Crystal structures and electronic properties of solid fluorine under high pressure*

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As the previously proposed structures of $C2/m$ and $C2/c$ possess similar enthalpies and x-ray diffraction patterns, the space group of fluorine at ambient pressure is in controversy. We successfully obtain its thermodynamically stable low-pressure phase, which shares the same structure as the earlier known $C2/c$. Further investigations on phonon spectra reveal the instability of the $C2/m$ structure with imaginary frequency in the Brillouin zone and confirm the dynamically stable property of the $C2/c$ structure at the same time. Compressing fluorine up to 8 GPa, the $C2/c$ phase is found to undergo a phase transition to a new structure with a space group of *Cmca*. Electronic energy band structures indicate the insulating feature of $C2/c$ and *Cmca* with no bands across the Fermi level. The infrared (IR) and Raman spectra of $C2/c$ and *Cmca* at selected pressures are calculated to provide useful information to future experiments.

Keywords: fluorine, structure, insulating feature

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1. Introduction

As a long-lived issue in physics and chemistry, high-pressure properties of diatomic molecules, such as H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2, have aroused keen interest. Among these molecular systems, hydrogen is the simplest and most abundant element in the universe. Since Wigner and Huntington[1] put forward that sufficient high pressure could induce both a molecular to atomic transition and an insulator to metal transition, the research door was opened. As an all-important dimension independent of temperature and chemical compositions, pressure can effectively change the internal structures and properties of materials, and then form high pressure structures with new physical properties or new matters that cannot exist at ambient pressure. Actually, pressure-induced transitions such as insulator to metal,[2–9] metal to semiconductor,[10] metal to insulator[11–13] transitions, have been widely reported in a variety of elements and compounds. Metallic hydrogen was predicted to be a superconductor with a high transition temperature according to Ashcroft[14] in 1968. Since then, extensive high pressure experimental and theoretical investigations of solid hydrogen have been conducted.[15–21] However, to the best of our knowledge, as a result of the strong bond interaction between internal hydrogen,[18,22] neither metallic hydrogen nor molecular dissociation has been reported up to now. The pressure-induced metallization and phase transition of molecular-to-monatomic in the other diatomic molecular systems such as nitrogen[23,24] and halogens[25–28] have been detected in both experiments and theories.

Fluorine, the first of the halogens and the last of the first-row diatomic elements, has many characteristics similar to hydrogen. On the other hand, elemental fluorine is also an abundant element in the universe and it is a system of particular interest and exhibits many unusual physical and chemical properties by virtue of the strongest oxidability and electronegativity. The fluorine-related systems have also been studied extensively, for example, BaF_2 is the fastest luminescent material that has been found to date,[29,30] MgF_2 is an archetypal simple ionic solid,[31] BaF radical is a promising candidate for laser cooling and magneto-optical trapping,[32] and some new fluoride-arsenides can be used as diluted magnetic semiconductors.[33–35]

The crystal structure of β-F_2 is determined[36] to be cubic, with space group $Pm3n$ and eight molecules per unit cell, which is very similar to the structure of γ-O_2.[37] β-F_2 is stable between the melting point 53.5 K and a solid-solid transition point 45.6 K. However, the structure of the low-temperature phase of fluorine at atmospheric pressure (α-F_2), which is stable up to 45.6 K, has not been identified in spite of many theoretical and experimental researches on the crystal structures of halogen.[38] The x-ray powder diffraction studies of Meyer *et al.*[39] indicated that α-F_2 is monoclinic, and provided two controversial candidate space groups $C2/m$ and $C2/c$ of solid fluorine at ambient pressure. A later interpretation of this x-

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ray data by Pauling *et al.*[40] supported that the space group is $C2/c$ ($a = 5.50$ Å, $b = 3.28$ Å, $c = 7.28$ Å, $\beta = 102.17°$ with four fluorine molecules in the conventional cell, but cannot rule out $C2/m$ completely. Afterwards, many spectroscopic studies and theoretical calculations[41–45] were carried out to determine the space group of solid fluorine at ambient pressure, yet provided no new insights as to whether $C2/m$ or $C2/c$ is the good candidate. Therefore, the symmetry group of fluorine at ambient pressure hitherto is in dispute.

