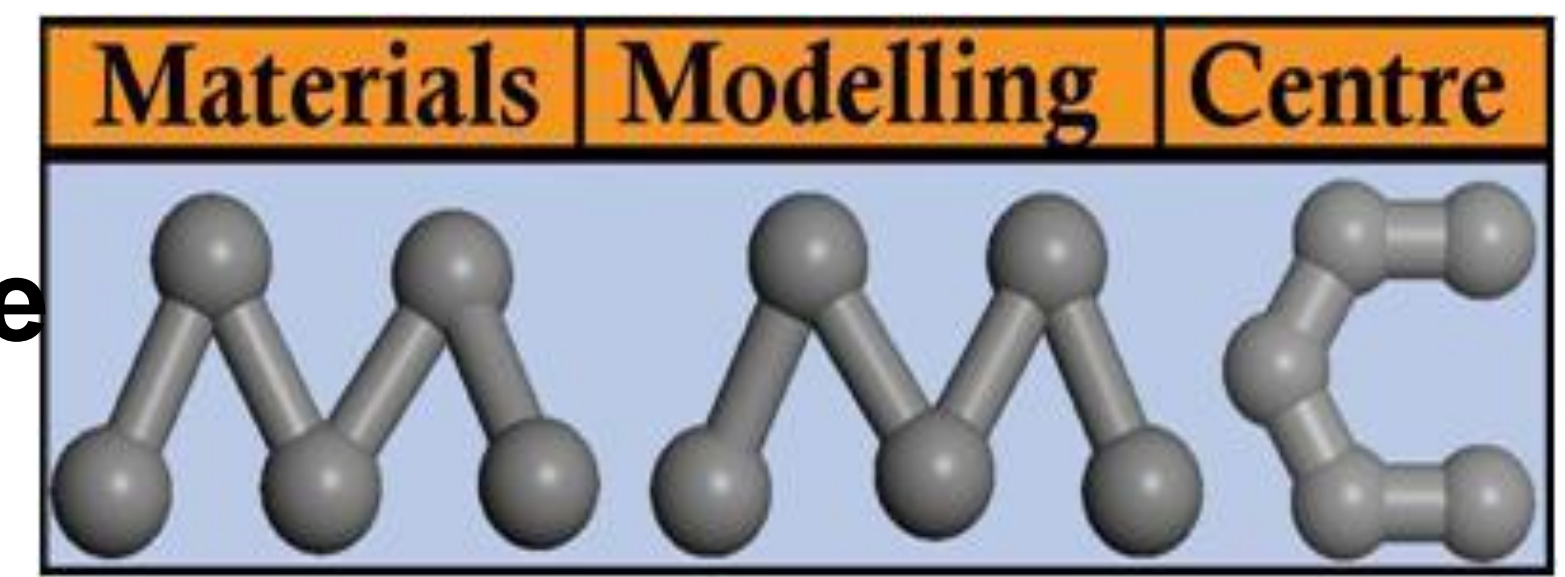


Computational Modelling Studies of Pentlandite (Fe,Ni)₉S₈ (111) surface: Oxidation and hydration

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Introduction

- Pentlandite (Fe,Ni)₉S₈ is an iron-nickel sulphide and it has Ni:Fe ratio of close to 1:1 [1].
- Most minerals are exposed to oxidation over time due to weathering and aging, as such oxidation has been found to affect the floatability of minerals.
- The oxidation of pentlandite, naturally is an important process to understand extraction of mineral ore [2].
- It has been reported that iron migrate outward on the surface which results in preferential oxidation of iron [1, 3].
- Hydration of surfaces is an important factor that determines the hydrophobicity and hydrophilicity character of the minerals.
- In this study we investigate the adsorption of water (hydration) and oxygen (oxidation) molecules on the nickel-rich pentlandite (111) surface using density functional theory method.

