First-principles reinvestigation of bulk WO$_3$

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Using first-principles calculations, we analyze the structural properties of tungsten trioxide WO$_3$. Our calculations rely on density functional theory and the use of the B1-WC hybrid functional, which provides very good agreement with experimental data. We show that the hypothetical high-symmetry cubic reference structure combines several ferroelectric and antiferrodistortive (antipolar cation rotations, rotations, and tilts of oxygen octahedra) structural instabilities. Although the ferroelectric instability is the largest, the instability related to antipolar W motions combines with those associated to oxygen rotations and tilts to produce the biggest energy reduction, yielding a $P2_1/c$ ground state. This nonpolar $P2_1/c$ phase is only different from the experimentally reported $Pm$ ground state by the absence of a very tiny additional ferroelectric distortion. The calculations performed on a stoichiometric compound so suggest that the low-temperature phase of WO$_3$ is not intrinsically ferroelectric and that the experimentally observed ferroelectric character might arise from extrinsic defects such as oxygen vacancies. Independently, we also identify never observed $R3m$ and $R3c$ ferroelectric metastable phases with large polarizations and low energies close to the $P2_1/c$ ground state, which makes WO$_3$ a potential antiferroelectric material. The relative stability of various phases is discussed in terms of the anharmonic couplings between different structural distortions, highlighting a very complex interplay.

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I. INTRODUCTION

Tungsten trioxide, WO$_3$, has been extensively studied due to its very attractive and rich properties for technological applications. WO$_3$ and its derivatives H$_2$WO$_3$ and WO$_{1-x}$ are electrochromic [1–6], thermochromic [7,8], and superconducting [3,8–14]. It has been envisaged that WO$_3$ may become one of the best materials for electrochromic applications such as in energy-efficient windows, smart glasses, antiglare automobile rear-view mirrors, sunroofs, displays, or even tunable photonic crystals [15] and to reduce photocorrosion [16]. The wide variety of the underlying electronic instabilities for these properties is mirrored by a multitude of related structural instabilities, which have been investigated ever since 1975 [17,18] and refined later [19–24].

All known WO$_3$ phases are characterized by very large distortions of the archetypal perovskite structure so that even the notion of octahedra tilts is to be taken with some caution. The WO$_6$ octahedra are so largely distorted that the variance of W–O distances in any observed structure is far greater than in most other known perovskite structures [25–29]. In this paper we make the fundamental connection between the electronic and structural structure properties of WO$_3$ and show that most, if not all, structural instabilities can be derived from a careful analysis of its intrinsic cubic phonon instabilities, despite these large deformation amplitudes.

The structural properties can be summarized as follows: WO$_3$ shows no proper melt; surface melting of crystalline material occurs at 1746 K. Crystal growth proceeds typically by sublimation and gas transport at temperatures below 1400 K. At the highest temperatures the structure is tetragonal (space group $P4/nmm$) with strong antiferrodistortive cation movements so that the WO$_6$ octahedra are strongly distorted [30] in an antipolar pattern. Additional rotational octahedral distortions condense in addition to the initial tetragonal displacements when lowering the temperature. They further reduce the symmetry from tetragonal to orthorhombic, monoclinic, triclinic, and finally to a second monoclinic phase. A structural sequence, which contains phases stabilized by temperature, is given in Fig. 1. A monoclinic phase ($P2_1/n$) [21] and a triclinic phase $P1$ exist at room temperature [25,26]. At higher temperatures, Vogt et al. [22] and Locherer et al. [19] concluded a transition from $Pbnm$ to the $P4/ncc$ phase and Howard et al. [23] observed an intermediate $P2_1/c$ phase. Locherer et al. [19] and Woodward et al. [26] found an additional transition from $P4/ncc$ to $P4/nmm$ at 980 to 1200 K. Below room temperature, Salje et al. [20] reported a transition from the triclinic $P1$ phase to a polar phase ($Pc$) with no further transitions down to 5 K.

WO$_3$ occurs (almost) always as oxygen deficient WO$_{3-x}$ with a metal-insulator transition to a metallic phase for high concentrations of oxygen vacancies or doping with alkali metals. Superconductivity occurs in the metallic phase [9] even if the reduced regions are restricted to nanoscale twin boundaries. Bulk superconductivity in WO$_{3-x}$ was found in a tetragonal phase with space group $P4_{2}m$ [10]. (Bi-)polaronic electron transport is a characteristic property of WO$_{3-x}$ [31–34].

Numerous first-principles studies were performed on WO$_3$ in order to characterize its electronic structure (bulk, thin films, and cluster phases [35–41]), the role of oxygen vacancies [42–45], and cation doping [46–53]. In this paper we do not only focus on the electronic structure but also extensively study the structural stabilities and metastabilities of the various phases. We show that the hybrid functional B1-WC is preferable for the study of the electronic and structural properties of WO$_3$ over previous approaches. In the first section we check the validity of the B1-WC functional against six known crystallographic phases. The sole disagreement exists for the crystallographic $\varepsilon$ phase ($Pc$), which yields a higher symmetric $P2_1/c$ structure. In the second section we analyze metastable phases starting from the phonon
knowledge of the origin of these different phases would be extremely valuable to understand the unique properties of WO$_3$.

In this section we start by characterizing the different phases of WO$_3$ observed experimentally to validate our approach and we will discuss the possible origin of the $Pc$ phase. We will also analyze the electronic structure of these phases and we will discuss how the B1-WC compares with the previous studies. Further analysis of these phases and other never observed metastable phases (comparison of relative internal energies, symmetry mode analysis of the distortions, coupling of modes) will be reported in Sec. IV B).

