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The multiferroic phase of DyFeO$_3$: an \textit{ab initio} study

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\textbf{Abstract.} By performing accurate \textit{ab initio} density functional theory (DFT) calculations, we study the role of 4f electrons in stabilizing the magnetic-field-induced ferroelectric state of DyFeO$_3$. We confirm that the ferroelectric polarization is driven by an exchange-strictive mechanism, working between adjacent spin-polarized Fe and Dy layers, as suggested by Y Tokunaga (2008 \textit{Phys. Rev. Lett.} 101 097205). A careful electronic structure analysis suggests that coupling between Dy and Fe spin sublattices is mediated by Dy–d and O–2p hybridization. Our results are robust with respect to the different computational schemes used for d and f localized states, such as the DFT + $U$ method, the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional and the GW approach. Our findings indicate that the interaction between the f and d sublattices might be used to tailor the ferroelectric and magnetic properties of multiferroic compounds.

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1. Introduction

Multiferroics (MFs) are compounds where long-range magnetic and dipolar orders coexist [1]. There is plenty of fascinating physics in these materials, owing to the strong entanglement of spin–charge–orbital degrees of freedom [2, 3] and great potential for technological applications has already been envisaged [4–6]. The coupling between magnetism and ferroelectricity can be used for sensing applications, but also for memory devices where data are typically stored as magnetic information and read out electrically. Recently, several manganese and iron oxides have been shown to possess strong coupling. However, ferroelectricity in these materials is rather weak and only the electrical polarization can be switched by a magnetic field (but not vice versa, a limitation for many applications). Within this framework, DyFeO$_3$ (DFO) is a very interesting compound [7, 8] because it shows large ferroelectric polarization combined with a strong magnetoelectric coupling, as has been shown experimentally by Tokunaga et al [9]. Furthermore, the ferroelectric polarization in DFO is induced by the peculiar magnetic structure, obtained on applying an external magnetic field.

DyFeO$_3$ belongs to the class of perovskite oxides, such as RMO$_3$ (where R is a rare-earth ion and M is a transition metal atom). The ordering temperatures of Dy and Fe magnetic moments are very different, $T_{N}^{\text{Dy}} \sim 4$ K and $T_{N}^{\text{Fe}} \sim 645$ K. In the following, we briefly recall the low-temperature behavior, i.e. for $T$ below $T_{N}^{\text{Dy}}$, upon the application of an external magnetic field. Two different situations have to be considered: (i) $H < H_{r}^{\text{Fe}}$ and (ii) $H > H_{r}^{\text{Fe}}$, where $H_{r}^{\text{Fe}}$ denotes a critical field of 24 kOe [9]. In both cases, Dy spins are ordered in a $G_x A_y$ configuration. However, the Fe magnetic ordering is different in the two cases: in situation (i) the ordering is $A_x G_y C_z$ but in (ii) it changes to $G_x A_y F_z$. According to symmetry considerations [10, 11], in (i) there is no ferroelectric polarization, while it appears in (ii). The notation can be understood as follows. For example, for the $G_x A_y F_z$ spin configuration of the Fe sublattice, the $x$-component of the spins describes a $G$-type antiferromagnetic (AFM) structure, i.e. all the nearest-neighbor moments are antiferromagnetically coupled; the $y$-component of the spins describes an A-type AFM structure, i.e. the nearest-neighbor moments are ferromagnetic (FM) coupled within a defined plane and AFM coupled between neighboring planes; finally, the $z$-component of the moments of Fe are FM coupled. Therefore, in (ii) the application of a strong magnetic field leading to the coexistence of a magnetic ordering and ferroelectric polarization...
characterizes DFO as MF. In order to model the complex experimental magnetic-field-induced phase, we start from the magnetic structure of the MF phase proposed in [9], where the magnetic configuration is $G_x A_y$ for Dy moments and $G_x A_y F_z$ for Fe moments. In order to simplify the theoretical approach, we retain only the $y$-component of Dy and Fe spins, i.e. we stick to a simple model with A-type AFM coupling for Dy and Fe spins. Despite the simplification made in our model compared to the experimental situation, it nevertheless allows us to describe the dominant mechanism giving rise to magnetically induced ferroelectricity, which is the main purpose of the present study.

