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Elastic properties of poly(vinylidene fluoride) (PVDF) crystals: A density functional theory study

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We computed structural and elastic properties of totally nine phases of poly(vinylidene fluoride) (PVDF) crystals using the density-functional theory (DFT) method with and without inclusion of the dispersion corrections. In addition to the four known crystalline forms, mechanic properties of five theoretically predicted crystalline forms of PVDF are also investigated. The all-*trans* form **I_p** exhibits the largest cohesive energy, bulk, and Young's modulus among the nine crystalline forms. The DFT calculations suggest that the δ crystalline forms (**III_{au}**, **III_{pu}**, **III_{pd}**, and **III_{ad}**) possess poor chain rigidity among the nine PVDF crystalline forms. In contrast, a change of relative orientation of PVDF chains does not lead to significant change in cohesive energy and mechanic properties. A comparison of the cohesive energies of nine crystalline forms of PVDF suggests that the theoretically proposed crystalline forms of PVDF are quite stable. © 2011 American Institute of Physics. [doi:10.1063/1.3574653]

I. INTRODUCTION

Fluoropolymers have attracted considerable interest from the industry for their unique elastic, thermal, chemical, piezo- and pyro-electric properties in comparison to their hydrocarbon analogous. Poly(vinylidene fluoride) (PVDF) - (C₂H₂F₂)_n - is one of the very important fluoropolymer materials that have many industrial applications.¹ Over past several decades, PVDF has been subjected to intensive studies.^{2–20} To date, it is known the PVDF exhibits four crystalline phases, namely: α , β , γ , and δ phases.^{2,3} These crystalline phases (or forms) possess different thermal, electrical, and elastic properties. The β type crystalline form has received the most attention owing to its piezoelectric and pyroelectric properties.^{4,5} Recently, the first-order ferroelectric phase transition in two-dimensional ultrathin crystalline PVDF films has been reported.⁶

The PVDF demonstrates different thermal behavior in comparison to other thermoplastic polymers due to its semi-crystalline structure. In experiments, the mixture of amorphous phases in the sample can affect accuracy of the measurement.¹⁴ Especially, the elastic properties of *pure* PVDF crystals can be greatly affected by the inner packing structure of the PVDF chains.^{2,3} In previous theoretical studies, classical force field parameters have been developed and applied to investigate elastic properties of PVDF crystals.^{15–18} In comparison to the available experimental data, it has been reported that the Young's module of the β form is overestimated by the empirical force field parameters.¹⁹ DFT calculations were also performed to study static and dynamical mechanical properties of crystalline forms of PVDF.²⁰ The DFT calculations suggested consistent tendency for the stability of four known PVDF crystalline forms. However, detailed

mechanic properties such as elastic constants and Young's modulus have not yet been computed based on the DFT method. Moreover, the conventional DFT within the general gradient approximation (GGA) and with perdue-burke-ernzerhof (PBE)²¹ exchange-correlation functional is poor in treating van der Waals interactions due to dynamical correlations between fluctuating charge distributions.²² New approaches that include empirical dispersion corrections for the DFT calculations have been developed to address this problem, such as the DFT-D and DFT-D2 methods.^{23,24} To our knowledge, the DFT-D or DFT-D2 method has not been applied to the study of the PVDF systems.

In this paper, we present results of elastic properties of totally nine crystalline forms of PVDF using the DFT (Refs. 25, 26) and DFT-D2 methods. The *elastic stiffness constants*, *Young's module*, and *bulk module* are all computed based on the optimized structure of various phases of PVDF. Our DFT/PBE calculations show that the cell parameters of four known crystalline forms are in good agreement with the experimentally measured ones. However, the inclusion of empirical van der Waals correction (in the DFT/PBE-D2 method) can lead to larger error in the cell parameters. On the basis of optimized crystal structures, the cohesive energies and elastic properties are computed. In addition to the known four crystal phases of PVDF (α , β , γ , and δ), we also study elastic properties of five new crystalline forms of PVDF proposed previously.¹⁵ We find that a slight change of relative orientation of PVDF chains in the α , β , γ , or δ form can induce little changes in the stability and elastic properties.

