Answers to the Reviewer (1) comments.

Comment: The comments by the reviewer were very insightful and useful, and the manuscript has improved significantly by incorporating the suggestions. In addition to the responses given below, the section of the manuscripts has been improved by making additions of figures and slight changes in the abstract and conclusion. The results section has been improved significantly to clarify on UNCLE cluster expansion, model description of PtAsS, heats of formations and also crystal structure morphology.

Abstract

The word small letter "m" in the word "miller" in the sentence "The calculated surface energies indicated that the (100) surface was the most stable amongst the low Miller index (100), (110) and (111) surfaces for $PtAs_2$, PtAsS and Pd_2As." was amended to "Miller" as highlighted.

The word "surface" in the sentence "The calculated thermodynamically equilibrium morphologies of the relaxed surface structures indicated that the (100) surface was the most dominant surface for all the studied surface structures." was removed.

1. Introduction

In the sentence "The stability of $PtAs_2$, PtAsS and Pd_2As is important in understanding their mineralogy formation which lead to their recovery." the two words "which lead" were replaced by "and therefore".

In the sentence "Furthermore, PGMs which contain both sulphur and arsenide are complex and needs a detailed understanding in their stability and for better extraction." The word "in" was changed to "of" and the words "and for better extraction" were removed.

The word "scientist" in the sentence "First principle calculations have become an important tool for surface scientist as they can determine facet-specific surface energies, surface electronic structures and crystal morphologies [4]." was modified to "scientists".

The words "will be" in the sentence "These will be complemented with surface morphology in order to identify the preferred plane cleavages." were removed.

2. Computational methodology

The word "the" in the sentence "The phonon dispersion spectra were computed using the PHONON code [9]." was inserted before PHONON code.

The word "were" in the sentence "The interaction range of 10.0 Å for phonon dispersion were used for all the studied models." was changed to "was".

3. Results and discussion

3.1. Cluster expansion and ground state structures of PtAsS model

The symbol "DHf" on the vertical axes of Figure 1(a) was changed to "ΔH_f" and the symbols on the legends have been changed from lines to crosses to match the representation of the Figure.

The sentence "**Figure 1**: The cluster expansion calculated ground states structure determination of Pt-As-S. The energies of formation are with reference to Pt, As and S." was modified to "**Figure 1**: (a) Shows the cluster expansion diagram obtained in determining the lowest ground states of Pt-As-S

structure, (b) shows the iterative obtained stable structures consisting of many pure phases and (c) shows the stable structures that were obtained in the ground state line at x = 0.5."

The sentence "Moreover, the cluster expansion showed a greater stability at 50/50 percentage (x = 0.5) where arsenic and sulphur atoms are equal with symmetry of the same structure." was modified to "Moreover, the cluster expansion showed a greater stability at 50/50 percentage (x = 0.5) where arsenic and sulphur atoms are equally distributed in the structure with formed S–As dimer bond at the centre."

The words "of the" In the sentence "Only three of the stable structures PtS_2, PtAsS and $PtAs_2$ were shown." were added and the word "were" was changed to "are".

3.2. Bulk properties of $PtAs_2$, PtAsS and Pd_2As

The word "predict" in the sentence "These comparisons confirm that our computational parameters are reasonably satisfactory and the DFT was able to predict the bulk structural properties." was removed and sentence modified to "These comparisons confirm that our computational parameters are reasonably satisfactory and the DFT obtained bulk lattice parameters were in agreement with experiments."

3.4 Surface terminations and slab convergence

The sentence "The slab depth was varied and the 15-layer slab depth was chosen for all structures, and it was used to create a 2x2 supercell structures, which was then optimized allowing only the atom position to relax." was modified to "A supercell surface slab of 2x2 was used for all surfaces for $PtAs_2$, PtAsS and Pd_2As (100) surface. The atomic positions were optimized, where for $PtAs_2$ and PtAsS systems the top two slabs were allowed to relax and the bottom three slabs fixed to the bulk coordinates, while for Pd_2As the top slab was allowed to relax and the bottom two slabs fixed to the bulk coordinates."

4. Conclusion

The two sentences "The PtAsS cluster expansion generated structures were found thermodynamically stable, with the 50:50 (x = 0.5) being the most stable phase. The phonon dispersion curves showed no soft modes along high symmetry direction suggesting stability for all structures." were swapped and reads as, "The phonon dispersion curves showed no soft modes along high symmetry direction suggesting stability for all structures. The PtAsS cluster expansion generated structures were found thermodynamically stable, with the 50:50 (x = 0.5) being the most stable phase."

Acknowledgements

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References

In the references the word "Vol" was removed in reference [9] and in reference [11] the word "Generalzed" was modified to "Generalised".

[9] Parlinski K, Li Z Q and Kawazoe Y 1997 First-principles determination of the soft mode in cubic ZrO2 Phys. Rev. Lett. vol. 78 4063–4066

[11] Sanchez J M, Ducastelle F and Gratias D 1984 Generalzed cluster description of multicomponent systems Physica A: Stat. Mech. Appl. 128 334–350

Major Concerns Comments Answers

1). Question: The last sentence of Section 2 is "Different terminations were tested and only less reactive (low positive surface energy) for (100), (110) and (111) surfaces were considered." This contrasts with the last sentence of the first paragraph of page 4: "The desired surface terminations precisely were cleaved considering all possible terminations." The situation is further confused by the previous sentence on page 4 which ends with "only the bulk terminations on the three low MI planes (100), (110) and (111) were considered."