Structures and Applications

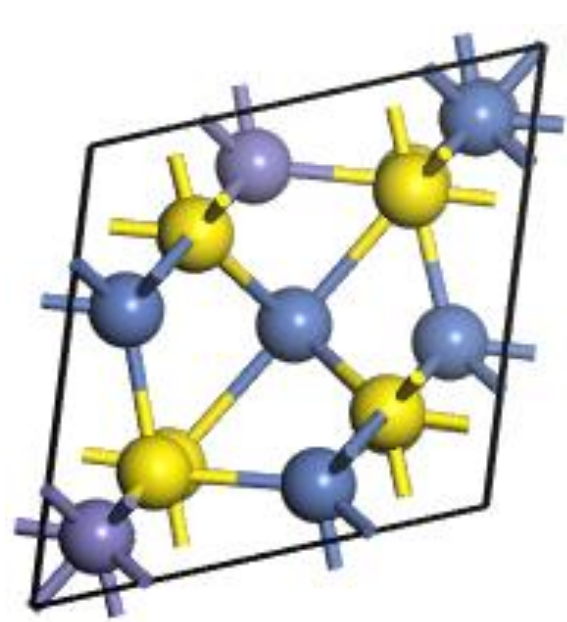


Figure 1: Bulk structure of Fe₄Ni₅S₈ Space Group, Fm3m (#225)