A. Structural and crystallographic analysis

In Table I we compare our calculated crystallographic data of the $P4/nmm$, $P4/ncc$, $Pbnm$, $P2_1/n$, $P1$, and $P2_1/c$ phases against the experimental measurements. Because the $P2_1/c$ phase is not observed experimentally at low temperature, we compare it with the closely related experimental $Pc$ phase.

Our calculations of the $P4/nmm$ phase are in very good agreement with the observed cell parameters and the atomic positions. The $P4/nmm$ phase is antipolar and consists of highly distorted WO$_6$ octahedra where the W–O bonds dimerize in opposite direction along the [110] perovskite direction. This W–O dimerization forms local dipole moments that are aligned along the [001] direction and antialigned along the [110] direction, so that the total dipole moment cancels. The crystallographic unit cell is elongated along the [001] direction and compressed along the [100] and [010] directions. This antipolar distortion remains present in all the phases discussed below in this section.

The $P4/ncc$ phase shows additional octahedra rotations around the $z$ axis ($a^0b^0c^-$ in the Glazer notation [65]), which induces a cell doubling along the [001] direction. The calculated $c$ cell parameter and the $z$ component of the atomic positions are in good agreement with experiments while the in-plane displacements are less well reproduced (Table I). The calculated $a$ and $b$ cell parameters are smaller than in experiments by 0.1 Å and the deviation from the tetragonal $O_2$ position is about two times larger than observed. We clearly overestimate the amplitude of the $a^0b^0c^-$ distortion (rotation angle of 13° instead of 7°; see also Fig. 7 further discussed in Sec. IV B). Although this could be partly intrinsic to the functional [66], it is worth noticing that our calculations ignore thermal effects while experiments were performed at high temperatures at which distortions might be reduced [67]. Although such a reduction does not seem to appear for the antipolar motions in the $P4/nmm$ and $P4/ncc$ phases, it might be more substantial for the rotations and we observe that the computed amplitudes of out-of-phase rotations are in much better agreement with experimental data for the low-temperature phases (see further discussed in Sec. IV B).

The orthorhombic $Pbcn$ phase can be characterized by an additional in-plane octahedra rotation about the crystallographic $y$ axis, yielding a rotation pattern $a^0b^+c^-$. We find a similar overestimate of the octahedra distortions as for the $P4/ncc$ phase while the calculated cell parameters are underestimated with respect to experiments. We note that

![FIG. 1. Schematic summary of the temperature phase diagram WO$_3$ as reported by three main experimental sources (Vogt et al. from Ref. [22], Locherer et al. from Ref. [21], and Howard et al. from Ref. [23]).](image)
TABLE I. Calculated lattice parameters in Å and Wyckoff positions of distorted WO$_3$ phases fully relaxed with the B1-WC functional. For each phase, we specify the space group and the experimental parameters are reported for comparison.

<table>
<thead>
<tr>
<th>P4/nmm</th>
<th>Present</th>
<th>Exp. [23]</th>
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<tr>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
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<tr>
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<td>5.299</td>
<td>3.930</td>
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<tr>
<td>$x$</td>
<td>$y$</td>
<td>$z$</td>
</tr>
<tr>
<td>$W_1$ (2c)</td>
<td>1/4</td>
<td>1/4</td>
</tr>
<tr>
<td>$O_1$ (2c)</td>
<td>1/4</td>
<td>1/4</td>
</tr>
<tr>
<td>$O_2$ (4d)</td>
<td>0</td>
<td>0</td>
</tr>
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<table>
<thead>
<tr>
<th>P4/ncc</th>
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<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
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<td>5.168</td>
<td>5.168</td>
<td>7.870</td>
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<tr>
<td>$x$</td>
<td>$y$</td>
<td>$z$</td>
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<tr>
<td>$W_1$ (4c)</td>
<td>1/4</td>
<td>1/4</td>
</tr>
<tr>
<td>$O_1$ (4c)</td>
<td>1/4</td>
<td>1/4</td>
</tr>
<tr>
<td>$O_2$ (8f)</td>
<td>0.0570</td>
<td>$-0.0570$</td>
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<td>7.684</td>
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<tr>
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<td>$z$</td>
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<tr>
<td>$W_1$ (3d)</td>
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<td>0.0260</td>
</tr>
<tr>
<td>$O_1$ (3d)</td>
<td>$-0.0010$</td>
<td>0.0430</td>
</tr>
<tr>
<td>$O_2$ (3d)</td>
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<td>0.2590</td>
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<tr>
<td>$O_3$ (3d)</td>
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<td>0.0100</td>
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<table>
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<tr>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
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<td>7.359</td>
<td>7.486</td>
<td>7.544</td>
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<td>$x$</td>
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<td>$z$</td>
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<td>$W_1$ (4e)</td>
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<td>0.0074</td>
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<td>$W_2$ (4e)</td>
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<td>0.0133</td>
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<tr>
<td>$O_1$ (4e)</td>
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<td>0.0410</td>
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<tr>
<td>$O_2$ (4e)</td>
<td>$-0.0056$</td>
<td>0.4576</td>
</tr>
<tr>
<td>$O_3$ (4e)</td>
<td>0.2883</td>
<td>0.2534</td>
</tr>
<tr>
<td>$O_4$ (4e)</td>
<td>0.2029</td>
<td>0.2530</td>
</tr>
<tr>
<td>$O_5$ (4e)</td>
<td>0.2795</td>
<td>0.0385</td>
</tr>
<tr>
<td>$O_6$ (4e)</td>
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<td>0.4630</td>
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<td>$b$</td>
<td>$c$</td>
</tr>
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<td>7.334</td>
<td>7.446</td>
<td>7.612</td>
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<tr>
<td>$x$</td>
<td>$y$</td>
<td>$z$</td>
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<tr>
<td>$W_1$ (2i)</td>
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<td>0.0172</td>
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<tr>
<td>$W_2$ (2i)</td>
<td>0.2540</td>
<td>0.5210</td>
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<tr>
<td>$W_3$ (2i)</td>
<td>0.2397</td>
<td>0.0228</td>
</tr>
<tr>
<td>$W_4$ (2i)</td>
<td>0.2456</td>
<td>0.5268</td>
</tr>
<tr>
<td>$O_1$ (2i)</td>
<td>0.0015</td>
<td>0.0395</td>
</tr>
<tr>
<td>$O_2$ (2i)</td>
<td>0.5022</td>
<td>0.5406</td>
</tr>
<tr>
<td>$O_3$ (2i)</td>
<td>0.0026</td>
<td>0.4582</td>
</tr>
<tr>
<td>$O_4$ (2i)</td>
<td>0.5012</td>
<td>0.0398</td>
</tr>
<tr>
<td>$O_5$ (2i)</td>
<td>0.2892</td>
<td>0.2571</td>
</tr>
<tr>
<td>$O_6$ (2i)</td>
<td>0.2081</td>
<td>0.7575</td>
</tr>
<tr>
<td>$O_7$ (2i)</td>
<td>0.2098</td>
<td>0.2569</td>
</tr>
</tbody>
</table>

