

A van der Waals density functional theory study of poly(vinylidene difluoride) crystalline phases.

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Abstract. Ferroelectric polymers, such as poly(vinylidene difluoride) (PVDF), have many potential applications in flexible electronic devices. PVDF has six experimentally observed polymorphs, three of which are ferroelectric. In this work we use density functional theory to investigate the structural properties, energetics and polarisation of the stable α -phase, its ferroelectric analogue, the δ -phase, and the β -phase, which has the best ferroelectric properties. The results from a variety of exchange and correlation functionals were compared and it was found that van der Waals (vdW) interactions have an important effect on the calculated crystal structures and energetics, with the vdW-DF functional giving the best agreement with experimental lattice parameters. The spontaneous polarisation was found to strongly correlate with the unit cell volumes, which depend on the functional used. While the rel-

ative phase energies were not strongly dependent on the functional, the cohesive energies were significantly underestimated using the PBE functional. The inclusion of vdW interactions is, therefore, important to obtain the correct lattice structures, polarisation and energetics of PVDF polymorphs.

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1 Introduction

Ferroelectric (FE) materials exhibit a spontaneous electric dipole moment that is switchable by an applied electric field and, hence, they play an important role in electronic devices, such as transistors, non-volatile memory, sensors, etc., [1]. To provide lightweight and flexible consumer devices, inflexible crystalline FE materials, such as perovskites, need to be replaced by low density, flexible FE materials, such as FE polymers, which have the additional benefit of being easy and potentially inexpensive to process [2,3].

Poly(vinylidene difluoride) (PVDF) is a particularly promising FE polymer due to its chemical stability and good ferroelectric, piezoelectric and pyroelectric properties [4]. The FE properties arise from a strong electric dipole moment in the PVDF monomer unit, which is due to the high electronegativity difference between fluorine and hydrogen atoms combined with a small enough monomer to allow switching at low coercive fields. Other polymers, such as poly(vinylidene dichloride) (PVDC), poly(vinylidene cyanide), and poly(aminodifluoroborane) also have monomer dipole moments but are not useful in FE devices due to either steric effects, which increase the coercive field, or chemical reactivity [4].

PVDF can exist in at least six known crystalline polymorphs, as well as in amorphous melt or glassy phases. The α -phase, which is thermodynamically stable at ambient conditions, is non-ferroelectric and chains have a TG^+TG^- -structure, where T and $G^{+/-}$ stand for trans and \pm gauche, respectively. The individual chains in this phase do have a dipole moment but are aligned antiparallel, which gives a zero net dipole moment of the crystal. If the chains are aligned parallel, this gives the ferroelectric δ -phase [5,6]. The β -phase has an (all-trans) planar zig-zag chain structure and is the polymorph with the highest spontaneous polarisation.

After crystallisation from melt or solution and subsequent thermal treatment, PVDF often exists as a mixture of polymorphs [7]. To estimate the fraction of each polymorph in a sample, experimentalists analyse diffraction patterns or vibrational spectra using information available about known crystal phases. Simulations are useful for providing information about the ideal crystal structures, and density functional theory (DFT) has been used to study crystalline phases of PVDF. Previous DFT studies have determined lattice parameters and polarisation of the β -phase [8, 9], phase energetics [10,11], chain rotational barriers [9,12], elastic constants [13], structural and electronic properties of thin films [14] and vibrational spectra [15–17]. While these studies provided valuable insight into PVDF crystalline phases, most did not account for van der Waals (vdW) interactions, which are important for weakly bonded systems [18]. Only the study by Pei *et al* [13] used the semi-empirical DFT-D2 vdW correction [19]. No one has previously applied the first-principles vdW-DF [20] or vdW-DF2 [21] functionals to studies of PVDF. A DFT vdW-DF study of polyethylene [18] showed that vdW interactions were essential to obtain accurate lattice parameters and cohesive energies and the results were in good agreement with experimental values.

The goal of this work is to investigate the structure and energetics of three common polymorphs of PVDF. We use density functional theory (DFT) with a variety of exchange and correlation (XC) functionals and vdW correction methods. We obtain crystal structures for the α , δ and β -phases and show that vdW interactions have an important impact on lattice parameters and cohesive energies. In addition, the value of the spontaneous polarisation for the β and δ -phases was found to correlate strongly with the calculated unit cell volume. The inclusion of vdW interactions is thus crucial for providing accurate information about PVDF crystal structures from DFT calculations.