Lattice Parameter (Å)	DFT
a	7.062
b	7.063
c	7.080
Cell angle (α=β=γ) = 90°	

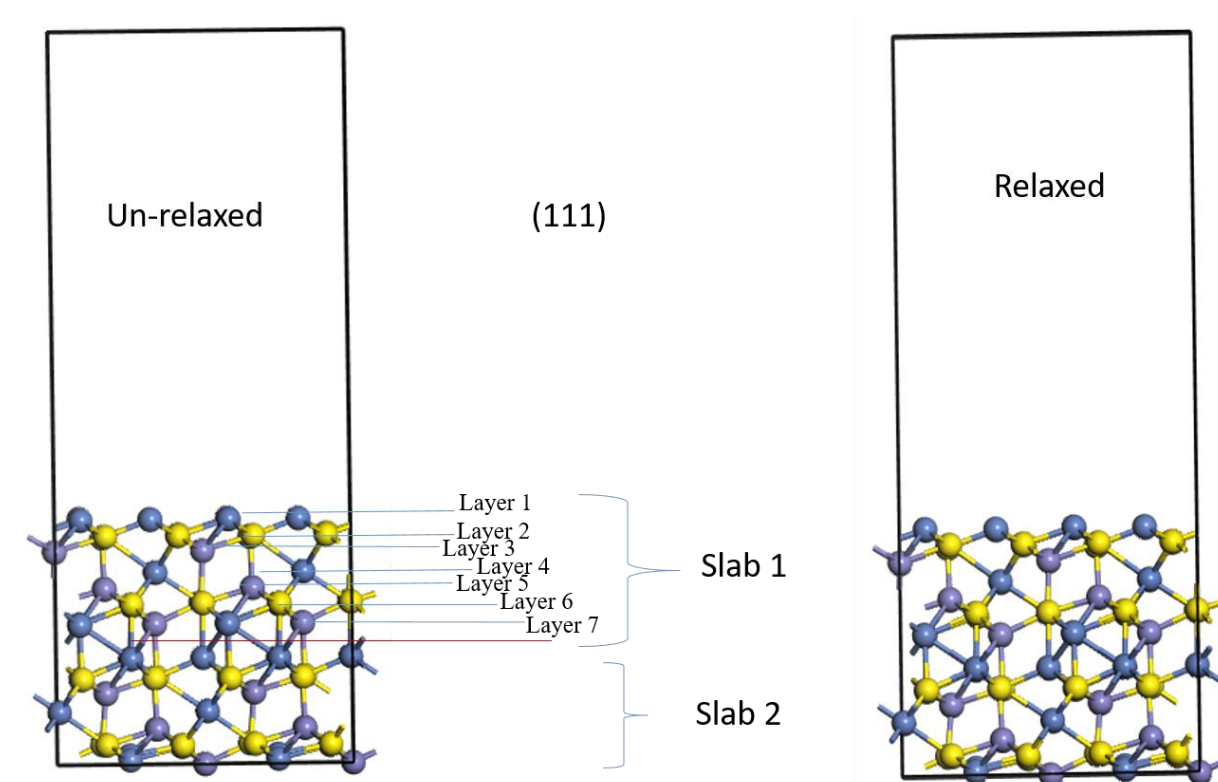
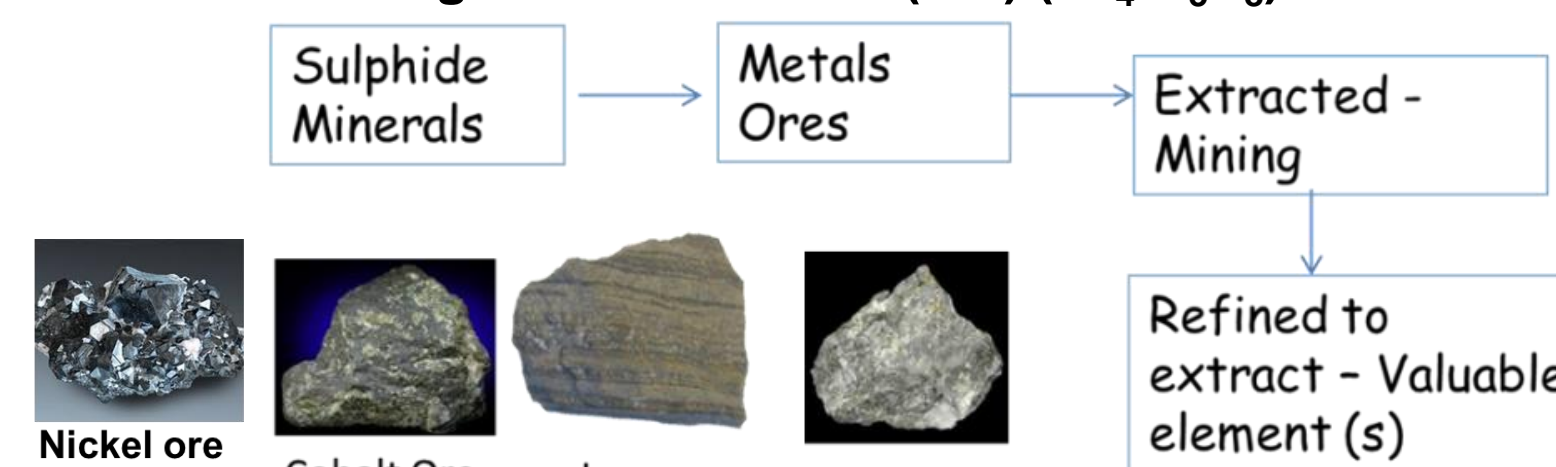


Figure 2: Low Miller (111) (Fe₄Ni₅S₈) surfaces



Flowchart showing how metal ores are extracted through mining and refined to obtain valuable elements.

Methodology

- The study is based on the *Ab-initio* quantum-mechanical Density Functional Theory (DFT) method [4].
- The DFT CASTEP (Cambridge Serial Total Energy Package) code was used to investigate the oxidation and hydration reaction on nickel-rich pentlandite (111) surface.
- A plane wave energy cut-off of 400 eV and (5×5×5) bulk and (5×5×1) surface proposed by Monkhorst-Pack [5] grid for the Brillouin zone integration were employed for the surface calculations.