II. COMPUTATIONAL METHODS

Two methods can be used to calculate the elastic stiffness coefficients (also called the elastic constants) of a solid. According to the definition of elastic stiffness coefficients

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(C_{ijkl}) in Eq. (1), the C_{ijkl} is the second derivate of Helmholtz free energy (A) to the applied strain (ε). Further simplification can be made, where the C_{ijkl} is expressed in terms of the first derivate of stress (σ) and applied strain (ε) at constant temperature T .

$$C_{ijkl} = \frac{1}{V} \left(\frac{\partial^2 A}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right)_{T, \tau_{ij}, \tau_{kl}} = \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \right)_{T, \tau_{ij}, \tau_{kl}}. \quad (1)$$

For very small deformations from the equilibrium state, the relationship between the strain (ε) and stress (σ) can be expressed by Eqs. (2) and (3), known as the generalized Hooke's law:

$$\sigma_{ij} = \sum_{k,l=1}^3 C_{ijkl} \varepsilon_{kl} \equiv C_{ijkl} \varepsilon_{kl} \quad (2)$$

or, conversely,

$$\varepsilon_{ij} = \sum_{k,l=1}^3 S_{ijkl} \sigma_{kl} \equiv S_{ijkl} \sigma_{kl}, \quad (3)$$

where S_{ijkl} is the elastic compliance constant

Considering the fact that both the strain and stress tensors are symmetric, i.e.,

$$\sigma_{ij} = \sigma_{ji},$$

and

$$\varepsilon_{ij} = \varepsilon_{ji},$$

the stress and strain components can be further simplified using the Voigt notation, as represented by

$$\sigma = [\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23}, \sigma_{13}, \sigma_{12}]^T = [\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6]^T, \quad (4)$$

$$\varepsilon = [\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, 2\varepsilon_{23}, 2\varepsilon_{13}, 2\varepsilon_{12}]^T = [\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6]^T, \quad (5)$$

where the superscript T denotes the transpose of matrix. The Hooke's law can be rewritten as:

$$\sigma_i = C_{ij} \varepsilon_j, \quad (6)$$

where the C_{ij} is a 6×6 symmetric matrix. Theodorou and Suter have shown that the contribution of configuration entropy on deformations is negligible in estimating the elastic constants.¹⁸ Thus, it is possible to estimate the elastic stiffness coefficients from the second derivatives of energy with respect to small deformations (called the method 1 here). Alternatively, one can compute the elastic stiffness coefficients via calculating $\Delta\sigma_i/\Delta\varepsilon_j$ according to Eq. 6 (the method 2).

The stress-based method (method 2) is more efficient than the energy-based method (method 1), especially for the systems with lower crystalline symmetry. For the energy-based method, one needs to estimate the strain energy of the system by applying various distortions. In the case of orthorhombic crystal, there are nine independent elastic constants: $C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}, C_{55}$, and C_{66} . One can calculate $C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}$ independently with the applied strain $(\delta, 0, 0, 0, 0, 0), (0, \delta, 0, 0, 0, 0)$ etc., one at a time by perturbing single stress vector. For example, by applying the distortion strain $(\delta, 0, 0, 0, 0, 0)$, one could obtain the stress tensors $(\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6)$. One can then

calculate the elastic constants $C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}$, via the $\Delta\sigma_i/\delta$ through changing the strength of strains (usually four to six times). So, the entire elastic-constant matrix can be determined by changing six strain vectors (δ_1 to δ_6 , respectively), which significantly reduces the computation cost when the DFT method is used.

Explicitly, the strain is applied by changing the optimized equilibrium cell parameter using the strain-cell parameter correlation:

$$\mathbf{h} = \mathbf{h}_0(1 + \varepsilon), \quad (7)$$

where $\mathbf{h}_0$ and $\mathbf{h}$ are the matrix formed from the equilibrium cell parameters and the deformed cell parameters. The strain is applied by slightly changing one of the strain vectors, while all others are fixed. Each strain vector is changed from the -0.005 to 0.005 with a step interval of 0.002 . The molecule configuration is then optimized after each distortion. The stress tensor (σ_i) of the optimized structure at each distortion step is recorded for calculating C_{ij} .