The antipodal distortions along the $z$ axis compare well with experiments for P4/nmm, P4/ncc, and Pbn.

The P2$_1$/n structure still contains an additional octahedra rotation around the crystallographic $x$ axis, yielding a rotation pattern $a^{+}b^{-}c^{-}$. The calculated cell volume is slightly too small (+0.7, −0.7, and −1.9% for $a$, $b$, and $c$ cell parameters, respectively) and the oxygen motions related to the octahedra tilt are overestimated (Table I).

The P1 phase is similar to the P2$_1$/n phase if one replaces the in-phase rotation by an out-of-phase rotation, yielding a rotation pattern $a^{+}b^{-}c^{-}$. The distortions are anisotropic in all three directions, which causes the cell to be triclinic with the angles $\alpha$, $\beta$, and $\gamma$ close to 90°. The calculated $a$, $b$, and $c$ cell parameters deviate from experiments by +0.4, −1.1, and −0.8%, respectively.

The $P2_1/c$ phase differs from the P1 by the fact that two out-of-phase rotations have the same amplitudes, yielding a rotation pattern $a^{+}a^{-}c^{-}$. This phase was never reported at low temperatures but is closely related to the experimental $\delta$ ($Pc$) phase, which only differs from the $P2_1/c$ phase by an additional polar distortion along the $c$ axis. While relaxing the low-temperature $Pc$ phase, we observed that the system always comes back in to the higher $P2_1/c$ symmetry. Wijs et al. using local-density approximation and generalized gradient approximation exchange-correlation functionals [38] found a similar effect. To further assess the dynamical stability of the $P2_1/c$ phase with respect to a potential $Pc$ ground state, we computed the zone-center phonons and did not observe any unstable mode: the lowest polar mode has a frequency of 158 cm$^{-1}$ and is far from being unstable. We also checked whether a soft polar mode can be induced by increasing the cell volume but did not observe any possibility to generate a polar instability. From our calculations, the ground-state structure of intrinsic WO$_3$ corresponds therefore to a $P2_1/c$ phase. Following the argument by Wijs et al. [38], we suggest

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that the polarity in the experimental ε (Pc) phase may be stabilized by the presence of oxygen vacancies or by another extrinsic parameter.

In Table I we compare our calculated atomic positions and cell parameters of the P21/c phase with the experimentally determined Pc phase. The deviations are surprisingly small for lattice parameters (+0.2, −0.2, and −0.5% for a, b, and c) and even smaller for the atomic positions. Comparing the structural parameters obtained with other hybrid functionals PBE0, B3LYP, and HSE06 reported by Wang et al. [42], we find close agreement with a typical smaller error margin for B1-WC. B1-WC gives a much better agreement for the P21/c phase with experimental data than using the three hybrid functionals tested by Wang et al.: HSE06, B3LYP, and PBE0 with errors of +0.6, +1.3, and +0.2% on a; +2.1, +2.5, and +0.6% on b; and +0.1, +3.0, and +1.7% on the c parameter. We notice, however, that the B1-WC often underestimates cell parameters while the three other hybrid functionals overestimate the cell parameters of WO3.

### B. Electronic structure

In Table II we compare the calculated electronic structures for the hypothetical cubic, P4/nmm, P4/ncc, Pnbn, P21/n, Pı, and P21/c phases and compare them with the experiments and previous DFT calculations using PBE0, HSE06, and B3LYP hybrid functionals and GW. For the P21/n and Pı phases, experimental data coincide with the B1-WC band gaps. The B1-WC results are similar to those obtained with the HSE06 functional while the PBE0 gives a slightly smaller gap energy and B3LYP larger values. The B1-WC band gap is closest to the results of GW calculations, an agreement also observed for the P21/c phase.