RESULTS AND DISCUSSIONS

Table 1: The calculated surface energy

Surface	Surface energy (J/m ²)
(111)	0.920

The stability of the surface terminations was calculated using: $E_{\text{surface}} = \left(\frac{1}{2A}\right) [E_{\text{slab}} - n E_{\text{bulk}}]$

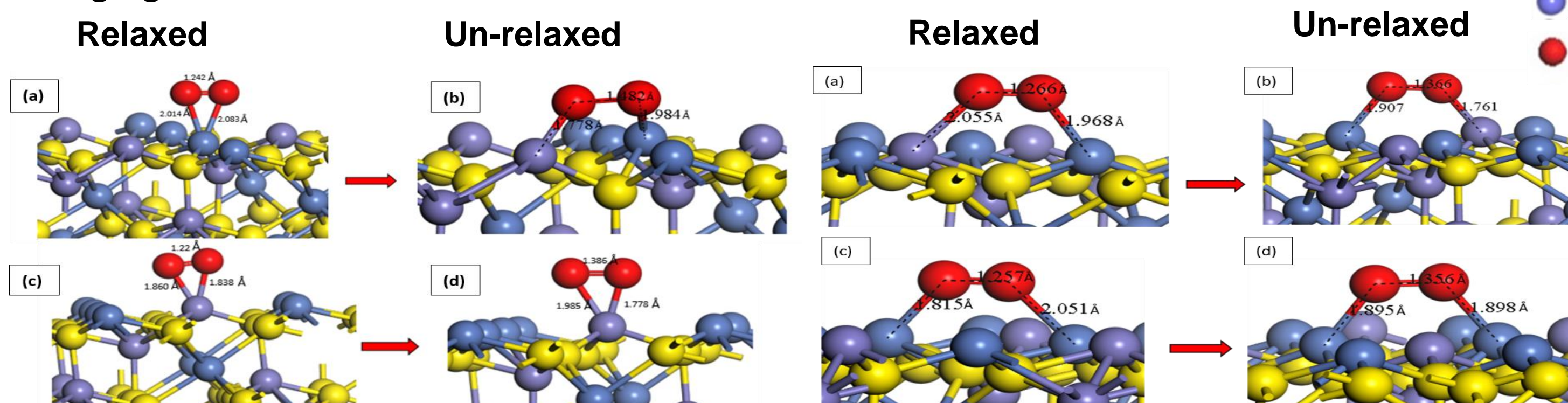
Table 2: Adsorption energies of oxidation on Ni-rich pentlandite (111) surface

Adsorption mode	Adsorption energies (kJ/mol)
Fe-peroxide	-187.73
Ni-Peroxide	-262.41
Ni-Superoxide	-252.77
Fe-Superoxide	-167.57
Ni-Bridge	-124.90
Fe-Ni-Bridge	-216.27
Hollow	-227.19

The strength of adsorption on the surface was determined by calculating the adsorption energies: $E_{\text{(ads.)}} = E_{\text{(system)}} - (E_{\text{(surface)}} + E_{\text{(adsorbate)}})$