The cell parameters of various crystalline forms of PVDF are optimized by using the periodic DFT/PBE method implemented in the vienna ab-initio simulation package (VASP).²⁷ To increase accuracy of the calculations, we use a relatively large plane-wave basis set cutoff (500 eV). The $\mathbf{k}$ -point set is varied according to the crystal parameters. Typically, a $\mathbf{k}$ -point mesh of $3 \times 5 \times 10$ is applied on the supercell with cell parameters $\sim 9\text{\AA} \times 5\text{\AA} \times 2\text{\AA}$. Moreover, the criteria of optimization convergence are set as 10^{-6} eV for the energy and 10^{-5} eV/\AA for the force. In addition, the DFT/PBE-D2 method²³ is used to compute the elastic constants of crystalline PVDF in different phases and to compare with those from the conventional DFT/PBE method. In the DFT/PBE-D2 method, the van der Waals interactions are described by a simple pair-wise force field. Here, the pair-wise van der Waals parameters such as C_6 and R_0 of C, H, and F atoms are taken from the original literature.²³ The global cutoff for the van der Waals interaction energy is set at 30 \AA. A global scaling factor 0.75 is used. The DFT/PBE-D2 calculations are carried out by using the latest version of VASP package (version 5.2.11).²⁷

III. RESULTS AND DISCUSSION

A. Cell parameters and cohesive energies of various crystalline forms of PVDF

Figure 1 displays packing structure in a unit cell for each of nine crystalline forms of PVDF. Based on the chains' configurations (*gauche* and *trans*) and relative orientations of two adjacent chains, the nine crystalline forms can be classified into four categories: **I**, **II**, **III**, and **IV**, corresponding to β , α , γ , and δ form, respectively.

In form **I** (β form), the unit cell contains two all-*trans* (T) chains. The two neighboring chains are *parallel* to each other, and they have the same orientations for the $-\text{CH}_2-$ and $-\text{CF}_2-$ units (polar form). Here, we use the suffixes *a* and *p* to denote the *anti-parallel* and *parallel* direction of the electric dipole moment (approximate from the $-\text{F}$ to $-\text{H}$ groups) between the two adjacent chains, respectively. The *u* and *d* are used to

FIG. 1. (Color online) Side and top view of packing structure in a unit cell for each of nine crystalline forms of PVDF. Gray, white, and blue spheres represent carbon, hydrogen and fluorine atoms, respectively. T and G refer to *trans* and *gauche* rotational conformation.

denote the *up-up* and *up-down* relative orientation of carbon backbones in each chain, respectively. If two chains have the same carbon backbone configuration and orientations, it is the *up-up* orientation, otherwise it is the *up-down* orientation. Therefore, form **I** can be further denoted as I_p .

Form **II** (α form) has two *anti-parallel* (II_a , nonpolar form) PVDF chains in the TGTG' configuration. In II_a , the functional groups at the corresponding location of two chains may take either *up-up* or *up-down* configuration with respect to each other, denoted as II_{au} and II_{ad} , respectively (cf. Figure 1).

Molecular chains in form **III** (γ form) have a configuration of T_3GT_3G' . If these chains are aligned parallel to each other, they are referred as III_{pu} or III_{pd} (polar forms). Otherwise, they are nonpolar forms III_{au} and III_{ad} , with the chains anti-parallel with each other.

Phase **IV** (δ form or II_p) is a counterpart of II_a , which includes the polymer chains in *parallel* arrangement and is thus, polar. The II_{pu} and II_{pd} are defined according to the *up-up* and *up-down* relative orientations of two adjacent chains.

The molecular conformations and relative chain orientations determine different crystalline forms of PVDF. It is thus possible to convert crystalline forms from one to another by altering the molecular conformation and relative orientation. The nonpolar II_{ad} phase can be achieved by cooling down PVDF from high temperature. The II_{ad} phase can be converted to II_{pd} phase in the presence of an external electric field of ~ 0.1 V/m (Ref. 20). The polar III_{pu} phase can be obtained by annealing the II_{ad} phase from high temperature. Phase I_p is the most interesting form due to its ferroelectricity. The all-*trans* I_p phase can be obtained by a mechanical stretching from the III_{pu} form, or by poling from the II_{pd} form through applying an external electric field (~ 0.5 V/m) (Ref. 20).

Table I lists the optimized cell parameters of nine crystalline forms of PVDF. For four known crystalline forms, I_p , II_{ad} , III_{pu} , and II_{pd} , the optimized cell parameters obtained from the DFT and GGA -D2 methods are compared with experimental data. To obtain the equilibrium cell parameters, the six structural parameters, a , b , c , α , β , and γ are scanned.

