Comment on "First-principles study of the influence of (110)-oriented strain on the ferroelectric properties of rutile TiO_2"

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In a recent article, Grünebohm *et al.* [Phys. Rev. **B** 84 132105 (2011)] report that they fail to reproduce the A_{2u} ferroelectric instability of TiO_2 in the rutile structure calculated with density functional theory within the PBE-GGA approximation by Montanari *et al.* [Chem. Phys. Lett **364**, 528 (2002)]. We demonstrate that this disagreement arises from an erroneous treatment of Ti 3*s* and 3*p* semi-core electrons as core in their calculations. Fortuitously the effect of the frozen semi-core pseudopotential cancels the phonon instability of the PBE exchange-correlation, and the combination yields phonon frequencies similar to the LDA harmonic values.

Grünebohm *et al.* also attempted and failed to reproduce the soft acoustic phonon mode instability under (110) strain reported by Mitev *et al.* [Phys. Rev. **B** 81 134303 (2010)]. For this mode the combination of PBE-GGA and frozen semi-core yields a small imaginary frequency of 9.8i. The failure of Grünebohm *et al.* to find this mode probably arose from numerical limitations of the geometry optimization approach in the presence of a shallow double well potential; the optimization method is not suitable for locating such instabilities.

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I. INTRODUCTION

Rutile TiO_2 is an incipient ferroelectric material. Over a 20 year period density functional theory has been used to develop an understanding of its dielectric response and lattice dynamical properties. It has also established the exquisite sensitivity of these properties to strain, volume changes and thus to approximations such as the treatment of electronic exchange and correlation[1].

In 2002 two of us demonstrated[2] that within the Perdew Burke and Enzerhof generalized gradient approximation (PBE-GGA)[3] the A_{2u} mode is unstable at the equilibrium geometry. The resulting structural instability corresponds to a ferroelectric distortion of the crystal in qualitative disagreement with the observed properties of rutile TiO_2[4]. In the local density approximation (LDA)[5] the equilibrium cell volume is slightly smaller and a stable structure is obtained, giving a quantitatively correct description of the lattice dynamics and dielectric properties. This motivated the choice of LDA functional for our study of Ref. 6 on the influence of strain on the ferroelectric properties and phonon modes of rutile TiO_2. The major conclusion of that work was the existence of a low frequency acoustic phonon branch over a broad region of the Brillouin Zone around (1/2,1/2,1/4) which became soft under negative pressure or anisotropic strain.

In article Ref. 7, Grünebohm, Ederer, and Entel, published another study on the same topic, in which they attempted and failed to reproduce those central findings of our work. Specifically they report that that the PBE-GGA does not predict a phonon instability of the rutile structure, that there is no softening of the A_{2u} mode under (110) strain, nor is there a destabilization under (110) strain at (1/2,1/2,1/4) by a soft acoustic mode.

It would be highly unsatisfactory for this discrepancy to remain unresolved in the literature; it would weaken the basis for future studies on this topic, and undermine confidence in the reproducibility of DFT plane-wave methods for this type of study. Grünebohm *et al.* offer a speculation that the discrepancy arises from "the different potentials used and the resulting difference in lattice parameters". We tested that hypothesis, and confirm it as the most likely origin of the discrepancy. We show that the error lies in the choice of pseudopotentials used by Grünebohm *et al.* specifically their treatment of the Ti 3*s* and 3*p* semicore electrons as part of the frozen pseudopotential core instead of as valence.

Textbook wisdom holds that in the case of titanate perovskites the frozen semicore approximation introduces significant errors in ferroelectric properties and that 3*p* and possibly 3*s* states must be explicitly included[8]. Indeed most pseudopotential studies of TiO_2 and titanate perovskites published since the mid 1990s have treated the Ti 3*s* and 3*p* electrons as valence, claiming that the frozen semicore approximation is inaccurate. However there is no report containing quantitative evidence of the consequences for phonon frequencies.

Ghosez *et al.*[13,14] performed band-by band decomposition of the Born effective charges and showed that the Ti 3*p* orbitals contribute a value of -0.22e to the effective

TABLE I. Pseudopotential configurations used. A single ultrasoft projector was used for each core or semi-core state. Two ultrasoft projectors were used for each valence state except for UF1 where a single projector was used for Ti 4s and UF3 where a single norm-conserving projector was used for Ti 4s. For all frozen core and semi-core states a pseudized core charge[9] was used.