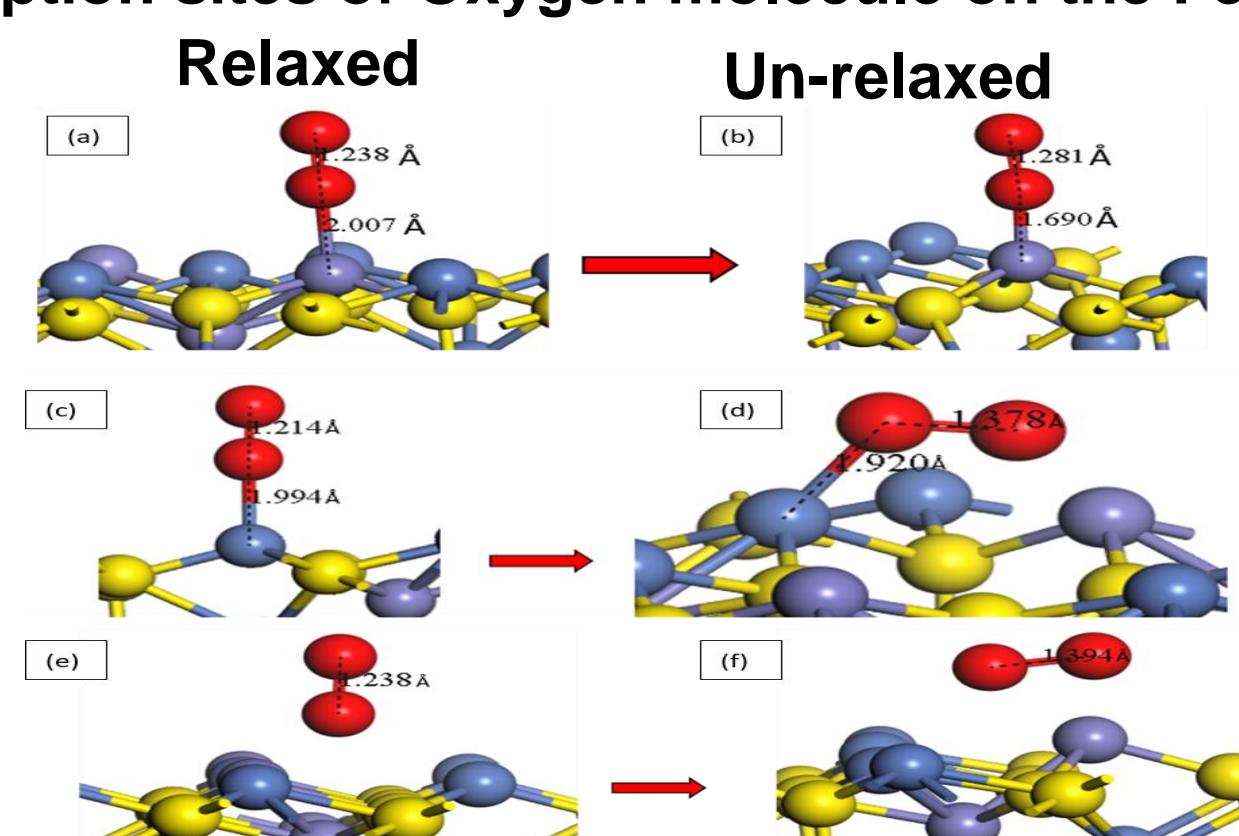
- The oxidation of the (111) surface of Ni-rich pentlandite indicated that the Ni-peroxide is the most preferred adsorption site.
- This further showed that the adsorption on this site results in bridging on Fe and Ni atoms on the surface.

Figure 3: Adsorption sites of Oxygen molecule on the Fe₄Ni₅S₈ (111) surface- Peroxide and Bridging