Method

All calculations were performed with Quantum ESPRESSO (QE) [22], versions 5.2 and 5.3, which implements density functional theory using a planewave basis set. The study investigated the performance of different exchange and correlation (XC) functionals including the LDA, the PBE generalised gradient approximation (GGA) [23], and the long range van der Waals (vdW) functionals vdW-DF [20,24,25] and vdW-DF2 [21], and the PBE-D2 [19] vdW correction scheme.

We tested both ultrasoft (US) PSPs and projector augmented waves (PAW) and found that the results were not significantly dependent on the PSP. Therefore, in the results section we present results using only US PSPs. Only pseudopotentials available from the QE website that were classification verified were used. The kinetic energy cutoffs were 80 Ry and 800 Ry for the wave function and for the charge density, respectively. These high cutoff energies were required to reach a total energy convergence of 1 mRy per atom. The Brillouin zone was sampled using a Monkhorst-Pack mesh of $2 \times 3 \times 4$ for the β phase and $3 \times 2 \times 4$ for the α and δ phases. In all cases, the self-consistent calculations were considered converged when the estimated energy error was less than 10^{-8} Ry. Cell and ionic relaxations were considered complete when the convergence threshold on the energy was 10^{-4} Ry and when forces less than 10^{-3} a.u. were reached.

The spontaneous polarisation was calculated using the modern theory of polarisation [26,27]. For all polymorphs we used 11 k-points in the dimensional reduced grid and 120 bands, which gave converged results for all cases.

2 Results and Discussion

2.1 Crystal structure

2.1.1 α phase

The α -phase is monoclinic with space group $P2_1/c$ [28] and has a TG^+TG^- chain structure with the dipoles aligned antiparallel resulting in a non-polar centrosymmetric structure. The chains have an antiparallel orientation along the c direction (chain axis), which corresponds to the experimentally determined space group [29, 28, 30, 13].

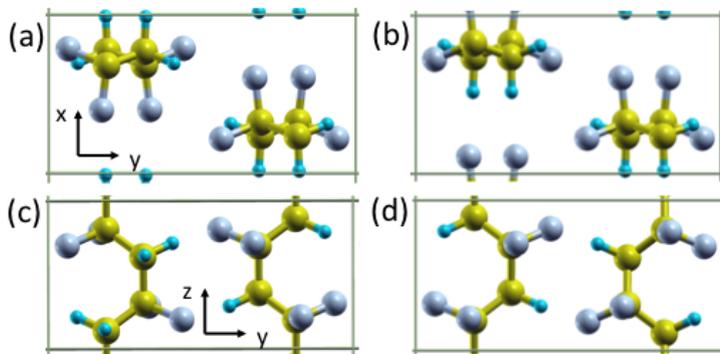


Fig. 1. α -phase in the a) xy -plane and c) yz -plane. δ -phase in the b) xy -plane and d) yz -plane. For an orthorhombic cell xyz directions correspond to abc lattice vectors.

The lattice parameters for the α -phase for various functionals are shown alongside previous calculations and experimental values from literature in Table 1. The c lattice parameter is along the chain and the a and b parameters are in the interchain directions. The LDA is seen to underestimate the a and b lattice constants by 6-7% but is in good agreement with the c lattice constant. In contrast, PBE significantly overestimates the a and b lattice constants by 4-5% but again is in reasonable agreement with the c lattice constant, which is in good agreement with previous PBE results [16, 13]. The lattice constant in the c direction is determined by the carbon backbone

and this length is less sensitive to the functional. However, the polymer chains are only weakly held together by van der Waals interactions and it is well known that for molecular systems the LDA overbinds, whereas the GGA underbinds.

Table 1. Lattice constants, angle β , and volume, V , for the α -phase for different functionals compared to DFT calculations and experimental results available in the literature.