Label	UF1	UF2	UF3
Ti ref.	$2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	$3s^2 3p^6 4s^2 3d^2$	$4s^2 3d^2$
r_c	1.2/1.2/1.8	1.8	2.2
r_{inner}/a_0	0.5	1.5	1.3
l_{loc}/a_0	d	d	s
O ref.	$1s^2 2s^2 2p^4$	$2s^2 2p^4$	$2s^2 2p^4$
r_c/a_0	0.8	1.3	1.3
r_{inner}/a_0	0.5	0.9	0.9
Cutoff /eV	1300	750	750

TABLE II. Calculated structural parameters of rutile TiO_2

	a/A	c/A	u
PW-LDA (UF1)	4.550	2.919	0.3039
PW-LDA (UF2)	4.549	2.919	0.3039
PW-LDA (UF3)	4.597	2.902	0.3023
LCAO-LDA[a]	4.548	2.944	0.305
FP-LAPW-LDA[b]	4.558	2.920	0.3039
PW-GGA (UF1)	4.642	2.963	0.3051
PW-GGA (UF2)	4.642	2.964	0.3051
PW-GGA (UF3)	4.684	2.953	0.3035
PW-GGA[c]	4.641	2.966	0.305
PW-GGA[d]	4.664	2.969	0.3047
LCAO-GGA[e]	4.623	2.987	0.306

[a] Ref. 1 and 10
[b] Ref. 11
[c] Ref. 2
[d] Ref. 7
[e] Ref. 12

charge on the Ti atoms in $SrTiO_3$ and -0.43e in the case of $BaTiO_3$ perovskites. The same authors also argue[15] that small contributions to this effective charge are responsible for the destabilization of the cubic phase by the softening of an optic phonon and a phase transition to the rhombohedral phase. Tegner *et al.*[16] performed a comprehensive investigation on the effect of inclusion of Ti $3s$ and $3p$ on cohesive energies, phase stability and electronic density of states of metallic Ti, concluding that frozen semicore Ti pseudopotentials result in poor transferability and that the relative stability of the ω and hcp phases is reversed. Deskins[17] found an 0.3 eV difference in the cohesive energy of TiO_2 and again that semicore Ti pseudopotentials exhibit worse transferability in the case of changes of oxidation state, with errors of up to 0.1 eV in dissociation reaction energies of $TiCl_n$ and absorption energetics of a variety of molecules and atoms on rutile TiO_2 surfaces. Holzwarth *et al.*[18] highlighted a large error in the atomic configuration energy for s-d promotion in Ti atoms of 90 meV obtained within the frozen-semicore approximation. However Perron *et al.*[19] showed that the effect of a frozen-core pseudopotential on *structural* parameters of TiO_2 rutile and anatase is less than 0.5% provided that a nonlinear core correction term is included[20].

The question of how many electrons to treat as valence is independent of other aspects of the pseudopotential construction or formalism, and holds equally for norm-conserving, ultrasoft or PAW pseudopotentials[18], as it concerns the inclusion or omission of the physics of polarizability of the Ti $3s$ and $3p$ electrons.

In summary, previous investigations are consistent with a picture in which structural parameters are little affected by the treatment of $3s$ and $3p$, relative energies of phases and cohesive energies are noticeably affected. Frozen semicore pseudopotentials have poor transferability resulting in significant errors in dielectric properties and chemical reaction energetics. As no results have been reported on the consequence for phonon frequencies and mechanical stability, we present them here.

II. GGA INSTABILITY OF RUTILE STRUCTURE

We performed calculations on bulk rutile TiO_2 using the CASTEP code[21], with a series of pseudopotentials to test the effect of the frozen-core approximation on successive shells. The pseudopotentials were of the ultrasoft variety generated using Vanderbilt's method[22]. Small core radii were chosen to generate accurate but "hard" pseudopotentials (*i.e.* which require a large cutoff) for both elements to leave the frozen-core approximation as the dominant contribution to the error. Details of these potentials are listed in table I. Three sets of pseudopotentials are designated UF1, UF2, and UF3 denoting that the Ti $1s$, $2s$ and $2p$, and $3s$ and $3p$ shells were frozen respectively. The UF3 set corresponds to the "large core" set used by Grünebohm *et al.* and the UF2 set corresponds to the "small core" set used by Montanari and Harrison and by previous authors. The UF1 set gives a "nearly all electron" calculation in which only the Ti $1s$ orbitals are in the core, and Ti $2s$ and $2p$ and O $1s$ are explicitly treated as valence. The computational cost of treating core states as valence is surprisingly reasonable because the sharply-peaked core orbitals are represented mostly by the pseudized augmentation functions of the Vanderbilt scheme. A very fine FFT grid is required only for the electron density to represent the augmentation charge, not for the soft orbital functions. This "all electron pseudopotential" approach has previously used successfully for calculations on iron at TPa pressures[23].

In each case a geometry optimization was performed to optimize both lattice parameters and the internal coordinate, followed by a finite displacement calculation of the dynamical matrix. This was diagonalized to yield

TABLE III. Calculated and experimental Γ-point phonon frequencies of bulk rutile TiO_2 (cm^{-1}). (TO frequencies only.)