From the computational point of view, the description of RMO$_3$ materials poses serious problems. These compounds are often (strongly) correlated materials, involving d- and f-electronic charge with significant spatial localization. First-principles density functional theory (DFT) calculations in the most commonly applied local density approximation (LDA) or generalized gradient approximation (GGA) have to face well-known deficiencies: the non-locality of the screened exchange interaction is not well taken into account and the electrostatic self-interaction is not entirely compensated [12]. Since semilocal functionals tend to delocalize f-states, the f-electrons are often kept ‘frozen’ in the core, and the origin of multiferroicity is generally attributed to the spin–charge–orbital degrees of freedom of the M sublattice. Although this ‘standard’ approach helped in clarifying many mechanisms leading to ferroelectricity in MFs [13], the influence of f-electrons on multiferroicity has not yet been extensively investigated by ab initio calculations, despite several experiments clearly pointing out f-electrons as playing an important role in the MF properties of RMO$_3$ compounds [14, 15]. This is especially so for DFO, where the application of a magnetic field induces an MF phase with the electric polarization appearing at a very low temperature, corresponding to the ordering of Dy spins [9, 10, 16]. Recall that Dy is expected to have a 3+ oxidation state, i.e. an f$^9$ configuration [17].

In this study, stimulated by the recent experimental demonstration of a magnetic-field-induced ferroelectric (FE) phase of DFO [9, 10, 16], we performed ab initio simulations in order to show the key role played by f-electrons in stabilizing the FE state. Our calculations support the experimental studies of [9, 16] and, at the same time, quantify the polarization and shed light on the microscopic mechanism (i.e. based on electronic structure analysis) of the origin of ferroelectricity. To the best of our knowledge, this is the first ab initio study of the above-mentioned effect. Our simulations were mainly carried out within a DFT+$U$ approach for localized electrons. In addition, we used the Heyd–Scuseria–Ernzerhof (HSE) screened hybrid functional [18, 19], which has been shown to improve the description of d- and f-electron systems [20–23] over LDA or GGA. Finally, our calculations were benchmarked by single-shot GW using HSE wave functions (G$_0$W$_0$@HSE). This treatment is expected to give a very accurate description of the electronic ground state [24].

2. Computational details

The most widely used methods to account for the localized nature of d- or f-electrons are (i) the LDA+$U$ method, (ii) self-interaction corrected (SIC) LDA/GGA, (iii) hybrid functional approaches and (iv) the GW method. These approaches usually improve the descriptions of many d- and f-electron systems within reasonable computation efforts. In the following, we give a brief description of the different methods. In (i), an additional ($U - J$) parameter is added to
the LDA (or GGA) energy functional in order to mimic an effective on-site Coulomb ($U$) and exchange ($J$) between electrons with the same orbital angular momentum [25]–[27]. This is a Hartree–Fock (HF)-like correction and is motivated by the fact that HF theory is free from self-interaction errors. Method (ii) relies on the original work of Perdew and Zunger [28, 29]. Their idea consists in removing directly the self-Hartree and self-exchange-correlation (xc) energy of all the occupied KS orbitals from the LDA xc functional or other semilocal functionals, thus defining a new SIC functional to be minimized. In this way, the self-interaction energy terms are subtracted on an orbital-by-orbital basis. In (iii), one way to minimize the self-interaction error is simply to add back some amount of Fock exchange. These functionals are known as hybrids because they admix a fraction of non-local HF exchange to a part of local/semilocal LDA/GGA exchange. They owe much of their success to the possibility of overcoming most of the previous limitations of standard functionals while retaining the successive rungs picture of the Jacob’s ladder of density functionals [30]. Since the evaluation of the HF exchange in extended systems, under periodic boundary conditions, requires large computational effort, hybrid functionals have mainly been applied in quantum chemistry. In computational solid-state physics, a breakthrough was achieved by Heyd, Scuseria and Ernzerhof, who proposed the HSE functional where the mixing is retained only on the short-range component of Coulomb interaction reducing the computational load for periodic systems due to the increased locality of the exchange interactions. The GW method (iv) is widely used for predicting quasi-particle band gaps. The central quantity is the XC self-energy, $\Sigma_{xc}$, which is non-local, energy dependent and non-Hermitian and includes all non-classical electron–electron interaction effects. The exact $\Sigma_{xc}$ can be obtained by solving a set of complicated integro-differential equations, Hedin’s equations after Hedin [31, 32], which are computationally very demanding even for simple systems like a homogeneous electron gas. Therefore one has to resort to various approximations. The state-of-the-art approach is GW approximation (GWA), which is the first-order term in a systematic many-body perturbation expansion of $\Sigma_{xc}$ with respect to the screened Coulomb interaction $W$. In practice, usually the quasi-particle energies are calculated as a first-order correction to some reference single-particle Hamiltonian $H_0$, and both $G$ and $W$ are calculated using eigen-energies and eigenfunctions of $H_0$, hence called $G_0W_0$. In our study, we have used the (i), (iii) and (iv) computational methods for the theoretical description of DFO.