Method	XC	Lattice parameters				Reference	
		a (\AA)	b (\AA)	c (\AA)	Angle β ($^\circ$)		V (\AA^3)
Exp	-	4.96	9.64	4.62	90	220.9	[29]
DFT	LDA	4.65	8.95	4.58	90.9	190.3	Present
DFT	PBE	5.21	10.00	4.68	90.7	243.7	Present
DFT	vdW-DF	4.99	9.57	4.69	90.6	224.0	Present
DFT	vdW-DF2	4.85	9.39	4.69	90.7	213.6	Present
DFT	PBE-D2	4.80	9.27	4.65	90.8	206.9	Present
DFT	PBE	5.18	10.30	4.70	91	250.7	[16]
DFT	PBE	5.02	9.77	4.67	90	229.0	[13]
DFT	PBE-D2	4.75	9.24	4.64	90	203.7	[13]
DFT	PBE0 hybrid	5.03	9.98	4.65	90.4	233.4	[31]

All calculations with vdW functionals or corrections give lattice constants that are much closer to experimental results. The vdW-DF2 and PBE-D2 calculations underestimate the experimental values by 2-4% for a and b lattice constants. The vdW-DF agrees with the experimental values to within 1% for a and b lattice constants and 1.5% for c . Our results for PBE-D2 are in close agreement to previously published results [13]. The type of pseudopotential used only has a small effect on the lattice constants compared to the effect of the exchange and correlation functional, with PAW giving slightly larger volumes, respectively, than US. In this space group the α and γ -angles are fixed by symmetry to 90° but the β -angle is not constrained to be

90° [16]. Our results for all functionals show a small deviation from 90°, similar to previous DFT calculations [16,31]. However, this is a small deviation that is within the DFT limits of accuracy.

2.1.2 δ phase

The α -phase can be transformed into the δ -phase by application of a strong electric field [5,6]. The δ -phase is similar to the α -phase except that the dipoles are aligned so that there is a net spontaneous dipole moment, as shown in Fig. 1(b). The crystal structure of δ is orthorhombic with space group $Pna2_1$ (or equivalently $P2_1cn$) [5,6], which corresponds to an antiparallel chain orientation [13]. The lattice parameters for the δ -phase are presented in Table 2. All angles in this space group are equal to 90°. The lattice parameters of the δ -phase are similar to those of the α -phase. The trends shown by the various functionals are similar to the trends observed for the α -phase.

Table 2. Lattice constants and volume, V , for the δ -phase for different functionals compared to DFT calculations and experimental results available from literature.

		Lattice parameters				
Method	XC	a (Å)	b (Å)	c (Å)	V (Å ³)	Reference
Exp	-	4.96	9.64	4.62	220.9	[5]
DFT	LDA	4.62	8.92	4.58	188.6	Present
DFT	PBE	5.17	10.09	4.69	244.4	Present
DFT	vdW-DF	4.98	9.53	4.70	223.2	Present
DFT	vdW-DF2	4.85	9.32	4.69	211.9	Present
DFT	PBE-D2	4.80	9.21	4.65	205.6	Present
DFT	PBE	5.02	9.71	4.67	227.6	[13]
DFT	PBE-D2	4.79	9.10	4.65	202.7	[13]
DFT	PBE0 hybrid	5.01	10.00	4.65	233.0	[31]

2.1.3 β phase

The β -PVDF structure is the crystal form with the highest spontaneous polarisation and therefore the most studied structure. The chain has an all-trans structure and the dipoles are in parallel alignment, as shown in Fig. 2.

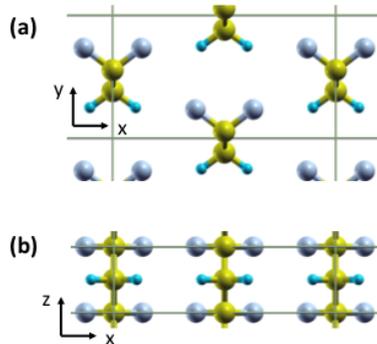


Fig. 2. View of the β -phase in the (a) xy -plane and (b) xz -plane. The xyz directions correspond to abc lattice vectors.

The lattice constants for the β -phase are shown in Table 3. First, we note that in the interchain directions, LDA underbinds by 7% and 9% for a and b , respectively and PBE overbinds by 4% and 2% for a and b , respectively. Our PBE calculation results in a considerably larger value for $a = 8.95 \text{ \AA}$ than the PBE values reported previously, which gave $a = 8.69 \text{ \AA}$ [13] and $a = 8.55 \text{ \AA}$ [17]. We attribute this to methodological differences, such as lower plane wave energy cutoffs of $\approx 38 \text{ Ry}$ (500 eV) [13] and 30 Ry [17]. We tested this by decreasing the plane wave cutoff from 80 Ry to 40 Ry and this resulted in a decrease in the a lattice parameter from 8.95 \AA to 8.57 \AA and a decrease in the volume from 115.7 \AA^3 to 106.6 \AA^3 .

