*Ab initio* studies of sperrylite, platarsite and palladoarsenide bulk and surface stabilities

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**Abstract.** In this study we employed the Vienna *Ab-initio* Simulation Package (VASP) along with the projector augmented wave (PAW) pseudopotential method to investigate the bulk structural and surface stabilities of sperrylite (PtAs$_2$), platarsite (PtAsS) and palladoarsenide (Pd$_2$As) minerals. The phase stability of PtAsS was obtained using UNiversal CLuster Expansion (UNCLE) code. The phonon dispersion curves showed no soft modes for all the structures, suggesting stability. 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$_2$As. The order of surface energies increased as: (100) < (111) < (110) for PtAs$_2$ and PtAsS and (100) < (110) < (111) for Pd$_2$As. The calculated thermodynamically equilibrium morphologies of the relaxed surface structures indicated that the (100) surface was the most dominant for all the studied structures. The findings offer more insight on the stability of these minerals and their surface stability.

1. **Introduction**

South Africa is one of the leading countries with high percentage of platinum group metal (PGM) in the igneous intrusion of Platreef Bushveld Complex [1]. The most predominant PGMs are platinum (Pt) and palladium (Pd) which consist of about 21% of arsenides [2]. Platinum is extremely resistant to physical and chemical degradation and has exceptional catalytic properties. These properties have led to extensive utilization of jewelry, high temperature industrial and automobile markets [3]. The stability of PtAs$_2$, PtAsS and Pd$_2$As is important in understanding their mineralogy formation and therefore to their recovery. Furthermore, PGMs which contain both sulphur and arsenide are complex and need a detailed understanding of their stability. First principle calculations have become an important tool for surface scientists as they can determine facet-specific surface energies, surface electronic structures and crystal morphologies [4].

In this paper, we performed density functional theory (DFT) calculations to study structural and vibrational stability of PtAs$_2$, PtAsS and Pd$_2$As models. The cluster expansion was implemented to generate the platarsite (PtAsS) mix bulk model. The surface calculations were computed to identify the most stable surface (working surface) for PtAs$_2$, PtAsS and Pd$_2$As minerals. These were complemented with surface morphology in order to identify the preferred plane cleavages.

2. **Computational methodology**

The bulk and surface stability calculations were performed within the framework of *ab-initio* quantum mechanical density functional theory [5]. The plane-wave (PW) projector augmented wave
pseudopotential with the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation [6], implemented within the VASP code [7], were employed. The plane-wave cut-off energy was set to 450 and 500 eV for (PtAs$_2$, PtAsS) and Pd$_2$As bulk models, respectively. The Brillouin zone k-points sampling of 4*4*4 for PtAs$_2$ and PtAsS and 7*7*7 for Pd$_2$As were used. In the case of surfaces the 4*4*1 for PtAs$_2$ and PtAsS and 5*3*1 for Pd$_2$As were employed. These were chosen according to the scheme proposed by Monkhorst-Pack [8]. The phonon dispersion spectra were computed using the PHONON code [9]. The interaction range of 10.0 Å for phonon dispersion was used for all the models. These were used to investigate the structural and vibrational properties of PtAs$_2$, PtAsS and Pd$_2$As minerals. In addition, the UNCLE code within Materials design (MedeA) was performed to generate new stable phase of PtAsS model [10].

To model the surface of the periodic boundary conditions, a slab of finite thickness perpendicular to the surface but infinite extension, i.e. using periodic boundary conditions was used. These slabs surfaces were obtained by cleaving the optimized bulk PtAs$_2$, PtAsS and Pd$_2$As structures. Slabs were separated from replicas repeating by a vacuum width of 20 Å. Different terminations were tested and only less reactive (low positive surface energy) for (100), (110) and (111) surfaces were considered.

3. Results and discussion

3.1. Cluster expansion and ground state structures of PtAsS model

In order to minimize the sensitivity of the cluster expansion to the user choices, and to make cluster expansion applicable beyond simple binary systems, a new UNCLE program package [11] has been developed. The UNCLE code [12] predicts the ground states of systems containing up to three and more elements. 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].

