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

A. Grünebohm,[1,*] C. Ederer,[2] and P. Entel[1]
[1]*Faculty of Physics, Universität Duisburg-Essen, Lotharstrasse 1, 47048 Duisburg, Germany*
[2]*Materials Theory, ETH Zürich, Wolfgang-Pauli-Strasse 27, 8093 Zürich, Switzerland*
(Received 2 July 2013; published 8 October 2013)

In their Comment, Refson *et al*. criticize the use of the "frozen-core" approximation for the Ti 3*s* and 3*p* semicore states in our Brief Report [Phys. Rev. B **84**, 132105 (2011)], and they dispute whether the methods employed by us are capable of supporting our conclusions. In this Reply we summarize the main features of our work and we show that indeed none of the conclusions of our Brief Report are affected by the frozen-core treatment of the Ti semicore states. The criticism of Refson *et al*. seems to be based mostly on a misinterpretation what the main goal of our study is and what the main conclusions of our work are. While the detailed comparison between different pseudopotentials containing different numbers of valence electrons presented in the comment by Refson *et al*. is very interesting and instructive in its own right, it has no consequences regarding the validity of our work.

DOI: 10.1103/PhysRevB.88.136102 PACS number(s): 77.22.−d, 77.80.bn, 77.84.−s

As the title suggests, our Brief Report[1] investigates the effect of (110)-oriented strain on potential ferroelectric instabilities in rutile TiO_2 using first-principles density functional theory calculations. It has been well known that (001)-oriented strain destabilizes an A_{2u} mode polarized along the strain direction in this material.[2–4] In our Brief Report we show that another polar mode, an E_u mode with polarization along the (110) direction, can be destabilized under (110)-oriented strain, which means that the polarization direction in TiO_2 can be changed depending on the specific strain conditions.[1] This is of particular relevance for the dielectric properties of the $(1\bar{1}0)$ surface, which is the most stable surface configuration of rutile TiO_2, and which can be strained either along the (001) or the (110) direction or both, depending on the substrate used. We point out that the Comment of Refson *et al*.[5] does not contain any evidence that would falsify this conclusion.

The main point of criticism of Refson *et al*. focuses on the fact that we do not include the Ti 3*s* and 3*p* states as valence states within our projector augmented wave (PAW) pseudopotential approach. This leads to some differences between our results and the former results of Refson and collaborators.[3,4,6] Specifically, within our approach the A_{2u} mode is stable at the corresponding theoretical equilibrium volume, whereas this mode is unstable in Ref. 6. In their Comment, Refson *et al*. assert that we claim that their old results are wrong, and that we also claim that our results are the "correct" Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) results for rutile TiO_2. However, in our Brief Report we do not make such a claim. In fact, we fully agree with Refson and co-workers that relaxing the frozen-core approximation for the Ti 3*s* and 3*p* states will lead to a result that should more closely resemble the result of an accurate all-electron calculation and thus can be viewed as being more representative of the "true" PBE-GGA result. In our work we simply notice the difference between the two results, and we correctly ascribe it to the use of the frozen-core treatment for the Ti 3*s* and 3*p* states in our calculations. In their Comment, Refson *et al*. call this a "speculation." However, considering that the frozen-core treatment is the only main difference between the two calculations and the well-known fact that semicore states can have pronounced effects on such structural instabilities, we do not consider this to be very speculative. We did not include a more elaborate discussion of this point in our paper[1] in order to stick to the short and focused format of a Brief Report, and since it has no consequences on our main conclusions (which focuses on qualitative trends rather than very specific quantitative results).

Before explaining why this seemingly crude approximation[7] (frozen Ti 3*s* and 3*p* states) does not affect the conclusions of our Brief Report, it is important to point out the following. While the prediction of the A_{2u} mode as either stable or unstable could be viewed as a severe *qualitative* difference, this is, however, only a mere *quantitative* difference for the purpose of our study. All approaches, local density approximation (LDA) and PBE-GGA, either with or without frozen Ti semicore states, will find a transition of this mode from stable to unstable with increasing volume or increasing (001) strain (see, e.g., Refs. 3, 6, and 8). The differences between the various methods are mainly small quantitative differences in the predicted equilibrium volume and (to a lesser extent) small differences in the predicted critical volume at which the transition from stable to unstable happens.