Comparing the trend of band gaps between the different phases, we find that both the appearance of antipolar motions in the P4/nmm phase and out-of-phase rotations in the I4/mcm significantly open the band gap with respect to the cubic phase. Only the in-phase rotations in the P4/mmb phase seem to play a more minor role and slightly close the band gap. The calculated electronic gaps are in reasonable agreement with the experimental values for the three low-temperature structures:

**TABLE II.** Electronic band gap (in eV) of different phases of WO3 as calculated in the present work with the B1-WC hybrid functional. We compare our results with previous hybrid functional calculations (PBE0, HSE06, and B3LYP), GW calculations, and experimental measurements.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>B1-WC</th>
<th>PBE0</th>
<th>HSE06</th>
<th>B3LYP</th>
<th>Exp1</th>
<th>Exp2</th>
<th>Exp3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>1.50</td>
<td>2.25</td>
<td>1.67</td>
<td>1.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4/mmb</td>
<td>1.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I4/mcm</td>
<td>1.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4/nmm</td>
<td>2.12</td>
<td>2.28</td>
<td>1.71</td>
<td>1.85</td>
<td>1.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4/ncc</td>
<td>2.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pcnb</td>
<td>2.65</td>
<td>3.35</td>
<td>2.57</td>
<td>2.89</td>
<td>3.21</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>P21/n</td>
<td>2.85</td>
<td>2.90</td>
<td>3.67</td>
<td>2.80</td>
<td>3.13</td>
<td>2.75</td>
<td>3.25</td>
</tr>
<tr>
<td>Pı</td>
<td>2.98</td>
<td>3.00</td>
<td>3.67</td>
<td>2.94</td>
<td>3.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P21/c</td>
<td>3.28</td>
<td>3.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 2.** Calculated density of states of the P1, P21/n, and P21/c phases with the B1-WC functional.

Eg = 2.85 eV for the room-temperature monoclinic phase P21/n, Eg = 2.98 eV for the triclinic phase Pı, and Eg = 3.28 eV for the monoclinic phase P21/c. Figure 2 shows the density of states of these three phases to demonstrate their similarity.

### IV. ORIGIN OF THE WO3 PHASES

The results presented so far give us confidence that the B1-WC functional reproduces well the experimental measurements so that we can now focus on the structural instabilities of the hypothetical Pm3m cubic parent phase and explain how their condensation gives rise to the various known phases of WO3. This also allows us to identify novel ferroelectric metastable phases. In each case, we analyze the crystallographic structure through a decomposition of the distortions with respect to the cubic parent phase in terms of symmetry-adapted modes.

#### A. Unstable modes of the cubic reference

Figure 3 shows the calculated phonon dispersion curves of hypothetical cubic WO3. Two branches of instabilities (imaginary frequencies plotted as negative numbers in Fig. 3) coexist in the Brillouin zone.

The first unstable branch has its largest imaginary value at Γ. The Γ unstable mode has the irreducible representation (irrep) Γ2 and corresponds to a polar mode. It suggests that the cubic phase of WO3 is mostly unstable via this polar instability and might be ferroelectric, which we will see later is not exactly the case. The polar instability at Γ propagates toward the X and M points with weak dispersion while it strongly disperses towards the R point. Aside from Γ, the modes of this branch are antipolar. The dispersion of this unstable branch is very similar to the one reported in BaTiO3 and corresponds to a ferroelectric instability requiring a chainlike correlation of displacements in real space [70].

The second branch of unstable modes appears between M and R points with smaller amplitudes and a nearly absent dispersion between these two points. The labels of the M and R point unstable phonon modes are M1 and R1 and...
they correspond to rotations of the oxygen octahedra. The

dispersion of this branch is comparable to what is observed

for similar modes in SrTiO$_3$ or PbTiO$_3$ and linked to a planar

character of the correlations of the atomic displacements in

real space [70].

Figure 4 represents a schematic view of the eigenvectors

related to the main instabilities of cubic WO$_3$. The polar

mode at $\Gamma$ ($\Gamma_4^-$, 373 i cm$^{-1}$) shows motion of W against the

O atoms, which is the source of a large electrical polarization.

The antipolar modes at the X ($X_5^-$, 256 i cm$^{-1}$) and M points

($M_3^-$, 147 i cm$^{-1}$) are associated to opposite displacements

from unit cell to unit cell along the [100] and [110] directions, respectively [71]. The $M_3^-$ (62 i cm$^{-1}$) and $R_1^+$ (69 i cm$^{-1}$)

unstable modes correspond rotations of the oxygen octahedra

about the central W atom with consecutive octahedra along

the rotation direction moving, respectively, in the same or

opposite directions. Using the Glazer notation [65], the $M_3^-$

mode corresponds to $a^3d^3a^+\times$ and the $R_1^+$ mode corresponds
to $a^3d^3a^-$. 

\[
\Gamma_4^- \quad M_3^- \quad X_5^- \quad R_1^+ \quad X_5^+
\]

B. Condensation and coupling of modes

Starting from the previous unstable modes, we now investig- 

te how their individual and combined condensations in the

hypothetical cubic structure give rise to various phases. We

then compare their energies and analyze the amplitudes of

distortions.

1. Condensation of modes of the unstable polar branch

We first consider the condensation of unstable $\Gamma_4^-$, $X_5^-$, and $M_3^-$ modes. Figure 5 shows the energy gain of the corresponding relaxed phase with respect to the cubic phase.