The calculations were performed using the projector augmented-wave (PAW) method [33, 34] with the Perdew–Burke–Ernzerhof (PBE) GGA functional [35]. We used DFT + $U$ within Dudarev’s approach [25]–[27] using $U_{eff} = U - J = 3$ and 4 eV for Fe-d and Dy-f states, respectively. The energy cutoff was set as 400 eV and a $4 \times 2 \times 4$ Monkhorst–Pack grid of $k$-points was used. We treated the Dy-f electrons both as valence and as core states [36]. The Berry phase approach [37, 38] was used to calculate the macroscopic polarization $P$. Non-collinear magnetism was treated in accordance with [39]. Spin–orbit coupling (SOC) was included for the end-point states of the adiabatic path, i.e. paraelectric (PE) and FE DFO (see below). For hybrid functionals, we used the HSE functional, recently implemented in VASP [40], and GW calculations [41, 42] were performed on top of the HSE ground state calculations [24]. The experimental lattice constants for orthorhombic DFO were used (space group $Pnma$, with $a = 5.596$ Å, $b = 7.629$ Å and $c = 5.301$ Å) [7]. Starting from experimental atomic positions, we performed atomic relaxations until the residual Hellman–Feynman forces were $< 0.01$ eV Å$^{-1}$.

In our notation, the $b$-axis corresponds to the $c$-axis in [9].
3. Switchable ferroelectric (FE) states

In figure 1, we show the two FE states of DFO, FE$_1$ and FE$_2$, with opposite polarizations. These represent a simplified version of the complex experimental magnetic-field-induced polar states (cf figures 1(c) and (d) of [9]), obtained by neglecting the $x$- and $z$-component of the Dy and Fe spins (see footnote 5).

In both the FE$_1$ and FE$_2$ cases, the Fe and Dy sublattices show an A-type magnetic structure, i.e. FM and AFM intralayer and interlayer coupling, respectively, with the spins pointing along the in-plane $c$-axis. In FE$_1$, the stacking of the spins along the out-of-plane $b$-axis is $\downarrow$ Fe$\downarrow$ Dy$\uparrow$ Fe$\uparrow$ Dy; the FE$_2$ state is obtained from the FE$_1$ state by rotating Dy spins by 180°, so that the spin stacking is $\downarrow$ Fe$\uparrow$ Dy$\uparrow$ Fe$\downarrow$ Dy. In the PE state, the atoms are arranged according to the $Pnma$ ($D_{2h}$) space group and the Dy spins are still intralayer FM coupled, but rotated with respect to the Fe spins by 90°. In FE$_1$, the spins of an Fe layer become parallel to the moments on one of the nearest-neighbor Dy layers and antiparallel to the other: Dy layers should then displace cooperatively toward Fe layers with parallel spins via exchange striction, giving rise to alternating short–long–short–long interlayer Dy–Fe distances. Accordingly, a polarization $P$ along the $b$-axis should be generated. In the FE$_2$ state, the flip of Dy spins would cause a reversal of $P$. Finally, in the PE state, each Fe sheet is sandwiched by layers with $\perp$ Dy spins, and no interlayer dimerization is expected. This microscopic mechanism, which involves frustrated interactions between rare earth and transition metal ions and its optimization by exchange striction, was proposed in [9, 16].