TABLE I. Computed cohesive energies, bulk modulus, Young's modulus, and optimized cell parameters of nine crystalline forms of PVDF, using either DFT/PBE or DFT/PBE-D2 method (see footnote below). The α , β , γ are angles between cell vectors a and b , b and c , and a and c , respectively. The data in the parentheses are experimental data.

Cell Parameters	Crystal Forms								
	β	α		γ				δ	
	$\mathbf{I}_p$	$\mathbf{II}_{ad}$	$\mathbf{II}_{au}$	$\mathbf{III}_{au}$	$\mathbf{III}_{pu}$	$\mathbf{III}_{pd}$	$\mathbf{III}_{ad}$	$\mathbf{II}_{pd}$	$\mathbf{II}_{pu}$
Space Group	$Cm2m$	$P2_1/c$	$Pca2_1$	$Pca2_1$	Cc	$Pna2_1$	$P2_1/c$	$P2_1cn$	Cc
Cohesive Energy	−0.24	−0.082	−0.078	−0.11	−0.094	−0.068	−0.061	−0.075	−0.077
(eV per CH_2 unit)	−0.44 ^a	−0.28 ^a			−0.31 ^a			−0.28 ^a	
Bulk Modulus	11.18	8.54	7.83	7.65	8.77	7.29	4.78	8.53	7.38
(GPa)	25.25 ^a	18.05 ^a			15.76 ^a			15.71 ^a	
E_c (GPa)	287.33	148.10	149.60	98.00	105.90	103.70	50.90	152.30	151.40
	341.30 ^a	175.13 ^a			119.90 ^a			179.94 ^a	
a (Å)	8.69/8.22 ^a	9.77/9.24 ^a	9.84	9.78	9.69/9.26 ^a	9.75	9.68	9.71/9.10 ^a	9.81
	(8.58)	(9.64)			(9.67)			(9.64)	
b (Å)	4.85/4.51 ^a	5.02/4.75 ^a	5.02	5.08	5.00/4.76 ^a	5.17	6.17	5.02/4.79 ^a	5.04
	(4.91)	(4.92)			(4.96)			(4.96)	
c (Å)	2.58/2.58 ^a	4.67/4.64 ^a	4.67	9.33	9.34/9.25 ^a	9.39	9.38	4.67/4.65 ^a	4.67
	(2.56)	(4.62)			(9.20)			(4.62)	
α (°)	90.0/90.0 ^a	90.0/90.0 ^a	90.0	90.0	90.0/90.0 ^a	90.0	90.0	90.0/90.0 ^a	90.0
	(90.0)	(90.0)			(90.0)			(90.0)	
β (°)	90.0/90.0 ^a	90.0/90.0 ^a	90.0	90.0	91.5/93.1 ^a	90.0	121.9	90.0/90.0 ^a	91.7
	(90.0)	(90.0)			(93.0)			(90.0)	
γ (°)	90.0/90.0 ^a	90.0/90.0 ^a	90.0	90.0	90.0/90.0 ^a	90.0	89.9	90.0/90.0 ^a	90.0
	(90.0)	(90.0)			(90.0)			(90.0)	

^aData calculated using DFT/PBE-D2 method.

We note that for the PVDF, the nonbonding interactions including the Coulomb and van der Waals interactions are dominant in chain packing. We also compare optimization results based on two different functionals, PBE and PW91 (Ref. 34). It is found that both PBE and PW91 give very close equilibrium structures for various PVDF crystals. However, cell parameters of b and c predicted by the PW91 functional are slightly larger ($\sim 10\%$) than those by the PBE functional. Here, only the PBE results are presented because they are closer to available experimental data. As shown in Table I, the cell parameters of four known forms, $\mathbf{I}_p$, $\mathbf{II}_{ad}$, $\mathbf{III}_{pu}$, and $\mathbf{II}_{pd}$ are in good agreement with the experimental measurements. The differences are generally less than 2%.

The optimized cell parameters of five new crystalline forms $\mathbf{II}_{au}$, $\mathbf{III}_{pu}$, $\mathbf{III}_{au}$, $\mathbf{III}_{pd}$, $\mathbf{III}_{ad}$ are also presented in Table I. These crystalline forms have been optimized previously based on the empirical force field (MSXX and MSXXS) by Karasawa *et al.*¹⁵ The optimized crystal parameters from the DFT calculations are close to those previously obtained based on the force field parameters. However, some differences are found for the $\mathbf{II}_{pu}$ form. The predicted α angle by DFT is 91.7° , much less than 104° predicted by the force field calculations. We find that the energy landscape for the parameters b , c , and γ near the equilibrium state is fairly flat. A slight change ($\pm 5\%$) of one of those parameters only induces very small energy rise (< 0.002 eV).