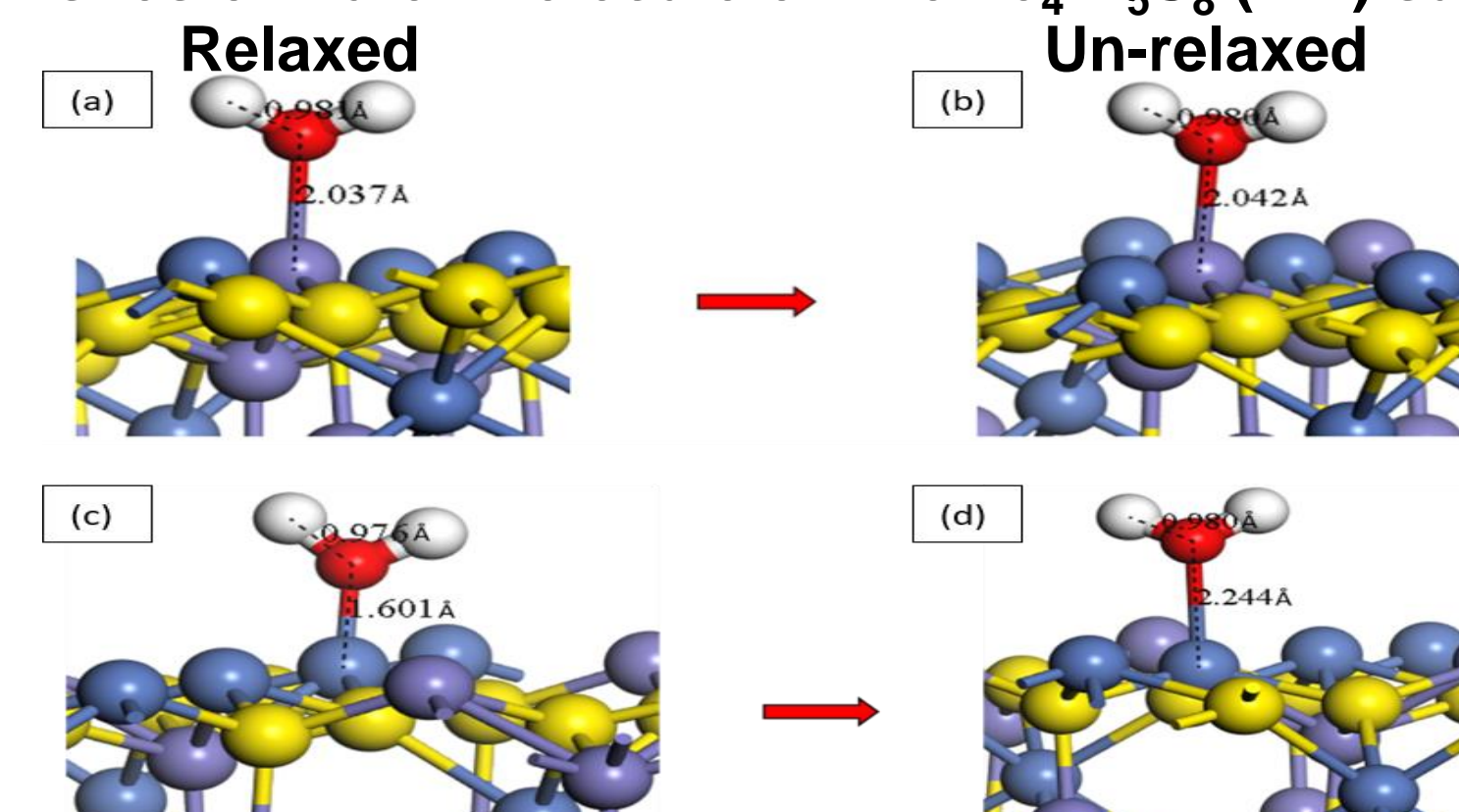
- The bond length between the Oxygen on the left hand side and Fe or Ni atoms is weakened (stretches to 2,509 Å and 1,985 Å).
- We noted that the Oxygen molecule forms a bridging bond (1,778 Å) with Fe atom (Ni-O₂-Fe), which suggest that the preferential oxidation of Fe atom.
- We noted that the O-O bond length of Fe-Ni- bridge was larger than for Ni-bridge.
- Furthermore, the Fe-O bond was shorter than that of Ni-O, indicating strong interaction between Fe and oxygen molecule.

Figure 4: Adsorption sites of Oxygen molecule on the Fe₄Ni₅S₈ (111) surface- Superoxide



- The adsorption of oxygen in superoxide on Fe did not change the orientation.
- The superoxide adsorption on Ni resulted in bent of oxygen molecule towards the Fe atom, however, it did not form bond with Fe.
- The hollow adsorption resulted in almost horizontal orientation on the surface and did not form any bonds on the surface.

Figure 5: Adsorption sites of water molecule on the Fe₄Ni₅S₈ (111) surface



- The water adsorption on Fe was more exothermic than on Ni atom, suggesting that the Ni-rich pentlandite is more hydrophilic on Fe atoms.
- We found that the Fe-OH₂ bond length was shorter than for Ni-OH₂.

CONCLUSION

The investigation of the surface properties and their interaction with Oxygen and Water molecules have been successfully performed using DFT. We used the cut-off energy of 400eV and 5x5x5 for bulk and 5x5x1 for the surface. The adsorption of O₂ and H₂O was found to be exothermic which indicated their interaction with the pentlandite surface. The oxidation preferred the Ni-peroxide mode, which resulted in bridging on Fe and Ni atoms. The hydration indicated that water has strong interaction with Fe than Ni on pentlandite surface.

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ACKNOWLEDGMENTS



National Research Foundation