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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Artem Samtsevich

PhD Program: Materials Science and Engineering

Title of Thesis: Simulation of the mechanisms of solid-solid phase transition

Supervisor: Professor Artem Oganov

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 25-07-2021**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The thesis submitted to my attention presents a methodological framework for modelling solid-solid (pressure-induced) phase transitions, by the integration of pre-existing methods and the development of ad hoc elements, capable of bridging and integrating functionalities. From this methodological sequence, 4 different systems are studied in detail, with respects to their conversion pathways. The elucidation of pathways is a preparatory step to a detailed kinetic study, which would also include the determination of kinetic rate constants. The dissertation is articulated over an introduction, which covers several concepts of phase transition definitions and their theories. Therein, transition state theory and harmonic approximation are discussed in a more specific way. This is followed by a chapter on the numerical simulations of phase transition. In particular, numerical algorithm from global optimization to free energy sampling are discussed. Chapter 3 discusses the mapping between limiting crystal structures, which can be addressed topologically (net/bond oriented) or geometrically (atom oriented). The overall target is to enable the generation of initial sequences of states/configuration, that can be enchained into an initial band, which can then be optimized within specific version of the NEB methods. This chapter contains original contributions by the candidate, in particular around the translation of the topological approach and its combination with the geometric approach, to generate a physically meaningful initial transition pathway guess. Chapter 4 contains the bulk of original results on the simulation of transition mechanisms/pathways, for 4 different compound classes. I found it very interesting that pathways to putative/predicted crystal structures were also included, as a further way to assess their synthetic realization. Chapter 4 is a very good, solid illustration of the methodology and its merit.

Given the success in suggesting transition pathways, and from them solid-solid reaction mechanisms, the thesis is making a valuable contribution to materials science in general, and to the further computability of difficult processes in the solid state, including critical processes. The bond-breaking nature of these processes and the reconstructive character of the transition makes the task of finding a mechanism difficult; therefore, this thesis is providing a valuable tool and a very interesting set of results.

From the methodological point of view, this work augments the capabilities of USPEX to suggest optimized transition pathways among existing and/or putative phases. As such, it takes the core functionality of the code beyond global optimization tasks, into a more path-oriented approach to crystal structure prediction.

The results on specific phase transition mechanisms are published in international journals, which confirms the importance of the message and the relevance for a broad community, which included solid state, mineralogy and phase transition simulations. There is no specific publication on methodological details, which is sometimes that could be planned or discussed. I think finding a trajectory/pathway map remains difficult, so this could be presented separately.

Systematic application of this approach to solids can represent and additional means not only to figure out pathways between crystal structures, but to also understand how an interesting compound (I'm thinking here for example of hardness, one of the examples discussed) can be actually synthesized. Additionally, like we learned from the last example, the changes of a mechanism under the effect of pressure can be an important knowledge for further tuning synthesis, including the targeted bypassing of intermediates, or again the specific attempt to quench an intermediate.

The quality of the publications is good, several important papers have been produced – I'm not familiar with the publication outlet #4, but I assume this is a relevant journal for the mineralogical community. So, all in all the results have been to some good extent validated.

I would ask the candidate to consider these changes before thesis defense:

I found several images from chapter 1 (1.2, 1.3, 1.4 1.5) and chapter 2 (2.4) not duly referenced, this must be fixed. There are also several of our contribution to solid-solid phase transitions that are not cited, I was surprised by this choice.

The discussion of TST follows the reference to TPS, I think that the connection between the two should be better clarified – also Chandler is the original author of the TPS method, this cannot be attributed to Bolhuis alone, like it is currently the case on p. 12.

The problem of mapping two crystal structure onto each other, in a way that the resulting pathway is meaningful, is a non-trivial problem, particularly in the absence of a relationship of a group to an isotropic subgroup. Examples are made, but it would improve clarity and didactic message if the candidate would illustrate a full set of topological mappings and the meaningful geometric models that can be connected thereof – I found the explanation of the topological mapping sound but somehow too much biased by the content and approach of the original publications (Blatov et al.) – it would help, maybe for the first system studied, to provide details of actual and even unlikely, rejected mappings, and how the mapping choice may affect the final results.

NEB methods also suffer from local PES rugosity, meaning that a sufficiently high local energy barrier can prevent bands to fully relax – I think some discussion on how NEB copes with this problem will be appropriate. Towards doing so, several stages of band relaxation could be presented and discussed.

In general, while nucleation is indicated as the main mode of solid-solid first order phase transitions, the method of interest in this thesis does not allow nucleation – this is discussed. I would welcome some reasoning about the extent to which a collective mechanism can still represent a nucleation-based one, where phase coexistence and interfaces are present.

I would like to discuss and possibly challenge the choice of the MEP as representative of the real mechanism.

Stefano Leoni

Provisional Recommendation

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*