The cohesive energies of nine phases of PVDF are presented in Table I. The $\mathbf{I}_p$ (β form) possesses the greatest cohesive energy (−0.24 eV per CH_2 unit) among the nine crystalline forms. For the α form $\mathbf{II}_{ad}$, the calculated cohesive energy is −0.082 eV/ CH_2 unit, which is only 0.004

eV greater than that of $\mathbf{II}_{au}$ form. For the γ and δ forms, the cohesive energies of experimentally observed phases, $\mathbf{III}_{pu}$ and $\mathbf{II}_{pd}$, are also comparable to those of theoretically predicted $\mathbf{III}_{pd}$, $\mathbf{III}_{ad}$, and $\mathbf{II}_{pu}$ forms. In particular, for the theoretically predicted phase $\mathbf{III}_{au}$, its cohesive energy is even slightly greater (0.01 eV/ CH_2) than the $\mathbf{III}_{pu}$ phase.

B. Elastic properties of crystalline forms of PVDF

Despite of extensive studies of PVDF polymers, mechanical properties of the crystalline forms of PVDF are less studied due in part to the difficulty in obtaining perfect crystals. Based on the optimized crystalline structures, we have computed elastic stiffness constants, the Young's modules, as well as the bulk modulus for all nine crystalline forms of PVDF. The bulk modulus (β) and Young's modulus (E_c) in the chain direction are computed based on the definition

$$\beta^{-1} = \sum_{i,j=1}^3 S_{ij},$$

$$E_c = \sigma_c / \varepsilon_c,$$

where ε_c is the strain applied along the chain direction and σ_c is the stress induced by the applied strain along the chain direction, and the results are presented in Table I. As mentioned in the method section, the complete elastic constant matrix (having 36 elements) can be computed using the stress-strain relationship. The calculated elastic constants for the nine crystalline forms of PVDF using the DFT/PBE method are presented in the supplemental materials.³⁵ For the orthorhombic crystalline forms $\mathbf{I}_p$, $\mathbf{II}_{ad}$, $\mathbf{II}_{au}$, $\mathbf{III}_{au}$, $\mathbf{III}_{pu}$,

FIG. 2. (Color online) The strain-stress relationships used for computing elastic constants, C_{11} , C_{22} , and C_{33} , of all nine crystalline forms of PVDF.

and II_{pd} , each has nine independent elastic constants, C_{11} to C_{66} , C_{12} , C_{13} , and C_{23} . The calculated elastic constants (See Ref. 35 for supplemental materials) from the stress-strain relation indicate that the elastic constants other than the nine mentioned above are close to zero for these crystalline forms. The crystalline forms III_{pu} , II_{pu} , and III_{ad} are monoclinic crystal, which have four additional nonzero elastic constants, C_{16} , C_{26} , C_{36} , and C_{45} . However, the calculated elastic constants, C_{16} , C_{26} , C_{36} , and C_{45} for the crystalline forms III_{pu} , II_{pu} are fairly small compared to C_{11} , C_{22} , and C_{33} .

Figure 2 shows the stress-strain relationship used to calculate C_{11} , C_{22} , and C_{33} for each of nine crystalline forms of PVDF. It can be seen that the stress and strain show a linear relationship. For the phase I_{p} , we also

compare the results from the stress-strain method and the energy-strain method of three main elastic constants: C_{11} , C_{22} , and C_{33} . Figure 3 shows the energy-strain curve of phase I_{p} under different strains. The estimated elastic constants, C_{11} (9.19 GPa), C_{22} (11.30 GPa), and C_{33} (270.81 GPa), from the energy-strain relationship are close to those obtained from the stress-strain method (19.83, 24.50, and 287.33 GPa, respectively). In PVDF crystals, the weak interactions are dominant in a and b directions. This makes the accurate estimation of the cell parameters difficult. As a consequent, one may find in Figs. 2 and 3 that the stress-strain and energy-strain curves may not be exactly symmetric with respect to the zero-point corresponding to the equilibrium structure.