While all methods will predict values that are within the typical uncertainty of current state-of-the-art first-principles methods (about 1% for lattice parameters, significantly less for internal structural parameters, somewhat more for elastic properties), none of the methods will, however, make quantitative predictions that are in exact agreement with experimental measurements for all quantities of interest. In the present case of rutile TiO_2, LDA and GGA underestimate (respectively overestimate) the lattice parameters by approximately the same amount. Due to this slight underestimation of the volume, the A_{2u} mode is correctly predicted as stable within LDA whereas it is unstable at the slightly overestimated volume within GGA.[6] Thus, rutile TiO_2 is wrongly predicted to be ferroelectric within GGA, and an LDA treatment seems to be more appropriate. On the other hand, it has been shown recently that the elastic constants calculated within GGA are

closer to the experimental values than the ones calculated within LDA.[9] Considering all this, it seems fair to say that neither LDA nor GGA (semicore states included or not) are getting all quantities exactly right.

For the purpose of our study an accurate description of both dielectric as well as structural and elastic properties of rutile TiO_2 is required. In addition, a longer term goal of our research is to investigate TiO_2 surfaces[10] and heterostructures of TiO_2 and ferromagnetic Fe.[11] However, it is well known that within LDA the energy of nonmagnetic fcc Fe is underestimated relative to the ferromagnetic bcc structure, which leads to a qualitatively wrong ground state of Fe within LDA.[12] Therefore, since our studies of Fe-TiO_2 heterostructures require structural relaxations of Fe in a low symmetry environment, these calculations need to be performed using the GGA approach. As described above, there is no clear preference between LDA or GGA for the study of combined elastic and dielectric properties in rutile TiO_2, and we therefore use the GGA approach also for our studies of strain effects in bulk TiO_2. This allows us to use the corresponding results as a reference for our calculations of Fe-TiO_2 heterostructures.

The latter require large supercells with many atoms, and it is important to keep the computational effort manageable without a significant decrease in accuracy. We therefore decided to use the frozen-core approximation (in combination with nonlinear core corrections) for the Ti ion. This reduces the number of valence electrons, and thus the number of bands that have to be obtained from the Kohn-Sham equations. In the present case, the frozen-core approximation has the additional benefit of reducing the polarizability of the Ti ions and thus suppressing the incorrect GGA prediction of a polar instability at the equilibrium volume. As Refson *et al.* correctly point out, this effect is due to a cancellation of errors between the GGA volume overestimation and the reduced polarizability of the Ti ion within the frozen-core approximation. However, taking advantage of such a cancellation of errors is common practice and is entirely justified in this case. After all, it is not our interest to study the fictitious material "PBE-GGA TiO_2" in the most accurate way possible, but rather to understand certain features of "real-world TiO_2."

As already mentioned above, we did not include results of elaborate test calculations confirming the consistency of the so-obtained results in our paper[1] in order to stick to the short and focused format of a Brief Report. We did not consider this to be essential for establishing the main conclusions of our work. However, in Ref. 8 we have demonstrated that our approach leads to the same qualitative trends for the strain dependence of the phonon frequencies as "small-core" LDA calculations. In addition, we have shown in Ref. 10 that our approach even leads to a pressure dependence of the structural parameters that is in better agreement with experimental data than the LDA calculations of Ref. 3 (see Table II of Ref. 10). In fact, the data presented in the comment of Refson *et al.* further confirm that our approach works rather well and leads to phonon frequencies that are in good quantitative agreement with LDA calculations including semicore states and with experiment (compare columns "LDA-UF1," "PBE-UF3," and "Expt." in Table III of the Comment). The calculations of Refson and collaborators thus give further evidence that our results are reliable and are indeed fully capable of supporting our conclusions.

