, 1928.
21. Reuss, A. Berechnung der Fließgrenze von Mischkristallen auf Grund der Plastizitätsbedingung für Einkristalle. *J. Appl. Math. Mech.* **1929**, *9*, 49–58. [[CrossRef](#)]
22. Hill, R. The Elastic Behaviour of a Crystalline Aggregate. *Phys. Soc. Lond. Sect. A* **1952**, *65*, 349–354. [[CrossRef](#)]
23. Pugh, S.F. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *Lond. Edinb. Dublin Philos. Mag. J. Sci.* **1954**, *45*, 823–843. [[CrossRef](#)]
24. Ranganathan, S.I.; Ostoja-Starzewski, M. Universal Elastic Anisotropy Index. *Phys. Rev. Lett.* **2008**, *101*, 055504. [[CrossRef](#)] [[PubMed](#)]
25. Feng, J.; Xiao, B.; Zhou, R.; Pan, W.; Clarke, D.R. Anisotropic elastic and thermal properties of the double perovskite slab-rock salt layer Ln₂SrAl₂O₇ (Ln = La, Nd, Sm, Eu, Gd or Dy) natural superlattice structure. *Acta Mater.* **2012**, *60*, 3380–3392. [[CrossRef](#)]
26. Ravindran, P.; Fast, L.; Korzhavyi, P.A.; Johansson, B.; Wills, J.; Eriksson, O. Density functional theory for calculation of elastic properties of orthorhombic crystals: Application to TiSi₂. *J. Appl. Phys.* **1998**, *84*, 4891–4904. [[CrossRef](#)]
27. Wei, Q.; Zhang, M.; Yan, H.; Lin, Z.; Zhu, X. Structural, electronic and mechanical properties of Imma-carbon. *Europhys. Lett.* **2014**, *107*, 27007. [[CrossRef](#)]
28. Marmiera, A.; Lethbridge, Z.A.D.; Walton, R.I.; Smith, C.W.; Parker, S.C.; Evans, K.E. ELAM: A computer program for the analysis and representation of anisotropic elastic properties. *Comput. Phys. Commun.* **2010**, *181*, 2102–2115. [[CrossRef](#)]
29. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [[CrossRef](#)] [[PubMed](#)]
30. Clark, S.J.; Segall, M.D.; Pickard, C.J.; Hasnip, P.J.; Probert, M.I.J.; Refson, K.; Payne, M.C. First principles methods using CASTEP. *Z. Kristallogr.* **2005**, *220*, 567–570. [[CrossRef](#)]
31. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871. [[CrossRef](#)]

32. Kohn, W.; Sham, L.J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138. [[CrossRef](#)]
33. Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* **1990**, *41*, 7892–7895. [[CrossRef](#)]
34. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192. [[CrossRef](#)]
35. Pfrommer, B.G.; Côté, M.; Louie, S.G.; Cohen, M.L. Relaxation of Crystals with the Quasi-Newton Method. *J. Comput. Phys.* **1997**, *131*, 233–240. [[CrossRef](#)]



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