Besides, the high-pressure properties of solid fluorine have not been sufficiently covered, thus the structures of crystal fluorine in a wide pressure range of 0–100 GPa are explored by using first-principles calculations based on the density functional theory (DFT)[46,47] in this paper. In this work, the thermodynamically stable phase $C2/c$ at low-pressure is obtained by us, which possesses the same structure as earlier known $C2/c$.[40] Our high precision calculations on enthalpies of $C2/m$ and $C2/c$ fluorine through the VASP code suggest that the $C2/c$ phase is slightly more energetically stable than $C2/m$ at low pressure. Further investigations indicate that $C2/m$ has imaginary phonon frequencies, while $C2/c$ establishes dynamical stability. Theoretically, $C2/c$ is determined to be the better candidate of solid fluorine at ambient pressure. At about 8 GPa, $C2/c$ transforms to a new high-pressure phase *Cmca* proposed by us. *Cmca* remains intact at the pressure of 100 GPa, which is not similar to the other halogen molecules that readily exhibit molecular dissociation. The electronic properties demonstrate that both $C2/c$ and *Cmca* are insulators. The nonmetallic property of *Cmca* fluorine is different from that of the other halogen crystals with the prototypical structure of *Cmca*.

2. Calculation methods

We use the ELocR[48] code to predict the structure of fluorine under high pressure. The energetic and electronic structure calculations are performed with the Vienna *ab initio* simulation package (VASP)[49] within density-functional theory using the Perdew–Burke–Ernzerh (PBE) of generalized gradient approximation (GGA).[50] The $2s^2 2p^5$ electrons are treated as the valence electrons. A plane-wave cutoff of 900 eV and appropriate Monkhorst–Pack k-meshes are employed with the resolution of $2\pi \times 0.03$ Å^{-1} for Brillouin zone (BZ) sampling to ensure that all the enthalpy calculations are well converged to less than 1 meV/ atom. The phonon, infrared (IR), and Raman spectra are calculated by CASTEP.[51] In the calculation of phonon, IR, and Raman spectra, the norm-conserving scheme is used to generate the pseudopotential, the tolerance in the self-consistent field (SCF) calculation is 1.0×10^{-6} eV/atom.

3. Results and discussion

The crystal structures of fluorine are explored through ELocR, the calculated enthalpy difference ΔH relative to $C2/m$-4 as a function of pressure is summarized in Fig. 1. Geometry optimization performed with all structures acquired by us indicates that the thermodynamically stable low-pressure phase is $C2/c$, which shares the same structure as the previously proposed one by the experiment.[40] Actually, the x-ray powder diffraction experiment[40] carried out on solid fluorine provided two controversial candidates with the space groups of $C2/m$ and $C2/c$.Because the energies and x-ray patterns of $C2/m$ and $C2/c$ are very similar, the debate on the structures of solid fluorine continues. Our high precision calculations on enthalpies of $C2/m$ and $C2/c$ fluorine through the VASP code, as shown in Fig. 1(a), reveal that the differences between the two structures are 0.97 meV/atom, 8.65 meV/atom, and 9.52 meV/atom at 1 GPa, 4 GPa, and 6 GPa, respectively, which suggests that the $C2/c$ phase is slightly more energetically stable than $C2/m$ at low pressure. As the pressure is raised on fluorine up to 8 GPa, the $C2/c$ structure is found to experience a transformation into a new structure with a space group of *Cmca*. The *Cmca* phase is superior to the other structures in energy in the pressure range of 8–100 GPa, as presented in Fig. 1(b). The other six energetic competing structures detected in our structure searches are R-3m, $I4/mmm$, $Immm$, $C2/m$-4,$C2/m$-16, and $C2/c$-16. Here, $C2/m$-4,$C2/m$-16, and $C2/c$-16 are labeled in this way for differentiating the earlier proposed structures $C2/m$[39] and $C2/c$,[40] and the digits represent the number of atoms in the conventional cell of the crystal lattice.

The favored structures of solid fluorine obtained in this work are illustrated in Fig. 2 and the corresponding parameters at the selected pressures are presented in Table 1. In the $C2/c$ phase, there are eight fluorine atoms in the conventional cell occupying the position $8f$, with the position ($x = -1.10808$, $y = 0.07600$, $z = -0.09642$) in the fractional coordination at ambient pressure. The diatomic molecules of fluorine consist of a layered structure with different inclination directions of bonds in the adjacent two layers, where different colors are painted for comparison, as can be seen in Fig. 2(b). The layered structure possesses the feature associated with the equivalent intramolecular bond length. The intramolecular bond lengths of solid fluorine are detected as 1.418 Å, 1.421 Å, and 1.422 Å at 1 bar, 1 GPa, and 6 GPa, respectively, and the corresponding shortest intermolecular distances are 2.710 Å, 2.613 Å, and 2.397 Å. The pressure dependencies of the intramolecular and intermolecular distances in the $C2/c$ phase plotted in Fig. 3(a) demonstrate that the intermolecular distance declines continuously with pressure, while the changed trend of the bond length is just the opposite.