FIG. 3. (Color online) The energy-strain relationship used for fitting to the elastic constants (a) C_{11} , (b) C_{22} , (c) C_{33} of phase I_{p} . The red line is a fit of the points from the DFT calculations.

As shown in Fig. 2, the all-*trans* phase $\mathbf{I}_p$ (β form) exhibits the largest elastic constant (C_{33}) among nine phases. Here, the Young's modulus along the chain direction (E_c) nearly equals to C_{33} . As shown in Table I, the calculated Young's modulus of phases $\mathbf{II}_{ad}$, $\mathbf{II}_{au}$, $\mathbf{II}_{pu}$, and $\mathbf{II}_{pd}$ (α and δ forms) along the chain direction are much less than that of phase $\mathbf{I}_p$, whereas, they are larger than those of phases $\mathbf{III}_{pu}$, $\mathbf{III}_{ad}$, and $\mathbf{III}_{pd}$ (γ form). One may find the change of neighboring chain's orientation has almost no effect on the mechanical properties of PVDF crystals. For example, the phases $\mathbf{II}_{ad}$, $\mathbf{II}_{au}$, $\mathbf{II}_{pu}$, and $\mathbf{II}_{pd}$ have very similar elastic constants. Moreover, the elastic constants of phases $\mathbf{III}_{au}$, $\mathbf{III}_{pu}$, and $\mathbf{III}_{pd}$ are also close to each other. Phase $\mathbf{III}_{ad}$ has the elastic constants distinct from $\mathbf{III}_{au}$, $\mathbf{III}_{pu}$, and $\mathbf{III}_{pd}$ due to its distorted cell shape. On the basis of E_c , the phase $\mathbf{I}_p$ seems to possess the highest mechanic stiffness. The monoclinic phase $\mathbf{III}_{ad}$ has the least cohesive energy, implying its lowest mechanical stability. Among the crystalline forms, β , α , δ , or γ , the $\mathbf{I}_p$, $\mathbf{II}_{ad}$, $\mathbf{III}_{pu}$, and $\mathbf{II}_{pd}$ possess the largest bulk and Young's modulus. Note that these four crystalline forms have been observed in experiments.

The δ forms ($\mathbf{III}_{au}$, $\mathbf{III}_{pu}$, $\mathbf{III}_{pd}$, and $\mathbf{III}_{ad}$) possess smaller Young's modulus along the chain direction, suggesting their poor chain rigidity. To date, the experimental data on the mechanic properties of PVDF crystals are scarce. For the phase $\mathbf{I}_p$, the measured Young's module is 177 GPa,¹⁹ significantly less than the calculated value (~ 287 GPa). The discrepancy between the theory and experiment may be due to the mix of different PVDF crystalline phases in the experimental sample. In fact, an earlier experiment has shown some kink bands existing within the crystallites of planar-zigzag form $\mathbf{I}_p$, which may lower the Young's modulus along the chain direction.³⁶

C. DFT calculation with inclusion of the van der Waals corrections (DFT-D2)

As mentioned above, the DFT/GGA cannot properly describe van der Waals interactions (resulting from dynamical correlations between fluctuating charge distributions). In the PVDF crystals, the chain-chain interactions entail nonbonding interactions such as electrostatic and van der Waals interactions. To study the influence of the van der Waals interactions on the elastic properties of PVDF crystals, we employ the recently developed DFT-D2 method.^{23,24} First, we have performed benchmark calculations using the DFT/PBE-D2 method and four solid systems, Ne, Ar, Kr and Si, as a test bed, as both experimental and previous DFT/PBE-D2 calculation results for these elemental solids and their lattice constants are available.^{28–33} As shown in the Appendix, our DFT/PBE-D2 calculations reproduce recent theoretical results for these systems very well.³² However, one difference between DFT/PBE-D2 and DFT/PW91-vdW result of Si is found, which will be discussed below.

The results for the four PVDF crystalline forms ($\mathbf{I}_p$, $\mathbf{II}_{ad}$, $\mathbf{III}_{pu}$, and $\mathbf{II}_{pd}$) are presented in Table I. Compared with the results from the conventional DFT/PBE calculations, the inclusion of van der Waals corrections (DFT-D2) leads to shorter length of unit cell along the a and b direction (domi-

nated by the nonbond interactions). The predicted unit cell parameters (a and b) are also much smaller than the experimental data. In contrast, the inclusion of van der Waals corrections has little effect on the predicted unit cell length along the chain direction, as it involves mainly covalent bond interactions.