![Figure 1](image_url)

**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 binary ground state diagram in Figure 1 shows that all generated structures have negative heat of formation ($\Delta H_f$), hence they are stable. 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. 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 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. 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\(_4\)As\(_4\)S\(_4\)) has P2\(_{13}\) and P3 space group. We have considered the PtAsS (Pt\(_4\)As\(_4\)S\(_4\)) phase with P3 space group as it had a CVS of 1.2 meV/pos and thus preferred phases. This suggested that two stable structures exist on the convex ground state line within the studied concentration range. This revealed that the structure of PtAsS model is quite complex with various stable compounds existing at different arsenic and sulphur concentrations.

3.2. Bulk properties of PtAs\(_2\), PtAsS and Pd\(_2\)As

The crystal structures of sperrylite (Pa-3 space group), platarsite (P3 space group) are cubic [13] with 12 atoms, while palladoarsenide is monoclinic with space group of P-62m [14] and contain 9 atoms. The full structural relaxations of the bulk models were performed and the calculated structural lattice parameters of the bulk structures are given in Table 1. We found that the lattice constants were in agreement with the experimental data. These comparisons confirm that our computational parameters are reasonably satisfactory and the DFT obtained bulk lattice parameters were in agreement with experiments.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Calculated Lattice parameters (Å)</th>
<th>Experimental Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtAs(_2)</td>
<td>a = b = c = 6.061</td>
<td>a = b = c = 5.970 [15]</td>
</tr>
<tr>
<td>PtAsS</td>
<td>a = b = c = 6.024</td>
<td>a = b = c = 5.790 [13]</td>
</tr>
<tr>
<td>Pd(_2)As</td>
<td>a = b = 6.737, c = 3.664</td>
<td>a = b = 6.620, c = 3.600 [16]</td>
</tr>
</tbody>
</table>

Figure 2: The relaxed bulk structure: (a) sperrylite (PtAs\(_2\)), (b) platarsite (PtAsS) and (c) palladoarsenide (Pd\(_2\)As).

3.3. Vibrational properties of PtAs\(_2\), PtAsS and Pd\(_2\)As

The analysis of vibrational properties of PtAs\(_2\), PtAsS and Pd\(_2\)As phases with respect to the phonon dispersion are shown in Figure 3. The vibrational stability of the structures PtAs\(_2\), PtAsS and Pd\(_2\)As were carried out along the symmetry directions within the first Brillouin zones.
We observed positive frequencies in all the Brillouin zone directions. As such, our phonon dispersion calculations confirm that PtAs$_2$, PtAsS and Pd$_2$As structures are vibrationally stable due to the absence of negative vibrations (soft modes) along all directions. However, the PtAsS and Pd$_2$As system were found to give a scale up to $-1$ THz, which may suggest a slight overlap of the vibrations to negative. These were ignored and considered as imaginary modes.

3.4. Surface terminations and slab convergence

Considerations must be given to the large number of the Miller index planes (MI), and within each plane, all possible bulk terminations that exist. 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. The slab depths were varied as shown in Figure 4(g) for PtAs$_2$ and PtAsS (100) surface and 4(h) for Pd$_2$As (100) surface. These showed a linear decreasing trend of total energy with an increase in slab thickness. The principal concern is that the slab depth should be sufficient such that both surfaces act as an effectively infinite amount of the bulk solid (i.e. the surfaces do not interact with one another through the solid). Ideally to achieve this, a large slab depth would be required but the computational cost of modelling very deep slabs was avoided. As such the 15-layer slab depth for PtAs$_2$ and PtAsS (100) surface and 21-layers for Pd$_2$As (100) surface were chosen and considered as thick enough for adsorption.