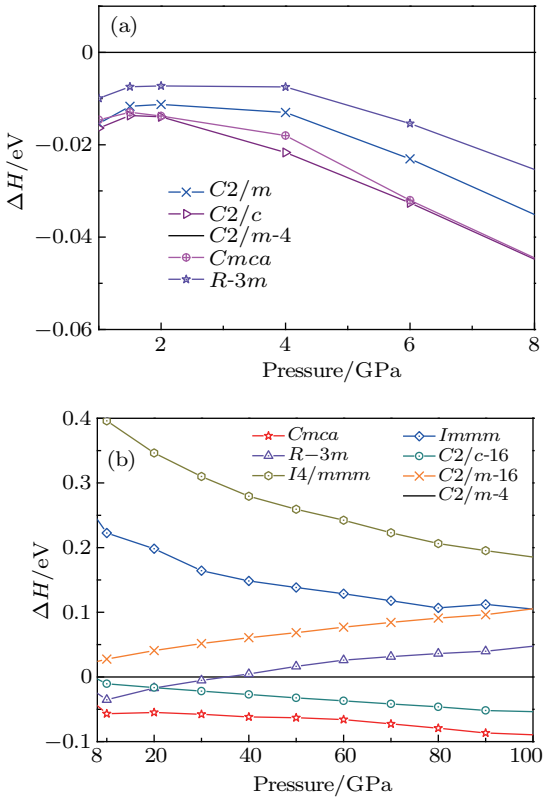


Fig. 1. (color online) Calculated enthalpy per fluorine atom relative to $C2/m$-4 as a function of pressure in the pressure ranges of (a) 1–8 GPa and (b) 8–100 GPa.

The phenomena are also observed in the $C2/c$ structure of solid hydrogen.[52] The differences between hydrogen and fluorine are that the $C2/c$ fluorine has an equivalent intramolecular bond length, while the $C2/c$ hydrogen possesses two different bond lengths. Moreover, the shorter intramolecular distance and the typical intermolecular distance of solid hydrogen reach equality at 600 GPa upon compression and the hydrogen molecules start to dissociate. However, the intermolecular distance of the $C2/c$ fluorine remains longer than the intramolecular bond length all the time. With increasing pressure, the $C2/c$ fluorine transforms into *Cmca* without any dissociation. The lattice parameters as a function of pressure in solid fluorine are presented in Fig. 3(b). It can be seen that the lattice parameters a and b decrease smoothly with pressure, while c shows a sudden decline near 8 GPa, revealing a phase transition in the vicinity.

The lattice of *Cmca* is orthorhombic with axes $a = 4.3115$, $b = 2.8812$, $c = 8.8082$ at 20 GPa. The cyrstallographic sites of the eight atoms in the conventional cell are in the position $8f$ ($x = -0.5000$, $y = 0.3799$, $z = 1.39328$). The crystal fluorine of the *Cmca* phase also has a layered structure and the distribution of fluorine molecules is similar to that of $C2/c$ structure as shown in Fig. 2(c). The bond lengths of fluorine molecules are 1.425 Å, 1.423 Å, and 1.416 Å at 10 GPa, 60 GPa, and 100 GPa, respectively, and the corresponding nearest intermolecular distances are 2.314 Å, 2.017 Å, and 1.931 Å. The decreases of the bond length and intermolecular distance with pressure indicate the strong covalent chemical bond between the fluorine atoms. Moreover, the intermolecular distance is longer than the intramolecular bond length in the *Cmca* phase, suggesting that *Cmca* remains intact at the pressure of 100 GPa. The molecular feature of *Cmca* is different from that of the other halogen molecules, which readily exhibit molecular dissociation. For example, solid bromine begins to undergo a phase transition of molecular-to-monatomic near 80 GPa,[25] and a molecular dissociation in solid iodine is observed at 21 GPa.[26,53,54]

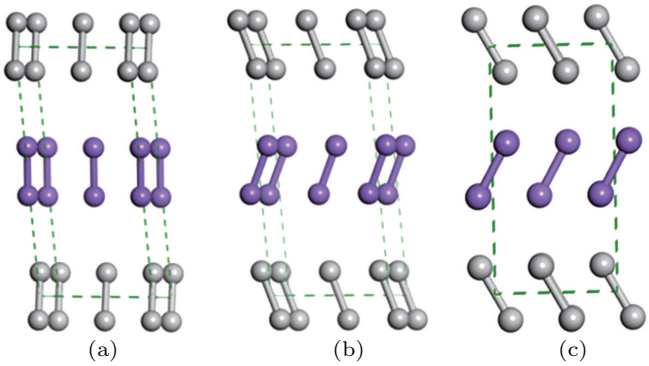


Fig. 2. (color online) The structures of fluorine at selected pressures: (a) $C2/m$ at 0 GPa, (b) $C2/c$ at 0 GPa, (c) *Cmca* at 20 GPa. Different color fluorine molecules represent different kinds of molecules.