The vdW calculations lie between the two extremes of the LDA and GGA. Our results for the PBE-D2 calculations are in close agreement with the previous D2 calculations of Pei *et al* [13]. Of the vdW calculations, vdW-DF gives the best overall

Table 3. Lattice constants for the β -phase from compared to previous DFT calculations and experimental results.

Method	XC	a (\AA)	b (\AA)	c (\AA)	V (\AA^3)	Reference
Expt	-	8.58	4.91	2.56	107.8	[28]
DFT	LDA	7.97	4.46	2.54	90.2	Present
DFT	PBE	8.95	5.00	2.59	115.7	Present
DFT	vdW-DF	8.62	4.80	2.60	107.5	Present
DFT	vdW-DF2	8.40	4.66	2.60	101.8	Present
DFT	PBE-D2	8.27	4.55	2.58	97.0	Present
DFT	PBE	8.55	4.83	2.58	106.5	[17]
DFT	PBE	8.69	4.85	2.58	108.7	[13]
DFT	PBE-D2	8.22	4.51	2.58	95.6	[13]
DFT	PBE0 hybrid	8.69	4.89	2.57	109.2	[31]

agreement with experimental values, with a volume of 107.5 \AA^3 , compared to the experimental volume of 107.8 \AA^3 [28].

2.2 Polymorph energetics

2.2.1 Phase energies

To compare the relative stability of the different polymorphs of PVDF we calculated the energy per monomer using the various functionals. The energy differences relative to the α -phase are presented in Fig. 3.

First we note that all functionals predict the δ -phase to be the lowest energy polymorph, although the energy difference of less than 1 kJ/mol is marginal and within the margin of error for these calculations. The β -phase has the highest energy, ranging from 2 kJ/mol for LDA up to 7 kJ/mol for PBE. Our results agree with previous PBE results [10], which found δ to be marginally stable, and a very small

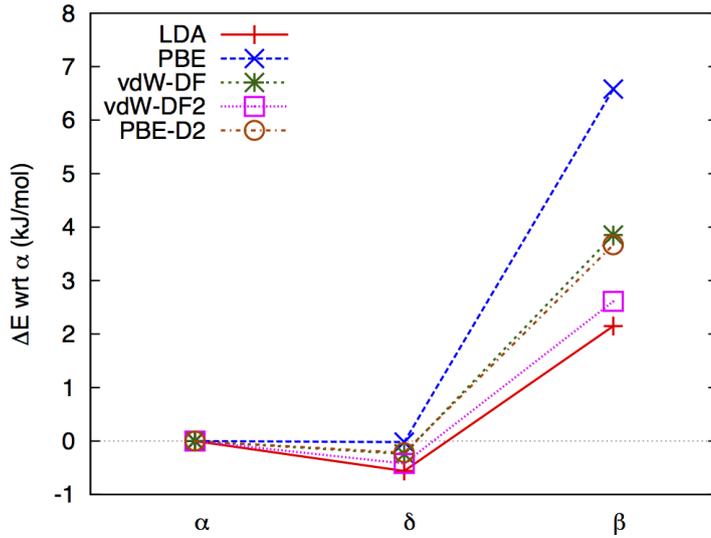


Fig. 3. Energy difference per monomer of PVDF polymorphs relative to α -phase.

energy range of less than 5 kJ/mol between the polymorphs studied. Another DFT study calculated the energy difference between the α and β -phases and found the α -phase to be 4.4 kJ/mol per monomer (23 meV per carbon atom) lower than the β -phase [11]. Another PBE study found that the α -phase is 2.6 kJ/mol (0.027 eV) per monomer lower in energy than the β -phase [16]. A study using the PBE0 functional found that the α , β , δ -phases differ in energy by less than 3 kJ/mol, with the α -phase being only marginally lower in energy than δ [31]. A study into the possible routes from α to β -phase transformations found the α and δ -phases to be almost equi-energetic, and the β -phase to have a higher energy of 3.4 kJ/mol [32].

2.2.2 Cohesive energies

We expect the inclusion of vdW interactions to have a significant effect on the cohesive energy of the polymorphs. We define the cohesive energy per monomer of the polymorphs to be

$$E_{\text{coh}} = \frac{E_{\text{cry}} - N_{\text{chain}}E_{\text{chain}}}{N_{\text{mon}}N_{\text{chain}}}$$

where E_{cry} is the total energy of the crystal, E_{chain} is the total energy of one relaxed chain in vacuum, N_{chain} is the number of chains in the crystal unit cell and N_{mon} is the number monomers per chain.