Figure 1. Ball-and-stick model of DFO in the PE and FE states (FE$_1$ and FE$_2$). Upper part: side views; bottom part: top view along the $b$-axis. Blue (large), red (medium) and black (small) spheres show Fe, Dy and O atoms, respectively. O$_{eq}$ and O$_{ap}$ refer to equatorial and apical oxygens, respectively. Arrows represent spin moments.
Our calculations confirm the above interpretation. First of all, the total energies of FE1 and FE2 are degenerate\(^6\). Furthermore, from the symmetry point of view, the rotation of Dy spins from PE to FE1 or to FE2 causes a symmetry lowering from the non-polar space group $62(D_{2h})$ to a polar space group $3\bar{3} (C_{2v})$, giving rise to a polarization along the $b$-axis. Indeed, the distortions lead to an alternate short–long–short–long interlayer distance, with $d_{FM} = 1.898 \text{ Å}$ and $d_{AFM} = 1.910 \text{ Å}$, while $d_{ideal} = 1.904 \text{ Å}$ in the unrelaxed non-spin-polarized case\(^7\). The Dy–f electrons play a key role in stabilizing the FE state. In order to prove this, we froze the f-electrons in the core and calculated the electronic ground state using the previously relaxed FE1 structure. First, the electronic contribution to the polarization, $P_{ele}$ (as defined below), vanishes; then, by allowing the ions to relax, the ionic contribution, $P_{ionic}$ (as defined below), becomes negligible as well, and the final crystal structure is non-polar. In summary, when treating the f-electrons as valence states, the PE state becomes unstable, the $D_{2h}$ point group symmetry is spontaneously broken to $C_{2v}$, and the system evolves toward a stable and polar state. If the f-electrons are removed from the valence and frozen in the core, the PE state remains stable. This unambiguously confirms that f-states are a necessary ingredient for ferroelectricity in DFO.

4. Discussion

4.1. Adiabatic path

To shed light on the onset of ferroelectricity, we construct an adiabatic path by progressively rotating the Dy spins from $90^\circ$ to $0^\circ$, i.e. from the PE to the FE1 state. In order to discuss the spontaneous polarization $\vec{P}_{tot}$ of the polar phase, it is useful to represent it as a summation of the ionic contribution, $\vec{P}_{ion}$, and the electronic, $\vec{P}_{ele} = \vec{P}_{tot} - \vec{P}_{ion}$. The ionic contribution is simply described as $\vec{P}_{ion} = \frac{|e|}{\Omega} \sum_{i=1}^{N_{atom}} Z_i^v \Delta \vec{r}_i$, where the symbols $e$, $\Omega$, $N_{atom}$, $|e|Z_i^v$ and $\Delta \vec{r}_i$ represent the electron charge, the unit-cell volume, the number of atoms in the unit cell, the valence charge of the $i$th atom and the displacement of the $i$th atom, respectively. The electronic contribution to the polarization is determined by evaluating the phase of the product of overlaps between cell-periodic Bloch functions along densely sampled strings of neighboring points in $k$-space, according to the procedure proposed by King-Smith and Vanderbilt within the Berry phase formalism\(^{[37, 38]}\). Furthermore, it is sometimes useful to estimate classically the polarization within a point-charge-model (PCM). It is calculated analogously to $\vec{P}_{ion}$, but $Z_i^v$ is replaced by $Z_i^{ion}$, the latter being the formal charge of the ion within a fully ionic model. For instance, for Fe, $Z_{Fe}^{ion} = +8$ (eight electrons are considered as valence electrons), while $Z_{Fe}^{ion} = +3$, i.e. formally equal to the oxidation number of Fe. If there is a large difference between PCM polarization and $\vec{P}_{ion} + \vec{P}_{ele}$, this has to be ascribed to covalency effects. Obviously, the partition in electronic and ionic components of the total polarization depends on how the electrons are partitioned in valence or core electrons, i.e. it depends on the valence electronic configuration used to generate the pseudopotential. Although the ionic and electronic components are a useful tool for qualitative discussions, one has to keep in mind that only the total polarization should have a sound physical meaning. However, there is the possibility of breaking down the total $P$ into a pure electronic part and an ionic part, as follows: (i) freeze atoms into the centrosymmetric

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\(^6\) The two values differ by less than 1 meV cell\(^{-1}\).

\(^7\) Further relaxations including SOC give $d_{FM} = 1.899 \text{ Å}$ and $d_{AFM} = 1.909 \text{ Å}$, whereas HSE gives $d_{FM} = 1.899 \text{ Å}$ and $d_{AFM} = 1.910 \text{ Å}$.
Figure 2. Adiabatic path connecting the PE and FE\textsubscript{1} phases through step-wise rotation of the Dy spin direction from 90\degree to 0°. PE refers to the PE phase when Dy and Fe spins are perpendicular (i.e. represented by perpendicular arrows at the bottom of the figure); FE\textsubscript{1} refers to the FE phase when the Dy and Fe spins are parallel (represented by parallel arrows at the bottom of the figure). See text for details. Units are (eVcell\textsuperscript{−1}) for $\Delta E$, $\mu$C cm\textsuperscript{−2} for FE polarization, Å for interlayer distance ($d$) and decimal degree ($\Theta$) for angles ($\Theta$). In panel (I), blue and red colors refer to relaxed and ideal ionic structures, i.e. with or without ionic relaxations, for each spin configuration held fixed.