The elastic properties of PVDF in $\mathbf{I}_p$, $\mathbf{II}_{ad}$, $\mathbf{III}_{pu}$, and $\mathbf{II}_{pd}$ forms are also computed by the DFT-D2 method. As shown in Table I, the Young's modulus along the chain direction, bulk modulus, and cohesive energies are much larger than those obtained from conventional DFT calculations, but both show consistent tendency. For example, both the DFT and DFT-D2 predict that the all-*trans* $\mathbf{I}_p$ form possesses the largest Young's modulus and bulk modulus. So which method is more accurate? In present, only limited experimental data are available for the four crystalline forms of PVDF. Based on the measured cell parameters, we find the DFT/PBE method gives better agreement than the DFT/PBE-D2 method. On the other hand, the Young module of the $\mathbf{I}_p$ form predicted from the DFT/PBE-D2 method is much larger than that from DFT/PBE and available experimental data. On basis of these considerations, we suggest the DFT/PBE method can provide reasonable description of structural and elastic properties of PVDF crystals. Also, the large plane-wave cutoff and dense k -point mesh are required to provide accurate calculations of mechanical properties of PVDF crystals.

The unexpected effect of inclusion of the dispersion correction (DFT/PBE-D2) on the predicted lattice constants of PVDF crystals might be due to several reasons. Bučko *et al.* have shown that the DFT/PBE-D2 method may fail sometimes in reproducing equilibrium lattice constants of certain systems such as the Ne solid (Ref. 32) (see Table II in the Appendix section). In addition, by comparing DFT/PBE-D2 results with DFT/PW91-vdW (Ref. 31) results of the lattice

TABLE II. Benchmark calculations of equilibrium lattice constant (a) of noble-gas element Ne, Ar, and Kr fcc solids, and cubic diamond Si. A plane-wave cutoff of 1000 eV and a $8 \times 8 \times 8$ k -point mesh are used.

Element	Method	a (Å)
Ne	Expt. ^a	4.464
	PBE-D2	4.226
	PBE-D2 ^c	4.23
	PW91 + vdW ^d	4.562
Ar	Expt. ^b	5.300
	PBE-D2	5.378
	PBE-D2 ^c	5.38
	PW91 + vdW ^d	6.002
Kr	Expt. ^c	5.646
	PBE-D2	5.640
	PBE-D2 ^e	5.64
Si	Expt. ^f	5.431
	PBE-D2	5.412
	PW91-vdW ^d	5.450

^aReference 28.

^bReference 29.

^cReference 30.

^dReference 31.

^eReference 32.

^fReference 33.

constants of Ne, Ar, and Si, one can see that not only the vdW parameters, but also the reference GGA functional (PBE or PW91) may affect the prediction of lattice constants. Hence, as far as the PBE functional is concerned, improved empirical vdW parameters are needed for accurate prediction of mechanical properties of the PVDF systems.

IV. CONCLUSION

We used the first-principles methods to calculate elastic properties of nine phases of PVDF, including four experimentally observed phases and five theoretically proposed crystalline forms. The all-*trans* phase **I_p** has the largest cohesive energy and greatest mechanic strength, in agreement with the experimental observations. Our DFT calculations for the theoretically proposed crystalline forms suggest that the δ forms (**III_{au}**, **III_{pu}**, **III_{pd}**, and **III_{ad}**) would show poor chain rigidity among the nine crystalline forms for PVDF. However, the change of relative orientation of PVDF chains does not lead to significant change in cohesive energy and mechanic properties. The comparison of cohesive energies of nine crystalline forms of PVDF suggests that the theoretically proposed forms of PVDF are also quite stable. Whether some of these crystalline forms may exist in nature must await future experiments. Finally, a comparison between conventional DFT/PBE and DFT/PBE-D2 calculations suggest that the conventional DFT/PBE method can provide better description of structural and mechanic properties of PVDF crystals.

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APPENDIX: BENCHMARK CALCULATIONS OF EQUILIBRIUM LATTICE CONSTANTS FOR SELECTED SOLID SYSTEMS BASED ON THE DFT-D2 METHOD

Benchmark Calculations of Equilibrium Lattice Constants for Selected Solid Systems Based on the DFT-D2 method.

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