Mode	LDA-UF1	LDA-UF2	LDA[a]	LDA-LAPW[b]	PBE-UF1	PBE-UF2	PBE[a]	PBE-UF3[c]	PBE-UF3	Expt[a]
B_{2u}	99.2	101.7	104.0	111.5	31.0i	28.4i	79.2	96.1	91.2	113
A_{2u}	125.1	128.7	154.4	153.0	89.6i	106.6i	86.3i	143.7	115.7	142
E_u	135.2	138.8	191.4	156.4	69.8i	62.5i	124.0	137.7	111.2	189
B_{2g}	136.9	137.1	137.0	138.2	127.1	150.5	154.2	131.2	144.4	142
E_u	381.5	382.4	383.9	384.8	353.8	355.1	353.5	383.2	366.4	388
B_{2u}	390.9	392.4	393.0	398.2	362.3	356.4	357.5	400.5	380.3	406
A_{2g}	417.6	419.5	421.7	416.0	408.5	417.9	423.6	407.6	405.6	–
E_g	463.1	463.5	463.2	463.7	429.1	428.9	429.2	472.2	464.3	455
E_u	486.7	487.3	488.4	487.0	469.6	469.7	488.4	480.0	491.4	494
A_{1g}	609.9	610.4	611.6	612.0	567.8	567.3	565.9	626.9	611.1	610
B_{1g}	817.3	818.2	824.7	816.1	770.8	771.4	774.3	815.2	794.6	825

[a] Ref. 2
[b] Ref. 11. These are pseudopotential-LAPW, not all-electron FP-LAPW calculations
[c] Calculated using the optimized lattice parameters of UF2

the gamma-point phonon frequencies. The Brillouin zone was sampled using a Monkhorst Pack[24] grid of dimensions $4 \times 4 \times 6$ and plane-wave cutoffs for each USP set are listed in table I. These choices yield a convergence of better than 1 meV/atom in total energy, 0.00025 A in lattice parameter. The geometry was relaxed until the force residual on each atom was less than 0.005 eV/A. For most phonons the frequencies were converged to better than 0.1 cm^{-1}; for the most sensitive phonon modes (which become imaginary) the maximum error was 3 cm^{-1}.

The calculated structural parameters are shown in table II. LDA lattice parameters for UF1 and UF2 are within 0.2% of those calculated using the reference all-electron techniques[1,11]. Freezing the Ti semicore states slightly increases the lattice parameters but by less than 1%, consistent with the values reported by Grünebohm *et al.* and by previous studies[19,20].

Phonon frequencies are presented in table III. This shows clearly that *(a)* the rutile structure is predicted to suffer from a phonon instability within PBE and *(b)* that freezing the semicore states has the effect of eliminating the instability and yields all real frequencies. As the atomic reference configuration is the same as used by Grünebohm *et al.* it is highly likely that this explains the failure to reproduce the instability in their calculation. The change in frequencies when the UF3 pseudopotentials are used at the lattice parameters of the UF2 calculation is much smaller than the UF2-UF3 change. This proves that the discrepancy between Grünebohm's result and ours is a direct consequence of the omission of electronic polarizability and hybridisation of the Ti $3s$ and $3p$ states and not an indirect consequence of the volume change.

The accuracy of the pseudopotentials is confirmed by the LDA results which are in excellent agreement with previous work including FP-LAPW calculations. The similarity of the UF2 results to the nearly all-electron UF1 values for both LDA and PBE demonstrates that the UF2 configuration contains all of the electronic freedom required for accurate lattice dynamics. This confirms the correctness of the "small-core" pseudopotential results of Ref. 2 where it was demonstrated that all-electron LCAO methods gave the same A_{2u} instability as the plane-wave pseudopotential calculations. We note one discrepancy with the prior results of Ref. 2, namely that the B_{2u} and E_u modes also exhibit an instability in addition to the A_{2u} instability previously described.

TABLE IV. Frequencies of the lowest mode at q=(0.5,0.5,0.25) calculated using using a $\sqrt{2} \times \sqrt{2} \times 4$ supercell (cm^{-1}).