(CS) structure, calculate the total polarization and refer to this as electronic, $P_{\text{ele}}$; (ii) relax the ions in the FE phase, calculate the total polarization, subtract the previously found electronic $P_{\text{ele}}$ and refer to this as ionic, $P_{\text{ion}} = P_{\text{tot}} - P_{\text{ele}}$ [43, 44]. In the following, we will consider only the absolute magnitude of the polarization vectors, since the polarization is always along the same direction.

The results are summarized in figure 2. Panel (I) shows the energy difference between the FE\textsubscript{1} and the PE phases, evaluated at the ideal CS ionic structure (in blue) and relaxed configuration (in red). In panels (II)–(IV), we show the electronic, ionic and total FE polarization, respectively. In (IV), the PCM estimate of the polarization is also reported (in black). In (V), the change in the interlayer distances along the path (see also figure 1) is shown. Panel (I) shows that ferroelectricity in DFO is spin induced. In fact, fixing the ions in their CS positions but rotating the spins from the perpendicular to the parallel configuration (blue bars in the figure, as explained above), there is an energy gain with respect to the PE phase, which increases from left to right, as represented by the heights of the blue bars. In this case, the energy gain is solely due to spin rotations and not to the ionic degrees of freedom, since the ions are fixed. If we allow the ions to relax, there is a further stabilization (as shown by the red bars). In other words, the spin rotation from perpendicular to parallel Dy and Fe spins induces a symmetry lowering from the PE to the FE phase and a concomitant decrease
in the system’s energy. In the charge densities associated with the new spin configurations, the ions are no longer in their equilibrium positions, and they move so as to minimize the residual Hellman–Feynmann forces, further stabilizing the structure. Note that the relaxation of the electronic degrees of freedom accounts for most of the total stabilization energy (cf blue and red bars). The energy gain increases from left to right in panel (I), i.e. toward a collinear configuration. It is important to point out that the polarization increases from left to right, even when keeping the ions fixed in the CS structure. This is shown in panel (II). Thus, by progressively rotating the spins, the electronic contribution to the polarization increases. As a matter of fact, in the case of ions fixed at CS positions, $P_{\text{ion}}$ is equal to zero for each spin configuration, and $P_{\text{tot}} = P_{\text{ele}} + P_{\text{ion}} = P_{\text{ele}}$: thus, the charge density associated with each spin configuration becomes progressively ‘polar’. This polarization is usually called $P_{\text{ele}}$ [43, 44]. If the ions are allowed to relax, they will adopt a polar configuration that will differ, in general, from the initial CS configuration. At this point, it is useful to calculate $P_{\text{ion}}$. From panel (III), we see that $P_{\text{ion}}$ is opposite to $P_{\text{ele}}$ and of the same order of magnitude. However, $P_{\text{ion}}$ does not fully compensate for $P_{\text{ele}}$: $P_{\text{tot}} = P_{\text{ele}} + P_{\text{ion}}$ is different from zero (see panel (IV)), giving rise to a total polarization $P_{\text{tot}}$ of $\sim 0.20 \mu \text{C cm}^{-2}$ for collinear spins. We thus arrive at the following important conclusion for our simple model of DFO: starting from a CS ionic configuration, the rotation of spins causes symmetry breaking, which drives the system toward a new stable configuration that is also FE. The fact that FE polarization arises solely by the spin rotation (and it is further enhanced by subsequent ionic relaxations) characterizes the ferroelectricity in DFO as spin induced [45]. The inclusion of SOC confirms $P_{\text{tot}}$, i.e. $0.18 \mu \text{C cm}^{-2}$. Notably, this value is in good agreement with the estimate given in [9]. HSE also yields a sizeable FE polarization. However, $P_{\text{pcm}}$ is not only opposite to $P_{\text{tot}}$ but also smaller in absolute value. The fact that the ab initio value and the point charge model are significantly different suggests that there is a large redistribution of the charge density upon spin rotations, due to strong covalency effects, as expected in spin-induced MFs [45]. The complex charge redistribution following the spin rotation and the subsequent ionic displacements to minimize the total energy result in a change in interlayer distances measured along the polar axis. The changes are such that the Dy and Fe layers that have FM (AFM) spin alignment move toward (opposite to) each other. This spin-driven interlayer dimerization is in line with the mechanism proposed in [9, 16].