Another point raised by Refson *et al.* is that we "claim not to reproduce the soft acoustic [with wave vector $\vec{q} \approx (1/2,1/2,1/4)$] phonon mode instability under (110) strain reported by Mitev *et al.* [(Ref. 4)]." Again, Refson *et al.* assume that reproducing (or not) the destabilization of this soft acoustic mode was a central aspect of our Brief Report, and that we doubt the correctness of their calculations. None of this is the case. We simply performed structural relaxations under (110) strain using a supercell that would in principle be compatible with the emergence of this mode. However, the goal of these relaxations was not to verify (or falsify) the calculations by Mitev *et al.* but rather to confirm the energy landscape that we explored previously by freezing in different B_{3u} modes with varying amplitudes. As is clearly stated in our Brief Report, these structural relaxations were initialized by straining the initial bulk structure and then displacing one of the O atoms by 0.002 Å in order to break the initial symmetry. No attempts were made to change the initial conditions in order to search for alternative minima in the energy landscape. This was unnecessary for our purposes, since our starting configuration was quite different from the final relaxation pattern, which, however, agreed extremely well with the linear combination of B_{3u} modes predicted from the calculated energy surface without relaxation. In our work we simply mention as a side remark that the relaxation pattern we find does not contain any signature of the soft acoustic mode discussed by Mitev *et al.* Since the focus of our Brief Report is on a different aspect, we did not pursue this comparison any further, and it does not have any influence on the correctness of our conclusions (which, as explained above, are valid for "real-world TiO_2").

Finally, we also want to note, that in their Comment, Refson *et al.* incorrectly state that in our Brief Report it is claimed that "there is no softening of the A_{2u} mode under (110) strain." Refson *et al.* seem to have confused things here, since the claim in our paper is exactly the opposite, i.e., also the A_{2u} mode softens slightly under (110) strain [see Fig. 3(b) of Ref. 1].

In summary, the Comment of Refson and co-workers seems to be largely based on a misinterpretation of the goals and conclusions of our work. Our Brief Report[1] is focused on the destabilization of a polar E_u mode under (110)-oriented strain in rutile TiO_2, not on providing particularly accurate values for specific phonon frequencies. As described above, the "frozen-core" approximation for the Ti $3s$ and $3p$ states does not affect the validity of our results and conclusions. Even though we take advantage of a cancellation of errors between the GGA volume overestimation and the reduced polarizability of the Ti ion within the frozen-core approximation, the resulting trends are fully consistent with available experimental data and also with "small-core" LDA calculations. While the detailed comparison between different pseudopotentials containing different numbers of valence electrons presented in the comment by Refson *et al.* is very interesting and instructive in its own right, it has no consequences regarding the validity of our paper.

*anna@thp.uni-due.de

[1] A. Grünebohm, C. Ederer, and P. Entel, Phys. Rev. B **84**, 132105 (2011).
[2] C. Lee, P. Ghosez, and X. Gonze, Phys. Rev. B **50**, 13379 (1994).
[3] B. Montanari and N. M. Harrison, J. Phys.: Condens. Matter **16**, 273 (2004).
[4] P. D. Mitev, K. Hermansson, B. Montanari, and K. Refson, Phys. Rev. B **81**, 134303 (2010).
[5] K. Refson, B. Montanari, P. D. Mitev, K. Hermansson, and N. M. Harrison, Phys. Rev. B **88**, 136101 (2013).
[6] B. Montanari and N. M. Harrison, Chem. Phys. Lett. **364**, 528 (2002).
[7] We believe that it is also important to distinguish between an *error* and an *approximation* (which might or might not be well justified in a certain context). We make a set of well-defined approximations, which can of course be criticized, but our calculations do not contain any errors. In that respect, calling the frozen-core approximation for the Ti $3s$ and $3p$ states an "error in the pseudopotentials," as Refson *et al*. do, seems rather misleading to us.
[8] A. Grünebohm, M. Siewert, C. Ederer, and P. Entel, Ferroelectrics **429**, 31 (2012).
[9] E. Shojaee and M. R. Mohammadizadeh, J. Phys.: Condens. Matter **22**, 015401 (2010).
[10] A. Grünebohm, P. Entel, and C. Ederer, Phys. Rev. B **87**, 054110 (2013).
[11] A. Grünebohm, P. Entel, and H. C. Herper [Phys. Rev. B (to be published)], arXiv:1304.0570.
[12] J. Zhu, X. W. Wang, and S. G. Louie, Phys. Rev. B **45**, 8887 (1992).