A supercell surface slab of 2x2 was used for all surfaces for PtAs$_2$, PtAsS and Pd$_2$As (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$_2$As the top slab was allowed to relax and the bottom two slabs fixed to the bulk coordinates. Figure 4 shows the un-relaxed and relaxed supercell structures for (100) surface of PtAs$_2$, PtAsS and Pd$_2$As structures. Figure 4(e) showed the slabs that are not identical due to the stacking configuration [17]. The surface stabilities for different terminations were determined from the surface energies using equation 1:

$$E_{\text{surface}} = \left( \frac{1}{2A} \right) \left[ E_{\text{slab}} - (n_{\text{slab}}) (E_{\text{bulk}}) \right]$$

where $E_{\text{slab}}$ is the total energy of the cell containing the surface slab, $n_{\text{slab}}$ is the number of atoms in the slab, $E_{\text{bulk}}$ is the total energy per atom of the bulk and A is the surface area. A low positive value of $E_{\text{surface}}$ indicates stability of the surface termination [3].
Figure 4: The un-relaxed and relaxed supercell structures of surface layers convergence for (a) and (b) PtAs$_2$, (c) and (d) PtAsS and (e) and (f) Pd$_2$As (100) surface.

Table 2 shows the supercell surface energies after relaxation for PtAs$_2$, PtAsS and Pd$_2$As structures. The computed surface energies increase as: (100) < (111) < (110) for PtAs$_2$ and PtAsS and as (100) < (110) < (111) for Pd$_2$As. The (100) surface was identified as the most stable surface (working surface) since it displayed the lowest positive energies. Similar working surface for PtAs$_2$ was reported by Waterson et al. [3].

Table 2. The relaxed surface energies for PtAs$_2$, PtAsS and Pd$_2$As structures.

<table>
<thead>
<tr>
<th>Surface slab</th>
<th>PtAs$_2$</th>
<th>PtAsS</th>
<th>Pd$_2$As</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.065</td>
<td>0.035</td>
<td>0.070</td>
</tr>
<tr>
<td>111</td>
<td>0.085</td>
<td>0.062</td>
<td>0.109</td>
</tr>
<tr>
<td>110</td>
<td>0.091</td>
<td>0.717</td>
<td>0.097</td>
</tr>
</tbody>
</table>

3.5. Surface morphologies
The crystal morphology of PtAs$_2$, PtAsS and Pd$_2$As structures were predicted by using calculated surface energies of (100), (110) and (111) surfaces as shown in Table 2 using the METADISE code [17]. The input file for PtAs$_2$ 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. Our surface
morphologies results indicated that (100) surface was the most dominant surface exposed, followed by (111) and (110) surface for PtAs$_2$ model, with the (110) plane being the smallest. For PtAsS, the surface morphology showed that the mineral preferred to cleave only along the (100) surface plane, since the (110) and (111) surface plane did not appear on the morphology. Furthermore, the (100) surface was the dominant surface exposed on surface morphologies for Pd$_2$As model. However, in this case the (110) and (111) were also exposed largely, suggesting that these planes may cleave during mineral crushing.

![Figure 5: The calculated equilibrium morphologies. (a) Input file for METADISE code to calculate the PtAs$_2$ morphology, (b) PtAs$_2$, (c) PtAsS, and (d) Pd$_2$As morphologies.](image)

4. Conclusion
In this study, we have performed *ab-initio* DFT calculations to investigate the bulk structural, vibrational and surface properties of PtAs$_2$, PtAsS and Pd$_2$As minerals. The optimized bulk structural lattice parameters were in agreement with the available experimental values. 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. The calculated surface energies indicated that the (100) surface for PtAs$_2$, PtAsS and Pd$_2$As structures was the most stable amongst the low Miller index (100), (110) and (111). The thermodynamically equilibrium morphologies of the relaxed structures indicated that (100) surface was the most dominant surface. These outcomes gave more insights on the bulk and surface stability of these minerals which demonstrated the preferred plane cleavage of these minerals during mineral grinding.

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References