### 4.2. Ionic relaxations and origin of the ferroelectricity

In the PE phase, Fe, Dy, $O_{\text{ap}}$ (apical oxygens) and $O_{\text{eq}}$ (equatorial oxygens) occupy the 4$a$, 4$c$, 4$c$ and 8$d$ Wyckoff positions (WPs), respectively. When the symmetry is lowered to $C_{2v}$, Dy and $O_{\text{ap}}$ change their site symmetry to 4$a$ and the $O_{\text{eq}}$ become inequivalent ($8d \rightarrow 4a + 4a$). This is readily explained by considering the local spin configuration around $O_{\text{eq}}$: when the latter are sandwiched by FM-coupled Fe and Dy layers, they have two $\uparrow$Fe and two $\uparrow$Dy atoms as nearest neighbors (these will be labeled $O_{\text{eq}}^{\uparrow\downarrow}$); when sandwiched by Fe and Dy layers AFM coupled, they have two $\uparrow$Fe and two $\downarrow$Dy atoms as nearest neighbors (labeled as $O_{\text{eq}}^{\uparrow\downarrow}$). First of all, all $O_{\text{eq}}$ carry a spin-induced moment parallel to the neighboring Fe atom. Furthermore, by imposing the FE$_1$ spin configuration on top of the CS ionic structure, $O_{\text{eq}}^{\uparrow\downarrow}$ and $O_{\text{eq}}^{\downarrow\uparrow}$ become inequivalent: the $O_{\text{eq}}^{\uparrow\downarrow}$ has $\pm 0.194 \mu_B$ and the $O_{\text{eq}}^{\downarrow\uparrow}$ has $\pm 0.207 \mu_B$ as the induced spin moment. To rule out any numerical artifact on this small difference, we impose the PE spin configuration on top of the CS ionic structure. In this case, all $O_{\text{eq}}$ carry induced spin moments of exactly the same magnitude. In passing, we note that all oxygens remain equivalent when freezing the
Dy-f electrons in the core. Furthermore, we performed an analysis of the symmetry breaking distortions [46, 47]. The mode decomposition confirms that an FE mode is involved, called $\Gamma_{4\ldots}$. In figure 3, we show the pattern of atomic displacements with respect to the CS structure. The inequivalency of $O_{\text{eq}}$ is subtle: $O_{\text{eq}}^{\uparrow\downarrow}$ move in such a way as to decrease (increase) the distance to its neighbor Dy atom. For $O_{\text{eq}}^{\uparrow\uparrow}$, $d_{\text{Dy-O}}$ is 2.478 Å; for $O_{\text{eq}}^{\downarrow\downarrow}$, $d_{\text{Dy-O}}$ is 2.496 Å (the same distance in the PE phase is 2.487 Å), suggesting that a weak bonding interaction is active between the FM layers, leading to a polarization along $b$. A useful tool for studying tiny differences in bonding interaction in solid state systems is the electron localization function (ELF) [48, 49]. The ELF values lie by definition between zero and one. The values are close to 1 if in the vicinity of one electron no other electron with the same spin may be found, for instance as occurs in bonding pairs. Here, we consider the difference in ELF (DELF) between the situation when f-electrons are in the valence and when they are frozen in the core, for the same ionic configuration, i.e. $\text{DELF}(\vec{r}) = \text{ELF}_{\text{val}}(\vec{r}) - \text{ELF}_{\text{core}}(\vec{r})$. The physical interpretation is as follows: positive values of DELF show up in regions where the electron localization is higher, i.e. the bonding between FM layers is strengthened. In figure 3 (right part), we show a positive isosurface of DELF projected into the $ab$-plane. Clearly, it is mainly localized between FM layers and, more specifically, in the region between Dy and $O_{\text{eq}}^{\uparrow\downarrow}$. This points to a bonding interaction between FM layers mediated by $O_{\text{eq}}^{\uparrow\downarrow}$.