Table 1. Optimized structural parameters for solid fluorine at selected pressures.

Space group (pressure)	Lattice parameters/Å	Atomic coordinates (fractional)	Site
$C2/m$ (0 GPa)	$a = 5.4702$ Å $b = 3.2316$ Å $c = 10.0675$ Å $\alpha = \gamma = 90°$, $\beta = 135.4132°$	F1 0.16242 –0.0000 0.09619 F2 0.09906 –0.0000 0.59767	$4i$ $4i$
$C2/c$ (0 GPa)	$a = 5.4009$ Å $b = 3.2657$ Å $c = 9.4781$ Å $\alpha = \gamma = 90°$, $\beta = 133.5472°$	F1 –1.10808 0.07600 –0.09642	$8f$
Cmca (20 GPa)	a=4.3115 Å $b = 2.8812$ Å $c = 5.8363$ Å $\alpha = \beta = \gamma = 90°$	F1 –0.5000 0.3799 1.39328	$8f$

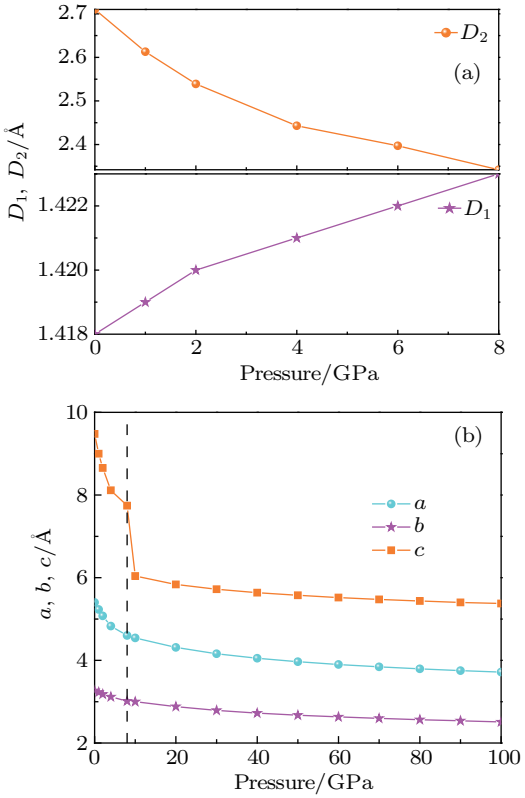


Fig. 3. (color online) Neighboring distances in the $C2/c$ phase and lattice parameters of crystal fluorine plotted as a function of pressure: (a) neighboring distances, D_1 and D_2 represent the intramolecular distance and the shortest intermolecular distance, respectively; (b) lattice parameters.

For a stable crystal structure, mechanical stability is a necessary condition and it requires the strain energy to be positive, i.e., the whole set of elastic constants C_{ij} satisfies the Born–Huang criterion.[55] For a monoclinic crystal, the independent elastic stiffness tensor consists of thirteen components C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, C_{23}, C_{15}, C_{25}, C_{35}, and C_{46}, the mechanical stability criteria are given by

$$\begin{aligned}
&C_{11}>0,\quad C_{22}>0,\quad C_{33}>0,\quad C_{44}>0,\quad C_{55}>0,\quad C_{66}>0,\\
&[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]>0,\\
&(C_{33}C_{55}-C_{35}^2)>0,\quad (C_{44}C_{66}-C_{46}^2)>0,\\
&(C_{22}+C_{33}-2C_{23})>0,\\
&[C_{22}(C_{33}C_{55}-C_{35}^2)+2C_{23}C_{25}C_{35}\\
&-C_{23}^2C_{55}-C_{25}^2C_{33}]>0. \qquad (1)
\end{aligned}$$

For an orthorhombic crystal, the independent elastic stiffness tensor consists of nine components C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, and C_{23}, and the mechanical stability criteria are given by

$$\begin{aligned}
&C_{11}>0,\quad C_{22}>0,\quad C_{33}>0,\quad C_{44}>0,\quad C_{55}>0,\quad C_{66}>0,\\
&[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]>0,\\
&[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]>0,\\
&(C_{11}+C_{22}-2C_{12})>0,\quad (C_{11}+C_{33}-2C_{13})>0,\\
&(C_{22}+C_{33}-2C_{23})>0. \qquad (2)
\end{aligned}$$