We tested several condensation schemes: (i) condensation of the polar $\Gamma_4^-$ mode along one ($P4mm$, two ($Amm2$), and 

three ($R3m$) directions; (ii) condensation of the $X_5^-$ along one ($Pmna$) and two ($P2_1/m$) directions; and (iii) condensation of the $M_3^-$ mode along one direction ($P4/nmm$).

We observe that the energy gain of the polar instabilities is large and that the $\Gamma_4^-$ polar mode drives a larger gain of energy (red columns in Fig. 5) than the antipolar $X_5^-$ and $M_3^-$

modes (green columns in Fig. 5). The space group related to the condensation of the $M_3^-$ mode corresponds to the high-

temperature phase observed experimentally ($P4/nmm$).

Condensation of the $\Gamma_4^-$ mode along two and three direc-

tions produces energy gains larger than its condensation in a single direction so that the $\Gamma_4^-$ mode alone will drive the system polar along the [111] direction with an energy difference between the $Amm2$ and $R3m$ phases of 6 meV. We calculated the polarization amplitude in the three $P4mm$, $Amm2$, and $R3m$ phases using the Berry phase technique and obtain 54, 69, and 69 $\mu$C cm$^{-2}$. These polarization values are comparable to those observed in robust ferroelectrics such as PbTiO$_3$.

They can be explained by the opposite motions of W and O atoms, associated with strongly anomalous Born effective charges (11.73 e for W and $-8.78/1.62$ e for O$_i$/O$_\perp$ in good agreement with previous calculations in Ref. [72]).
Combining the polar distortion of the low-energy $R3m$ phase with additional oxygen rotation modes does not further reduce the energy. Instead, it yields a $R3c$ phase slightly higher in energy but with a slightly amplified polarization of 71 $\mu$C cm$^{-2}$ and a slightly reduced oxygen rotation (with respect to the $R3c$). This emphasizes an unusual competition between these two types of distortions in WO$_3$ with respect to regular perovskite compounds, where in WO$_3$ the $R3c$ phase forms a local minimum between the $R3c$ and $R3m$ phases.

At the opposite, the mixing of the antipolar mode $M_3^-$ with oxygen rotation modes can drive larger energy gains so that the ferroelectric $R3m$ phase is not the ground state. This is in agreement with experimental observations where the observed phases at all temperatures contain antipolar motions. Among investigated phases, the $P2_1/c$ phase appears as the most stable but only marginally, as we observe that the $P2_1/n$, $P2_1/c$, and $P\overline{1}$ phases are all extremely close in energy (energy gains of 153, 155, and 155 meV, respectively, see Fig. 5). Consequently, within the precision of our calculations, we cannot unambiguously assess which one is the ground state. Nevertheless, as discussed in Sec. III A and further exemplified in the next section, the $P2_1/c$ phase is in excellent agreement with the experimental $P\overline{1}$ ground state, except for a tiny polar distortion. Our calculations highlight that, in fact, the $P2_1/n$ and $P\overline{1}$ phases observed at higher temperatures are also extremely close in energy.

We further notice that the ferroelectric $R3m$ phase, although never observed experimentally, is also relatively close in energy to the ground state (about 11 meV/f.u.). Following Rabe [74], the nonpolar (or eventually weakly polar in the experimental $P\overline{1}$ phase) ground state of WO$_3$ combined with an alternative low-energy ferroelectric phase obtained by polar distortions of the same high-symmetry reference structure makes it a potential antiferroelectric compound. Indeed, applying an electric field, it might be possible to open a typical double hysteresis loop from a field-induced first-order transition from the $P2_1/c$ ground state to the $R3m$ polar phase. Estimating the critical electric field required to stabilize the $R3m$ phase from $\varepsilon_c \sim \Delta E/\Omega_0 P_s$ [75], where $\Delta E$ is the energy difference between the two phases (11.43 meV/f.u.), $P_s$ is the spontaneous polarization of the polar phase (69 $\mu$C cm$^{-2}$), and $\Omega_0$ is its unit-cell volume (55 Å), we get the relatively modest value $\varepsilon_c \sim 480$ kV/cm. For the polar phase $R3c$ we need to apply a greater electric field $\varepsilon_c \sim 638$ kV/cm to stabilize this phase. This allows us to estimate that the critical field has similar value with respect to other antiferroelectric material, $\varepsilon_c \sim 470$ kV/cm for ZrO$_2$ [75] and $\varepsilon_c \sim 239$ kV/cm for PbZrO$_3$ [76]. Although this might not be easy to check experimentally on real samples that are typically oxygen deficient and highly conductive, the calculations reveal that stoichiometric WO$_3$ exhibits all the features of an antiferroelectric compound.

2. Condensation of modes of the oxygen rotation unstable branch

Figure 5 (blue columns) shows the energy gain given by the condensation of the $M_i^\pm$ and $R_i^\pm$ modes along one direction ($I4/mmm$ and $I4/mcm$), the $R_i^+$ mode in three directions ($R_3^c$), and the orthorhombic $Pnma$ phase where the $R_i^+$ mode is condensed in two directions and the $M_i^\pm$ mode in one direction ($a^{-}a^{-}c^+$). These distortions lower the energy much less than the polar and antipolar motions. This observation is in line with the modest amplitude of the related phonon instabilities: the energy curvatures at the origin are less negative for the octahedral rotations than for the polar motion. Nevertheless the amplitudes of octahedral rotations are 10.7 and 11.7 deg in $I4/mnm$ and $I4/mcm$, respectively.