The isolated chains were relaxed in a box with $a = b = 19 \text{ \AA}$ and with the c lattice parameter (backbone direction) allowed to vary. The TG^+TG^- chain is stable for all functionals, with the all-trans chain ranging from $\approx 16 - 19 \text{ kJ/mol}$ per monomer higher in energy than the TG^+TG^- chain. The chain energy differences, shown in Table 4, are similar for all functionals, which is expected since this is due to bonded interactions rather than van der Waals interactions. Su *et al* [10] also found the TG^+TG^- chain structure to be stable, with the all-trans chain to be 19.9 kJ/mol per monomer (2.38 kcal/mol per C atom) higher in energy.

Table 4. Cohesive energies and energy difference between the TG^+TG^- and all trans chains, denoted ΔE_{chain} . Units are kJ/mol per monomer.

Functional	α	δ	β	ΔE_{chain}	Ref
LDA	-25.5	-26.0	-41.7	-18.3	Present
PBE	-8.1	-8.1	-17.5	-16.0	Present
vdW-DF	-33.7	-34.0	-47.5	-17.6	Present
vdW-DF2	-30.9	-31.3	-46.8	-18.5	Present
PBE-D2	-27.0	-27.2	-41.6	-18.2	Present
PBE	-2.6	-2.8	-17.6	-19.9	[10]
PBE	-15.8	-14.5	-46.3	-	[13]
PBE-D2	-54.0	-54.0	-84.9	-	[13]

The cohesive energies are shown in Table 4. For all functionals the β -phase has the strongest cohesion, in agreement with previous results. It is clear that the PBE

functional gives the smallest cohesive energies, which is not surprising as it is known to underbind. The vdW methods result in slightly stronger cohesive energies than the LDA. These three functionals give very similar results, with vdW-DF giving slightly stronger cohesion and PBE-D2 giving weaker cohesion. We note that our cohesive energies for PBE and PBE-D2 are approximately half of the cohesive energies reported by Pei *et al* [13]. However, we note that their PBE values are much larger than both our results and the results of Su *et al* [10]. There is no experimental data on the cohesive energy for PVDF. However, we can compare our results qualitatively with a similar study on polyethylene [18]. GGAs gave cohesive energies of less than 1 kJ/mol per CH₂, compared to LDA, which gave ≈ 11 kJ/mol per CH₂. vdW-DF gave a result of ≈ 10 kJ/mol/CH₂, which is slightly smaller than the LDA and in good agreement with the experimental value of 7.8 kJ/mol/CH₂ [33].

Polarisation

In this subsection we investigate the polarisation of the polar phases for various XC functionals and vdW corrections. To calculate the polarisation using the Berry phase method it is necessary to construct a non-polar reference structure (see for example the description by Spaldin [34]). For PVDF, the non-polar reference state for the β -phase was constructed by fixing the dimensions of the unit cell and rotating one of the chains by 180° along the chain axis so that there is a zero net dipole moment in the unit cell. A similar approach was taken for the δ -phase. Our results for the spontaneous polarisation of the β -phase are shown in Table 5 alongside the results from previous calculations and experiments.

The β -phase has the highest spontaneous polarisation of all the known polymorphs of PVDF. In our DFT calculations the polarisation ranges from a maximum of 26.6 $\mu\text{C cm}^{-2}$ for the LDA to a minimum of 16.8 $\mu\text{C cm}^{-2}$ for PBE. Since the LDA and PBE give the smallest and largest unit cells, respectively, it is expected that

Table 5. Spontaneous polarisation, P ($\mu\text{C cm}^{-2}$), for the β -phase compared experimental results and previous DFT data.

P ($\mu\text{C cm}^{-2}$)	Method	Reference
7.6	Plasma poling	[35]
10.0	Extrusion	[36]
13.0	VDF oligomers	[37]
18.1	DFT PBE	[38]
17.8	DFT PBE	[9]
17.6	DFT PBE0 hybrid	[31]
26.6	DFT LDA	Present
16.8	DFT PBE	Present
19.8	DFT vdW-DF	Present
22.6	DFT vdW-DF2	Present
22.3	DFT PBE-D2	Present

their polarisations (dipole moment per unit volume) would be the largest and smallest, assuming that there is no significant change in dipole moment. The spontaneous polarisation is plotted against unit cell volume in Fig. 4. The results from the LDA, PBE, vdW-DF and vdW-DF2 functionals show an approximately linear trend, and the PBE-D2 falls below this trend.