	UF1	UF2	UF3
PBE	77.1i	72.6i	9.8i
LDA	50.0	55.1	74.8

III. MODE SOFTENING AT Q=(1/2,1/2,1/4)

Turning to the soft acoustic mode frequencies, we performed supercell phonon calculations using a $\sqrt{2}\times\sqrt{2}\times4$ supercell and diagonalized at the commensurate wavevector q=(0.5,0.5,0.25). Frequencies of the lowest acoustic modes are presented in table IV. Clearly the UF3 pseudopotential makes a substantial error in this mode, which is stiffened when the effect of semicore polarization is excluded. As with the Γ -point phonons, there is little difference between the unfrozen core UF2 compared with the nearly all-electron UF1 frequencies. The UF1 and UF2 LDA results are in good agreement with our earlier calculations in Ref. 6. However our current calculations predict that within the PBE approximation this acoustic mode has imaginary frequency for all three pseudopotential configurations considered. As with the Gamma point

results, we would expect the UF3 case to most closely reproduce the results of Ref. 7.

Grünebohm *et al.* state that "we could not reproduce the destabilization of the system along an acoustic phonon mode under (110) strain found in Ref. 8[25], for which an energy gain of several meV has been predicted, even if we use a $2.\sqrt{2} \times 2.\sqrt{2} \times 4$ supercell, which is commensurable with the displacement pattern of this mode".

However the geometry optimization method as employed by Grünebohm *et al.* is unsuitable for finding the soft displacement pattern. Our experience is that quasi-Newton type optimization methods usually fail any attempt to identify a shallow soft mode, or at best converge extremely slowly. Discovery of a single set of atomic displacements which slightly lowers the energy in a high-dimensional search space of otherwise stiff directions is a highly computationally challenging procedure. Several factors contribute to the difficulty. First is the high dimensionality of the search space, 576 for the $\sqrt{2}\times\sqrt{2}\times4$ cell employed (which is actually 4 times larger than strictly necessary to represent this soft eigenvector). Within this space the desired eigenvector is represented by a single direction.

The second factor is the shape and depth of the anharmonic potential, which has a well depth of only 2.5 meV (see Fig. 5 of Ref. 6) and a tiny gradient along the mode. For small displacement this yields a typical force on each Ti of 0.01 eV/A, with a maximum of 0.03 eV/A. Consequently the configuration at the initial points along the optimization would be deemed already converged according to the tolerance of 0.01 eV/A used by Grünebohm *et al.* In our experience a tolerance of 0.001 eV/A or even smaller is essential in such circumstances.

The third factor is the difficulty of finding a suitable starting configuration for the optimization. In a supercell of perfect rutile the gradient in every direction is zero, so an initial perturbation is required to break the supercell symmetry. A randomized displacement pattern must also excite the stiff modes and yield a much larger increase in the energy than the decrease being sought. The resulting geometry optimization almost always fails to find the soft mode displacement. We tested this for the soft acoustic mode in rutile TiO_2, using the UF2 pseudopotential, a force tolerance of 0.001 eV/A and as expected the optimization returned to the symmetric supercell configuration.

From the UF3 phonon frequency results in table IV we would expect an even shallower potential and even tinier gradient as a result of the additional stiffening resulting from the neglect of semi-core polarization. It is therefore doubly unsurprising that Grünebohm *et al.*'s attempt to search for the soft displacement using this method was unsuccessful. This is absence of evidence for the soft mode, not evidence of absence.

In our experience the only reliable way to explore a soft mode using geometry optimization is to first perform a phonon calculation, and to identify the soft eigenvector by diagonalization of a dynamical matrix. This eigenvector can be used as an initial perturbation from the symmetric supercell. The geometry optimization must use very tight force and energy tolerances, but is usually able to proceed without interference from the stiff modes.

IV. CONCLUSION

We have demonstrated that the finding of two of us that rutile TiO_2 is mechanically unstable to a ferroelectric A_{2u} soft mode in the PBE-GGA approximation is robust. Grünebohm *et al.*'s contrary finding can be attributed to an error in the PAW pseudopotentials they used, namely the frozen-core approximation applied to the Ti $3s$ and $3p$ electrons. Our convergent series of pseudopotentials to a highly accurate "nearly all electron" limit demonstrates that the effect of freezing Ti $3s$ and $3p$ is to stabilise the PBE rutile structure of TiO_2. In fact this error almost cancels the PBE instability to yield Γ point frequencies very similar to the LDA result but the cancellation is less complete elsewhere in the Brillouin Zone.

We further argue that the geometry optimisation methods with convergence tolerances reported by Grünebohm *et al.* are not capable of identifying shallow soft modes in the Brillouin zone. Our result[6] of a soft mode at q=(1/2,1/2,1/4) is also robustly confirmed.

Thus the situation is that in the incipient ferroelectric rutile-TiO_2 the LDA and PBE-GGA approximations to density functional theory yield qualitatively distinct descriptions. Within PBE-GGA, rutile TiO_2 is predicted to be ferroelectric with an equilibrium geometry that is unstable with respect to displacement along a number of phonon eigenvectors[4]. Within the LDA, rutile-TiO_2 is stable and a reasonable description of its dielectric response and lattice dynamics is obtained.

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