Such large distortions associated to a weak instability highlight relatively small anharmonicities, which might be explained by the absence of the A cation with respect to regular ABO$_3$ perovskites [73].

3. Combinations of modes

Beside the $P4/nmm$ phase, none of the previous single irrep mode condensations correspond to observed phases. Thus, we now explore the condensation of combined octahedral rotations and polar/antipolar modes. We depict in Fig. 5 the energy gain given by the joint condensation of polar and oxygen rotation modes along three directions ($R3c$, in purple color) and of antipolar and oxygen rotation modes ($P4/ncc$, $Pbcn$, $P2_1/n$, $P2_1/c$, and $P\overline{1}$, in cyan color).

4. Symmetry adapted mode analysis of the distorted phases

To quantify the distortions that appear in the various phases we project the structural distortions onto symmetry adapted modes of the cubic phase using AMPLIMODE software [77]. The results in Fig. 6 show the amplitudes of the modes in the fully relaxed phases from the calculations but nonobserved...
In the following we discuss the competition or cooperation character of the mode distortions. In perovskite oxides, it is established that the oxygen rotations are in competition with the ferroelectric displacements but less attention has been given to the combinations of other types of mode. Often, this cooperation or competition comes from the biquadratic energy term in the free-energy expansion with respect to two order parameters. In WO$_3$, we observe that the combination between the $\Gamma_4^-$ mode and the $R_3^+$ mode along the [111] direction in the R3c phase has the tendency to reduce the amplitude of the oxygen rotations with respect to the R3c phase (the $R_3^+$ mode is 13% smaller in the R3c phase than in the R3c phase, see Fig. 6) while the polar mode is unaffected. As discussed in the previous section, the combination of the $\Gamma_4^-$ and $R_3^+$ modes forms a local minimum (R3c phase) of higher energy than the R3m phase. This means that the polar distortions are in competition with the oxygen rotations as reported for perovskite oxides, with the difference that the polar mode amplitude is unaffected and that the R3c phase is locally stable (the system does not relax into the lowest-energy R3m phase). The strain can also play an important role [78], but when performing the same calculations at fixed cell parameters (fixed to the cubic ones), we find that the R3c phase still forms a local minimum of higher energy than the R3m phase. This unusual energy landscape can come from the marginal gain of energy of the oxygen rotations while large amplitudes of rotations are present.

On the other hand, the association of the oxygen rotations with the antipolar M$_3^-$ mode is cooperative. When we compare the amplitude of the $R_3^+$ and M$_3^-$ modes of the P4/nmm, I4/mcm, and P4/ncc (Figs. 6 and 7) we find that when both the $R_3^+$ and M$_3^-$ modes are present together in the P4/ncc phase, their amplitude is slightly higher (4% larger) than when condensed alone (P4/nmm and I4/mcm phases). Their combination, however, drives a sizable gain of energy: the P4/ncc phase is 63 and 126 meV lower in energy than the P4/nmm and the I4/mcm phases, respectively. This means that the combination of the oxygen rotations with the antipolar M$_3^-$ mode is much more cooperative than the combination with the polar mode $\Gamma_4^-$.

The Pbcn phase can be understood as a distorted P4/ncc phase with additional M$_3^-$ oxygen rotations along [010]. The resulting tilt pattern is $a^0b^+c^-$ with a small energy gain of 2 meV with respect to the P4/ncc phase and a reduction of mode amplitudes M$_3^-$, $R_3^+$, and M$_3^-$ (16, 7, and 22% reduction of the M$_3^-$, $R_3^+$, and M$_3^-$ modes with respect to the phases where they are condensed alone, i.e., P4/nmm, I4/mcm, and P4/mmm, respectively). The M$_3^-$ mode competes with the $R_3^+$ and M$_3^-$ modes in the sense their combination reduces their amplitude, but they cooperate to lower the energy of the system.

In the case of the monoclinic P2$_1$/n, P2$_1$/c, and triclinic P1 phases, the combination of the M$_3^-$ mode with several oxygen rotations ($a^0b^+c^-$ for P2$_1$/n, $a^-a^-c^-$ for P2$_1$/c, and $a^-b^-c^-$ for P1) lowers the energy of the crystal and with an increase of the mode amplitude with respect to the phases where these modes are condensed independently. For example, the antipolar M$_3^-$ mode has its amplitude increased by 11, 10, and 19% in the P2$_1$/n, P2$_1$/c, and P1 phases, respectively. This means that the dominant $R_3^+$ oxygen rotations cooperate with the antipolar M$_3^-$ mode to promote the ground state of WO$_3$.

We note that in the P4/nmm, P4mm, Amm2, R3m, I4/mcm, I4/mmm, R3c, P4/ncc, and R3c phases the mode decomposition shows only the primary modes we have condensed. This is different with the Pnma phase in which an additional mode X$_3^+$ appears with a small amplitude in the mode projections while we have condensed only the primary $R_3^+$ and M$_3^-$ modes (see Fig. 6). This additional mode appears by anharmonic coupling between the $R_3^+$ and M$_3^-$ modes such that the symmetry of the Pnma structure allows the X$_3^+$ mode to develop even though the X$_3^+$ mode is not unstable by itself [79]. Similarly, we observe the apparition of several additional modes in the Pbcn, P2$_1$/n, P2$_1$/c, and P1 phases, which we discuss in the next section.