The elastic stiffness constants C_{ij} of $C2/c$ and $Cmca$ at 0 GPa and 100 GPa, respectively, are illustrated in Table 2. Comparing the results with the stability criteria stated above, obviously, the C_{ij} calculated by us fulfills the stability criteria, suggesting that $C2/c$ and $Cmca$ are mechanically stable at the selected pressures. Besides, another essential requirement for a stable structure is lattice dynamic stability, thus the phonon spectra of $C2/c$ and $Cmca$ along several high symmetry directions at 0 GPa and 100 GPa respectively are calculated and depicted in Figs. 4(b) and 4(c). The absence of imaginary phonon frequencies in the Brillouin zone suggests that the two structures are dynamically stable.

Table 2. The calculated elastic stiffness coefficients (in GPa) of $C2/c$ at ambient pressure and $Cmca$ at 100 GPa.

Space group (pressure)	C_{11} C_{13}	C_{22} C_{23}	C_{33} C_{15}	C_{44} C_{25}	C_{55} C_{35}	C_{66} C_{46}	C_{12}
$C2/c$	415.63	388.05	299.58	119.83	96.07	113.78	126.68
(0 GPa)	92.13	116.42	–7.36	–4.16	9.02	–16.91	
$Cmca$	1725.71	1380.42	1612.33	738.07	276.18	528.91	704.77
(100 GPa)	415.14	999.42					

It is worth mentioning that the x-ray powder diffraction experiment carried out on solid fluorine provided two candidates with the space groups of $C2/m$ and $C2/c$. As geometry optimization is applied to the controversial structures of $C2/m$ and $C2/c$, the calculated lattice parameters of $C2/m$ phase ($a=5.4702$, $b=3.2316$, $c=10.0675$) and $C2/c$ phase ($a=5.4009$, $b=3.2657$, $c=9.4781$) at ambient pressure are comparable with the experimental values ($a=5.50$, $b=3.28$, $c=10.01$). Both $C2/m$ and $C2/c$ structures are monoclinic, the fluorine molecule distributions are analogous to each other, except they differ slightly in their molecular orientations as shown in Figs. 2(a) and 2(b). Comparing the theoretical x-ray diffraction patterns of the two controversial structures with the experimental data, it comes to a conclusion that the experimental data are in good coincidence with the spectra of $C2/c$ and $C2/m$ at ambient pressure. Thus, it is difficult to judge which is better for the crystal fluorine only based on the x-ray diffraction spectrum.

Although small different enthalpies between $C2/m$ and $C2/c$ crystals exist as mentioned above, $C2/c$ is more energetically stable than $C2/m$ at low pressure. Further investigations on the lattice dynamic stability reveal the dynamical stability of $C2/c$ comparing the instability of $C2/m$ with imaginary frequency in the vicinity of high symmetry points of M, G, and V in the Brillouin zone, as shown in Figs. 4(b) and 4(a). Theoretically, $C2/c$ is the better candidate for crystal fluorine at ambient pressure.

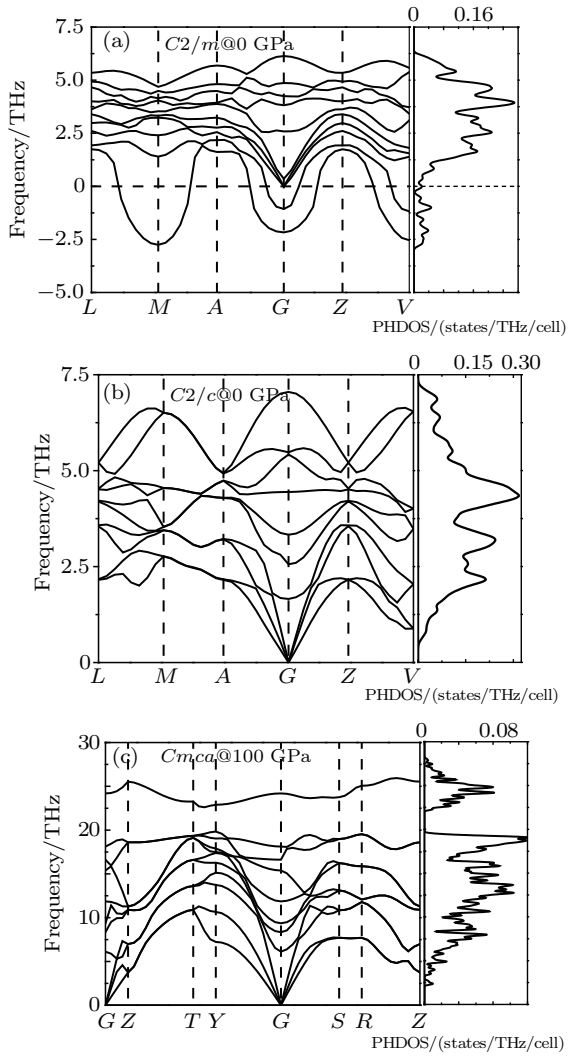


Fig. 4. Calculated phonon dispersion curves for (a) $C2/m$ at 0 GPa, (b) $C2/c$ at 0 GPa, and (c) *Cmca* at 100 GPa.