The bonding interaction between $O_{\text{eq}}^{\uparrow\downarrow}$ and the Dy atom allows the introduction of a simple description of the onset of ferroelectricity. In fact, the interaction between Dy and $O_{\text{eq}}^{\uparrow\downarrow}$ gives rise to an accumulation of electronic charge (bonding orbitals) in the region between Dy and $O_{\text{eq}}^{\uparrow\downarrow}$. These covalent bonds are heteropolar and therefore they will carry a small electric dipole between O and Dy, as schematically represented in figure 4. For the $+P$ state, these small bond dipoles, sandwiched by FM layers, have a component along the positive direction of the $b$-axis and therefore they sum up to give a finite contribution. On the other hand, for the $-P$ state, the bond dipoles point to an opposite direction with respect to the previous case, therefore reverting the finite polarization. The interpretation of bond dipoles as a source of the $+P$ and $-P$ states is shown in figures 4(a) and (b).
4.3. Electronic structure fingerprint

A careful inspection of the orbital-decomposed magnetic moments reveals that the Dy–5d states are polarized only if the 4f states are in the valence: the 4f states couple locally to the 5d spin moments by intra-atomic 4f–5d exchange interaction [50]. The 5d states are much more extended than 4f electrons, suggesting that the glue that finally couples FM Fe and Dy layers is the interatomic interaction between the Fe 3d states and the Dy 5d states mediated by the oxygen p states. In figure 5, we show the local density of states (DOS) at O\textsuperscript{eq}\textsuperscript{↑} atoms and the Dy–d and Dy–f states. In panel (I), a clear interaction between d and f states of Dy and oxygen states is visible (cf the dotted ellipse). Note that the same interaction involves the Fe 3d states as well (not shown in figure 5). Remarkably, the interaction disappears when freezing the f states in the core (see panel (II)), for which the intraatomic Dy–f–d and interatomic O–p interaction disappears. Panel (III) shows the Dy–f DOS calculated using DFT+U, HSE and G\textsubscript{0}W\textsubscript{0}@HSE calculations. In the (relevant) occupied manifold, the chosen U nicely fits the HSE DOS, which, in turn, is rather close to the G\textsubscript{0}W\textsubscript{0} calculations. The corrections beyond a mere DFT+U approach show up in the unoccupied states by opening the band gap. However, this does not change our conclusions, as far as the polarization is concerned. The local or on-site exchange between the Dy 4f–5d orbitals and a superexchange-like mechanism involving the interatomic interaction mediated by ligand p states is already known and studied for the EuO compound [51]–[55]. In our case, however, the superexchange mechanism involves the 4f and 3d states of the Dy and Fe sublattices, respectively, mediated by oxygen 2p states, i.e. 4f–2p–3d; in EuO, the superexchange involves the 4f of the same Eu lattice, via oxygen 2p states, i.e. 4f–2p–4f.

The fact that the Dy and Fe interaction is mediated by O\textsubscript{eq}\textsuperscript{↑}-sp states suggests possible routes to tailor the FE polarization. For instance, compressive or tensile strain along the polar axis should change the tilting of the octahedra, favoring or disfavoring the interaction via the intermediate O\textsubscript{eq}\textsuperscript{↑} states, i.e. changing the FE polarization.
Figure 5. DOS for oxygen and Dy atoms for f as valence (panel (I)) or as core states (panel (II)). Panel (III) shows the f-DOS as calculated by DFT+U, HSE and G0W0@HSE. Vertical dotted lines refer to the Fermi level. Positive (negative) DOS values refer to minority (majority) states. See text for details.

5. Conclusions

Several results emerge from our study. (i) the FE state of DFO is driven by exchange striction, confirming the interpretation given in [9, 16]. (ii) two degenerate and switchable polar states exist, characterized by a sign reversal of the FE polarization ($\pm P$) and linked by an adiabatic path, connecting the two FE states FE$_1$ and FE$_2$ to the same PE reference structure, which can be obtained through a relative rotation of the direction of Dy spins (with respect to Fe spins). (iii) the coupling between Dy and Fe spin sublattices is mediated by Dy–d and O–2p states. (iv) the estimated FE polarization is in agreement with experiments. (v) by freezing the f-states in the core instead of relaxing them in the valence, we confirm the crucial role played by f-electrons in establishing the spin-driven FE. More generally, our study suggests that f-electrons might play an important role in the FE properties of other RMO$_3$ compounds (where 4f electrons are often neglected in theoretical calculations). (vi) last but not least, our electronic structure analysis suggests possible routes to tailor the FE polarization, owing to the strong Dy–Fe coupling via intermediate equatorial oxygens. Further study is in progress to confirm this expectation.

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