Answer: The sentence "Different terminations were tested and only less reactive (low positive surface energy) for (100), (110) and (111) surfaces were considered." was not modified. However, the statements in page 4 was modified to "To reduce the search for working surfaces to a computationally tractable problem, whilst also ensuring that the most likely surfaces were surveyed, we have considered the three low MI planes (100), (110) and (111) terminations that were less reactive (with lowest surface energy) and possessed the bulk terminations." to clear the contradiction and confusion.

2). Question: Section 3.1 is treated as a black box. The authors basically say that there is this software and they used it and these are the results. There is no discussion of input parameters or the basic physics that the programme uses. This must be corrected or the section removed.

Answer: Section 3.1 was modified to address the concern about the input parameters for UNCLE code. As such a statement was added, "For the cluster expansion method we started by searching for the ground state of the PtAsS system of the DFT energy formation. Our initial starting point was $PtAs_2$, where the sulphur atoms were added automatically by the UNCLE code at the same position as arsenic atoms. The X, Y and Z parameters were also fitted to be equivalent for both As and S atoms. The input methods for the cluster expansion using UNCLE are detailed elsewhere [12]."

3). Question: Section 3.1: It is not clear which structures are used. If they are the ones calculated in 3.2 then the two sections should be interchanged. However this cannot be the case as a large number of stoichiometries are shown, with no mention of their structures having been calculated.

Answer: A statement "In Figure 1(c) we show the pure phases (Ce1 and Ce22) that possessed the Pa-3 space group, while the mixed phase of PtAsS ($Pt_4As_4S_4$) has P2_13 and P3 space group. We have considered the PtAsS ($Pt_4As_4S_4$) phase with P3 space group as it had a CVS of 1.2 meV/pos and thus preferred phases." was added to indicate which structure was used for PtAsS structure and a Figure 1(c) was inserted to show the table with picture to show the structures present at pure and mixed phases.

4). Question: Section 3.1: It is shown that x=0.5 is the most stable structure. It should be noted that all stoichiometries between PtS2 and PtAs2 are more stable than the PtS2 and PtAs2. It is therefore conceivable that a number of phases can form.

Answer: The concern of many stoichiometric structures that are stable than the $PtAs_2$ and PtS_2 are clarified by addition of statement "We found that all structures between PtS_2 and $PtAs_2$, i.e. phases of PtAsS are more stable than PtS_2 and $PtAs_2$ and it was therefore conceivable that a number of phases can form. Moreover, some stoichiometries have multiple DFT inputs and only three of the stable structures of PtS_2, PtAsS and $PtAs_2$ are shown in Figure 1(a)." as suggested.

5). Question: Figure 1 is very unclear. The figure has crosses while the legend has lines. The legend has “CE predictions” and “CE prediction”. There are a number of data points and a line which are from DFT, but whether these are from the authors or from elsewhere is not explained. Also the fact that some stoichiometries have multiple “DFT input”’s is not discussed.

Answer: The lines legends in Figure 1 were corrected with crosses to match the Figure graph representation. Also a statement “Moreover, some stoichiometries have multiple DFT inputs and only three of the stable structures of PtS_2, PtAsS and $PtAs_2$ are shown in Figure 1(a). As displayed in Figure 1(b) the last line (i.e. 20^{th} iteration), we can discern that the final cluster expansion contains 102 structures in the training set and has a Cross Validation Score (CVS) of 1.2 meV/pos which is very good for the system.” was added to address the multiple “DFT input” comment and a Figure 1(b) was inserted to number if iterations and structures obtained in the cluster expansion.

6). Question: Section 3.1: The sentence “This showed that the cluster expansion represents the interactions of Pt-As-S more accurately.” does not follow logically from the previous sentence. Firstly, it should be clarified “more accurately” than what? Secondly, showing that all structures are thermodynamically stable only proves the usefulness of the theory if this phase diagram matches the experimentally determined one.

Answer: The sentence “This showed that the cluster expansion represents the interactions of Pt-As-S more accurately.” was removed and the sentence “The binary ground state diagram in Figure 1 shows that all generated structures have negative heats of formation (ΔH_f), hence they are thermodynamically stable.” Was modified to “The binary ground state diagram in Figure 1 shows that all generated structures have negative heat of formation (ΔH_f), hence they are stable.”

7). Question: Section 3.5: Again this is a black box. Code was used, with no details of input parameters, underlying physics etc. As with Section 3.1 this should be corrected or the section removed. The conditions linking the calculated surface energies with the shown morphologies also need to be given.

Answer: The section “3.5. Surface morphologies” was modified by addition of input file picture (Figure 5(a)) for calculating the morphology and a statement “The input file for PtAs2 morphology calculation is shown in Figure 5(a). The calculated equilibrium morphologies of the relaxed (100), (110) and (111) surfaces are shown in Figure 5.” was added.