To uncover the electronic properties of the $C2/c$ and *Cmca* phases, the electronic band structure and the corresponding density of states (DOS) of $C2/c$ at 6 GPa and *Cmca* at 100 GPa are calculated and illustrated in Fig. 5. It is obvious that solid fluorine can keep the insulting property at least up to 100 GPa by the observation of no bands crossing the Fermi level, for example, the gaps are 2.58 eV and 2.28 eV for $C2/c$ at 6 GPa and *Cmca* at 100 GPa, respectively. It is noticeable that the nonmetallic property of *Cmca* fluorine is a complete contrast to the other halogen crystals with the prototypical structure of *Cmca*, such as the pressure-induced metallization in the *Cmca* iodine at 20.6 GPa[27,56] and the insulator-to-metal transition in the molecular *Cmca* bromine with band overlap at 55 GPa.[28] While the decreasing band gap with pressure in the solid fluorine suggests a transition from insulator to metal at sufficient high pressure.

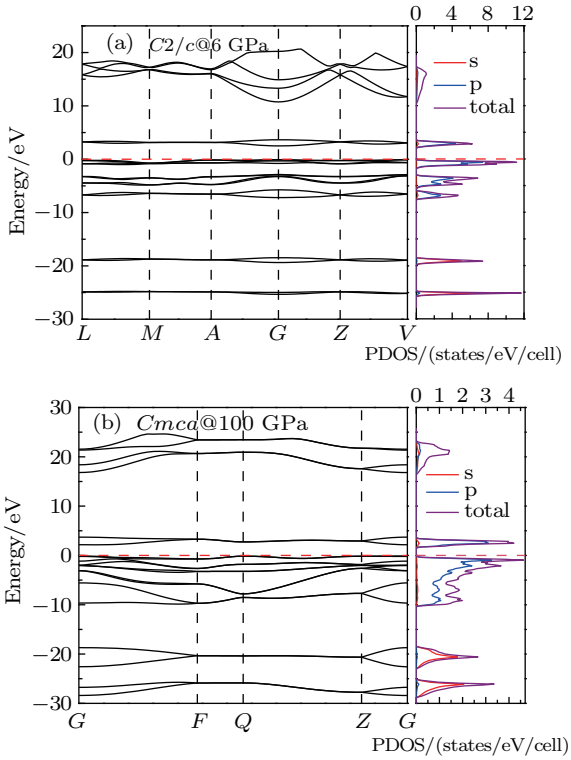


Fig. 5. (color online) The calculated electronic band structure and the corresponding density of states (DOS): (a) $C2/c$ at 6 GPa, (b) *Cmca* at 100 GPa.

Allowing for less high-pressure experimental data of crystal fluorine, we calculate the IR and Raman spectra of $C2/c$ and *Cmca* at 1 GPa and 20 GPa, respectively, as described in Table 3. The vibrational frequencies of IR and Raman can be obtained by calculating the optical phonons at the zone center (Γ point) and the phonons at the Γ point of the two phases can be classified by the irreducible representations of the point groups C_{2h} ($C2/c$) and D_{2h} (*Cmca*). Based on group theory analysis of the crystal, six Raman-active bands are expected in the $C2/c$ or $C2/m$ phase of solid fluorine, including two internal modes and four external modes.[41] For the $C2/c$ phase, $\Gamma_{\text{optic}} = 2A_u + B_u + 3B_g + 3A_g$, where A_u, B_u modes are IR active and B_g, A_g modes are Raman active. For the *Cmca* phase, $\Gamma_{\text{optic}} = B_{1u} + B_{2u} + 2A_g + B_{1g} + B_{2g} + 2B_{3g}$, where the B_{1u}, B_{2u} modes are IR active and A_g, B_{1g}, B_{2g}, B_{3g} modes are Raman active. At the low temperature of 15±5 K and the low pressure of 1 GPa, three external Raman modes locating at 57 cm^{-1}, 76 cm^{-1}, 109 cm^{-1} and one internal mode locating at 900 cm^{-1} have been clearly detected by the latest Raman data of solid fluorine.[45] The fourth external mode detected

in the experiment[41] is located at 93 cm^{-1}, but it is still uncertain due to its low intensity. Comparing the Raman modes to our calculated data of $C2/c$ fluorine, four external Raman-active modes in our work should be 49.41 cm^{-1}, 54.53 cm^{-1}, 104.13 cm^{-1}, 129.48 cm^{-1} and the one internal mode should be the merged peaks of 932.84 cm^{-1} and 933.86 cm^{-1}. The calculated values are expected to provide useful information to future high-pressure experiments of solid fluorine.