5. Energy invariants

The different phases arise from the condensation of one or several unstable modes (primary modes) of the cubic parent
<table>
<thead>
<tr>
<th>Space group</th>
<th>Irrep.</th>
<th>Direction</th>
<th>Subgroup</th>
<th>Calc.</th>
<th>Exp.</th>
<th>Linear invariants</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Pnma )</td>
<td>( R_4^+ ) (a,a,0)</td>
<td>14/mma</td>
<td>0.61</td>
<td></td>
<td></td>
<td>abc</td>
</tr>
<tr>
<td>( M_3^+ )</td>
<td>(0,0,e)</td>
<td>P4/mbm</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( X_5^- )</td>
<td>(0,a,b,0)</td>
<td>Cmcm</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Pbcn )</td>
<td>( R_4^+ ) (0,0,a)</td>
<td>14/mcm</td>
<td>0.47</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( M_3^+ )</td>
<td>(0,b,0)</td>
<td>P4/mbm</td>
<td>0.39</td>
<td>0.30</td>
<td>abc</td>
<td>adce</td>
</tr>
<tr>
<td>( M_3^- )</td>
<td>(c,d)</td>
<td>Ibam</td>
<td>0.23</td>
<td>0.25</td>
<td>abf</td>
<td>adcf</td>
</tr>
<tr>
<td>( X_5^- )</td>
<td>(0,e,-e,0)</td>
<td>Pnma</td>
<td>0.22</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( X_5^- )</td>
<td>(0,0,0,f,f)</td>
<td>Pmma</td>
<td>0.07</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P2_1/n )</td>
<td>( R_4^+ ) (a,b,a)</td>
<td>C2/m</td>
<td>0.60</td>
<td>0.48</td>
<td></td>
<td>aeg+bdf</td>
</tr>
<tr>
<td>( M_3^+ )</td>
<td>(c,0,0)</td>
<td>P4/mbm</td>
<td>0.34</td>
<td>0.37</td>
<td>acs</td>
<td>aei-bch+bci</td>
</tr>
<tr>
<td>( M_3^- )</td>
<td>(0,d,e)</td>
<td>Ibam</td>
<td>0.27</td>
<td>0.25</td>
<td></td>
<td>acdg-beef</td>
</tr>
<tr>
<td>( X_5^- )</td>
<td>(f,-f,0,g,g)</td>
<td>Pmnm</td>
<td>0.09</td>
<td>0.26</td>
<td>adeh+adei+bdeh</td>
<td></td>
</tr>
<tr>
<td>( X_5^- )</td>
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<td>P2_1/m</td>
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<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P2_1/c )</td>
<td>( \Gamma_4^+ ) (a,-a,-b)</td>
<td>Cm</td>
<td>0</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_4^+ )</td>
<td>(-b,-a,a)</td>
<td>C2/c</td>
<td>0.73</td>
<td>0.72</td>
<td>aed</td>
<td>bcd</td>
</tr>
<tr>
<td>( M_3^+ )</td>
<td>(c,0,0)</td>
<td>P4/nmm</td>
<td>0.27</td>
<td>0.30</td>
<td></td>
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</tr>
<tr>
<td>( X_5^- )</td>
<td>(0,0,0,-d,0)</td>
<td>Cmcm</td>
<td>0.10</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To clarify the origin of secondary modes in several low-symmetry phases of WO₃, we restrict ourselves here to the search of such multilinear invariant terms in the energy expansion around its cubic phase by using the INVARiANTS software [82]. We report these multilinear invariants up to the fourth order obtained for the Pnma, Pbcn, P2₁/n, and P2₁/c phases. The letters represent the mode amplitudes \((Q^i)\) in the directions specified in the third column where the bold letters refer to the primary modes in the structure \((Q^p)\) and the normal letters refer to secondary modes \((Q^q)\).

In the \( Pnma \) phase, we find that the \( X_5^+ \) mode appears through a trilinear coupling with the oxygen rotations modes \( R_4^+ \) and \( M_3^+ \) (abc invariant in Table III). This additional \( X_5^+ \) mode is also found in \( Pnma \) of ABO₃ perovskites [83,84] where the eigenvector corresponds to antipolar motions of the \( A \) cation. In WO₃ the \( A \) cation is absent and \( X_5^+ \) corresponds to similar antipolar motions but of oxygen instead of the \( A \) site (see Fig. 4).

In \( Pbcn \) the primary \( M_3^+ \) mode condenses along \( z \), the \( R_4^+ \) mode condenses along \( z \) and the \( M_3^+ \) and \( M_3^- \) modes condense along \( y \) and four additional secondary modes: \( X_5^- \) and \( X_5^+ \) with a large amplitude and \( M_3^- \) and \( M_3^+ \) with a small amplitude as well as an additional component of the \( M_3^+ \) mode about the \( x \) direction. If we restrict ourselves to the strongest \( X_5^- \) and \( X_5^+ \) modes we find that both are coupled with the \( R_4^+ \) and \( M_3^- \) modes through a trilinear coupling (abc and abf invariants in Table III) but also through a quadrilinear coupling with the \( R_4^+ \) mode and the two components of the \( M_3^- \) mode (adce and adcf invariants in Table III). We can thus explain the appearance of the \( X_5^- \) and \( X_5^+ \) modes through a trilinear coupling with the oxygen octahedral rotations and the appearance of the second \( x \) component of the antipolar \( M_3^+ \) mode through a coupling with the secondary \( X_5^- \) and \( X_5^+ \) modes and the primary \( R_4^+ \) mode. The final structure can thus be seen as antipolar through the \( M_3^- \) mode along \( z \) with a canting of its direction toward the \( x \) axis and through the \( X_5^- \) mode along the \( y \) direction, the whole distortions being associated with the \( a^-b^+c^- \) pattern of oxygen rotation distortions.