It is well known that the experimentally measured polarisation is lower than the value predicted by DFT calculations. This is normally attributed to the fact that DFT calculations use perfect PVDF crystal structures, whereas, experimentally, PVDF exhibits thermal fluctuations and can be partially amorphous or exist in several polymorphs simultaneously. However, there are many experimental studies focused on improving the crystallinity and purity of the β -phase. For example, Noda *et al* [37] formed thin films of VDF oligomers and measured a spontaneous polarisation of

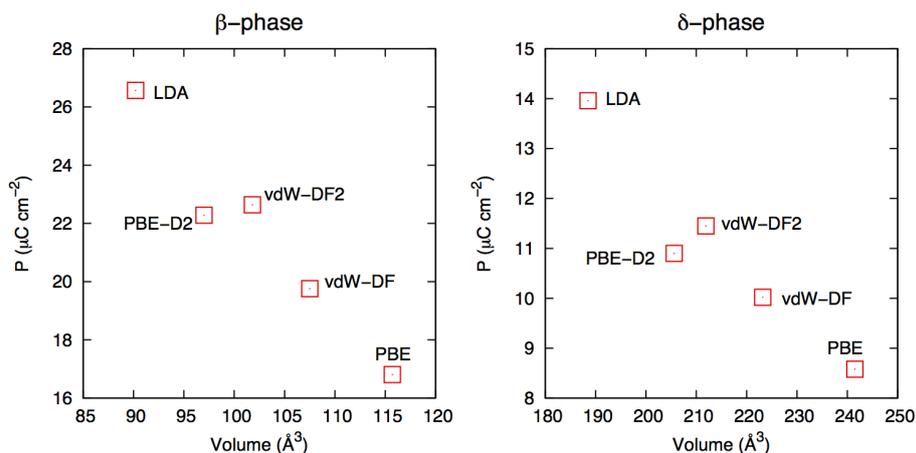


Fig. 4. Variation of polarisation with the volume of the unit cell for β -phase (left) and δ -phase (right).

$13 \mu\text{C cm}^{-2}$. Further work to control the crystallinity may result in experimental measurements of the polarisation to become even closer to the computationally predicted values.

The polarisation of the δ -phase is shown in Fig. 4 as a function of the unit cell volume and ranges from $8.6 \mu\text{C cm}^{-2}$ for PBE to $14.0 \mu\text{C cm}^{-2}$ for LDA. Similar to the β -phase there is a strong correlation between the polarisation and the volume. An experimental value for the polarisation of the δ -phase is $7 \mu\text{C cm}^{-2}$ [6] (see their Supplementary Information) and a previous DFT result using the PBE0 hybrid functional gave $8.5 \mu\text{C cm}^{-2}$ [31].

3 Conclusions

Structural properties, energetics and polarisation of three polymorphs of PVDF were studied using DFT calculations with various XC functionals and vdW corrections. The studied polymorphs were the α -phase, its polar analogue the δ -phase and the β -phase. For all phases it was found that vdW interactions were essential in pre-

dicting the correct interchain distances and corresponding lattice constants. Of the functionals studied, the vdW-DF functional was found to give the best agreement with experimental lattice constants.

The spontaneous polarisation for the polar phases, β and δ , was calculated for the different functionals. The variation in polarisation with functional/correction is primarily due to the different unit cell volumes and the spontaneous polarisation varies linearly with unit cell volume. The PBE-D2 method predicts a smaller polarisation for the predicted volume than the other functionals.

The relative energetics of the different polymorphs were compared with respect to the α -phase. All functionals predict that the δ -phase is slightly more stable than the α -phase, and that the β -phase is between 2-7 kJ/mol higher than α . However, the vdW corrections have an important effect on the cohesive energies, with the vdW cohesive energies being similar to or stronger than the LDA cohesive energies for all three phases. As expected, PBE predicts much weaker cohesive energies. In all cases the β -phase was found to have the strongest cohesive energies, in agreement with previous studies.

In summary, it is clear that the inclusion of vdW interactions is essential for predicting the lattice structure and energetics of PVDF polymorphs and future studies into phase transformations and new polymorphs should take vdW interactions into account.

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files for PVDF crystal structures are available from <http://dx.doi.org/10.15129/26e38705-5d3d-47c2-9b15-b2aef53641a2>. Files are embargoed until 31/05/17.

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