Table 3. Computed IR/Raman active frequencies for the $C2/c$ and *Cmca* structures at 1 GPa and 20 GPa, respectively. Here R and I stand for Raman and IR active, vm and f_q stand for vibrational mode and vibrational frequency, respectively.

$C2/c$ (1 GPa)	R	vm	B_g	A_g	A_g	B_g	B_g	A_g
		f_q/cm^{-1}	49.41	54.53	104.13	129.48	932.84	933.86
	I	vm	A_u	B_u	A_u			
		f_q/cm^{-1}	65.38	67.68	98.59			
Cmca (20 GPa)	R	vm	B_{1g}	B_{2g}	A_g	B_{3g}	A_g	B_{3g}
		f_q cm^{-1}	222.20	256.41	284.21	334.35	842.32	892.54
	I	vm	B_{1u}	B_{2u}				
		f_q/cm^{-1}	179.43	280.65				

4. Conclusion

In summary, high precision calculations on enthalpies of the controversial structures of $C2/m$ and $C2/c$ fluorine through the VASP code suggest that the$C2/c$ phase is slightly more energetically stable than $C2/m$ at low pressure. Further investigations on phonon spectra reveal the instability of the $C2/m$ structure and confirm the dynamically stable property of the $C2/c$ structure. Theoretically, $C2/c$ is determined to be the better candidate of solid fluorine at ambient pressure. Under compression, the $C2/c$ phase transforms to a new structure *Cmca* at about 8 GPa. The *Cmca* phase is superior to the other structures in energy in the pressure range of 8–100 GPa. Moreover, *Cmca* remains intact at the pressure of 100 GPa, which is not similar to the other halogen molecules. The electronic energy band structures indicate that both $C2/c$and *Cmca* structures are insulators at the selected pressures.

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References

[1] Wigner E and Huntingdon H B 1935 *J. Chem. Phys.* **3** 764

[2] Zhang H D, Jin X L, Lv Y Z, Zhuang Q, Liu Y X, Lv Q Q, Li Da, Bao K, Liu B B and Cui T 2015 *RSC Adv.* **5** 107637

[3] Li Y, Jin X L, Cui T, Zhuang Q, Lv Q Q, Wu G, Meng X, Bao K, Liu B B and Zhou Q 2017 *RSC Adv.* **7** 7424

[4] Monserrat B, Drummond N D, Pickard C J and Needs R J 2014 *Phys. Rev. Lett.* **112** 055504.

[5] Ma T, Li H, Zheng X, Wang S M, Wang X C, Zhao H Z, Han S B, Liu J, Zhang R F, Zhu P W, Long Y W, Cheng J G, Ma Y M, Zhao Y S, Jin C Q and Yu X H 2017 *Adv. Mater.* **29** 1604003

[6] Cui X Y, Hu T J, Wang J S, Zhang J K, Li X F, Yang J H and Gao C X 2017 *Chin. Phys. B* **26** 046401

[7] Xu X Y, Chai C C, Fan Q Y and Yang Y T 2017 *Chin. Phys. B* **26** 046101

[8] Feng S Q, Wang L L, Jiang X X, Li H N, Cheng X L and Su L 2017 *Chin. Phys. B* **26** 046301

[9] Guo Z C, Luo F and Cheng Y 2014 *Computational Materials Science* **84** 139

[10] Matsuoka T and Shimizu K 2009 *Nature* **458** 186

[11] Ma Y M, Eremets M, Oganov A R, Xie Yu, Trojan I, Medvedev S, Lyakhov A O, Valle M and Prakapenka V 2009 *Nature* **458** 182

[12] Rousseau B, Xie Y, Ma Y and Bergara A 2011 *Eur. Phys. J. B* **9** 10972

[13] Jin X L, Chen X J, Cui T, Mao H K, Zhang H D, Zhuang Q, Bao Kuo, Zhou D W, Liu B B, Zhou Q and He Z 2016 *Proc. Natl. Acad. Sci. USA* **113** 2366