The transition from \( Pbcn \) to \( P2_1/n \) can be seen as being induced by the condensation of the \( R_4^+ \) mode along the remaining direction for the oxygen rotation octahedral distortions to \( a^-b^+c^- \). This means that we find the same mode coupling as in the \( Pbcn \) phase plus some extra ones due to the additional mode condensation. Because we do not induce...
a new irrep, the couplings are the same (i.e., trilinear and
quadrilinear between the primary \( R_1^1 \), \( M_2^1 \), and \( M_3^1 \) modes and
the secondary \( X_5^1 \) and \( X_7^1 \) modes) but in different directions
from the \( Pbcn \) phase: we observe the \( X_5^1 \) and \( X_7^1 \) modes in
two directions instead of one. Other modes also appear in the
symmetry adapted mode analysis but with smaller amplitudes
(\( M_2^2 \), \( M_3^2 \), \( M_4^2 \), and \( M_5^2 \)), which we do not include in the
invariant analysis.

\( P\bar{1} \) and \( P2_1/c \) are very similar in the sense that for both
structures we can envisage the condensation of \( R_1^1 \) modes
in three directions and the \( M_3^1 \) mode in one direction. The
difference is that in the \( P2_1/c \) phase the \( R_1^1 \) mode is primary
with the same amplitude in two directions and a different
amplitude in the third direction (\( a^+a^-c^- \) where the \( M_3^1 \) mode
is primary in the \( z \) direction) while in the \( P\bar{1} \) phase the
condensation of the \( R_1^1 \) mode has different amplitudes in three
directions (\( a^-b^-c^- \)). In \( P2_1/c \) the presence of the \( X_4^1 \) and \( M_5^1 \)
secondary modes can be explained by trilinear coupling with
the \( R_1^1 \) and \( M_3^1 \) primary modes (\( abc+abd \) and \( abc \) invariants
in Table III) in a similar way as in the \( P3_2/n \) phase.

This analysis shows that the low-symmetry phases of \( \text{WO}_3 \)
are complex and involve numerous multilinear couplings of
modes if one expands the energy with respect to the cubic
phase. We note that, among possible couplings, the coupling
with the secondary \( X_5^1 \) mode is most important in all low-
symmetry phases.

Going further, in order to test whether symmetry arguments
lead to the polar \( P\bar{1} \) phase using anharmonic couplings,
we have tested if there exists any bi-, tri-, or quadri-linear
coupling involving a polar mode at the \( \Gamma \) point. We did not
find any couplings with the \( R_4^1 \), \( M_4^1 \), or \( M_6^1 \) modes. We thus
conclude that it is not possible to generate polarity in \( \text{WO}_3 \) in
the limit to these primary modes, which are the ones appearing
in other experimental phases.

V. CONCLUSIONS

In this study, we have performed a first-principles study of
\( \text{WO}_3 \) using the B1-WC hybrid exchange-correlation functional
which appears to yield good overall agreement with experi-
ments regarding electronic and structural properties together.

Starting from the inspection of the phonon dispersion
curves of a hypothetical cubic structure taken as reference,
we have identified two main branches of instabilities and
characterized various phases arising from the condensation of
one or more unstable modes. Although the dominant phonon
instability is associated to a zone-center polar mode, we found
a nonpolar \( P2_1/c \) ground state arising from the combination of
cooperative antipolar distortions and oxygen octahedra
rotations. This phase is very similar to the experimentally
reported polar \( P\bar{1} \) ground state, except for the absence of a
tiny polar distortion. Our calculations do not show, however,
any tendency of the \( P2_1/c \) phase to evolve to a \( P\bar{1} \) phase
suggesting that \( \text{WO}_3 \) is likely not intrinsically ferroelectric.
Instead the ferroelectric character might arise from extrinsic
defects such as oxygen vacancies. The \( P2_1/c \) phase is ant-
ipolar and defects could easily produce a slightly unbalanced
antidipole structure, yielding a weak net polarization. In this
sense, off-stoichiometric \( \text{WO}_3 \) might be better described as a
ferrielectric compound [85]. The ground state is determined by
two antiparallel movements of \( W \) off-centerings which exactly
compensate each other in the \( P2_1/c \) phase. The displacements
are almost identical in the \( P\bar{1} \) phase, but the two displacements
do not fully compensate each other. We suspect that such
weak ferrielectricity can be induced by defects such as oxygen
vacancies.

At the level of our calculations, the \( P2_1/c \) ground state
is almost degenerated in energy with the \( P3_2/n \) and \( P\bar{1} \)
phases observed at higher temperature. Also, we discovered
the existence of a never observed and low-energy ferroelectric
\( R3m \) phase with a large polarization. Although this might
not be of direct interest due to the conductive character
of usual off-stoichiometric samples, the proximity with the
\( P2_1/c \) ground state of this structurally unrelated \( R3m \) polar
phase toward which the system could be switched through a
first-order transition under moderate electric fields makes
\( \text{WO}_3 \) a potential antiferroelectric material.

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[7] C. Sella, M. Maaza, O. Nemraoui, J. Lafait, N. Renard, and
presented at the Fifth International Conference on Plasma
Surface Engineering.
[78] The volume of the cubic, R3c, R3m, and R3c phases are 54.01 Å³, 50.89 Å³, 55.35 Å³, and 52.71 Å³.