[14] Ashcroft N W 1968 *Phys. Rev. Lett.* **21** 1748

[15] Kitamura H, Tsuneyuki S, Ogitsu T and Miyake T 2000 *Nature* **404** 259

[16] Tse J S and Klug D D 1995 *Nature* **378** 595

[17] Natoli V, Martin R M and Ceperley D 1995 *Phys. Rev. Lett.* **74** 1601

[18] Narayana C, Luo H, Orloff J and Ruoff A L 1998 *Nature* **393** 46

[19] Mao H K and Hemley R J 1989 *Science* **244** 1462

[20] Mao H K and Hemley R J 1994 *Rev. Mod. Phys.* **66** 671

[21] Martin S and Richard M M 2000 *Phys. Rev. Lett.* **84** 6070

[22] Loubeyre P, Occelli F and Toullec R L 2002 *Nature* **416** 613

[23] Nellis W J, Holmes N C, Mitchell A C and van Thiel M 1984 *Phys. Rev. Lett.* **53** 1661

[24] Reichlin R L, Schiferl D, Martin S, Vanderborgh C and Mills R L 1985 *Phys. Rev. Lett.* **55** 1464

[25] Fujii Y, Hase K and Ohishi Y 1989 *Phys. Rev. Lett.* **63** 536

[26] Takemura K, Minomura S and Shimomura O 1980 *Phys. Rev. Lett.* **45** 1881

[27] Van Bolhuis F, Koster P B and Migchelsen T 1967 *Acta Cryst.* **23** 90

[28] Duan D F, Liu Y H, Ma Y M, Liu Z M, Cui T, Liu B B and Zou G T 2007 *Phys. Rev. B* **76** 104113

[29] Jiang H T, Pandey R, Darrigan C and Rerat M 2003 *J. Phys.: Condens. Matter* **15** 709

[30] Cui X Y, Hu T J, Wang J S, Zhang J K, Li X F, Yang J H and Gao C X 2017 *Chin. Phys. Lett.* **34** 046401

[31] Haines J, Le'ger J M, Gorelli F, Klug D D, Tse J S and Li Z Q 2001 *Phys. Rev. B* **64** 134110

[32] Xu L, Wei B, Xia Y, Deng L Z and Yin J P 2017 *Chin. Phys. B* **26** 033702

[33] Chen B J, Deng Z, Wang X C, Feng S M, Yuan Z, Zhang S J, Liu Q Q and Jin C Q 2016 *Chin. Phys. B* **25** 077503

[34] Chen B J, Deng Z, Li W M, *et al.* 2016 *Sci. Rep.* **6** 36578

[35] Xiong J J, Shen D, Zheng Z G and Wang X Q 2016 *Chin. Phys. B* **25** 096401

[36] Jordan T H, Streib W E and Lipscomb W N 1964 *J. Chem. Phys.* **41** 760

[37] Jordan T H, Streib W E, Smith H W and Lipscomb W N 1964 *Acta Cryst.* **17** 777

[38] Ian H H and Stuart A R 1967 *J. Chem. Phys.* **46** 3881

[39] Meyer L, Barrett C S and Greer S C 1968 *J. Chem. Phys.* **49** 1902

[40] Pauling L, Keaveny I and Robinson A B 1970 *J. Solid. State. Chem.* **2** 225

[41] Niemczyk T M, Getty R R and Leroi G E 1973 *J. Chem. Phys.* **59** 5740

[42] Gamba Z and Halac E B 1987 *J. Chem. Phys.* **87** 7184

[43] Kobashi K and Klein M L 1980 *Mol. Phys.* **41** 679

[44] Kirin D and Etters R D 1986 *J. Chem. Phys.* **84** 3439
[45] Schiferl D, Kinkead S and Hanson R C 1987 *J. Chem. Phys.* **87** 3016
[46] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864
[47] Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133
[48] A code for crystal structural prediction and analysis is based on evolutional local random computational method, and is developed by our group.
[49] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
[50] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[51] Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M I J, Refson K and Payne M C 2005 *Zeitschrift für Kristallographie-Crystalline Materials* **220** 567
[52] Liu H Y, Wang H and Ma Y M 2012 *J. Phys. Chem. C* **116** 9221
[53] Takemura K, Fujii Y, Minomura S and Shimomura O 1979 *Solid State Commun.* **30** 137
[54] Takemura K, Minomura S and Shimomura O 1982 *Phys. Rev. B* **26** 998
[55] Wu Z J, Zhao E J and Xiang H P 2007 *Phys. Rev. B* **76** 054115
[56] Shimomura O, Takemura K and Fujii Y 1978 *Phys. Rev. B* **18** 715