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Cleavage surface and oxygen adsorption on (001) monoclinic pyrrhotite – A DFT study

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Monoclinic pyrrhotite (Fe_7S_8) is one of the most abundant sulfide minerals in the Earth's crust, commonly found in ores containing metals such as copper, lead, zinc, platinum, and silver. The oxidation of monoclinic pyrrhotite can lead to the acidification of soil and rivers, as well as the leaching of heavy metals. These processes may result in the intoxication of various organisms, including humans [1].

The calculations to simulate pyrrhotite's surfaces were performed using Plane-wave Density Functional Theory as implemented in the Quantum Espresso Package. Ultrasoft pseudopotentials and the GGA PBE XC functional, together with the Hubbard correction (GGA+U), were used. Initially, different surfaces were tested using a slab model, with a vacuum, of 10 Å to prevent interactions between the slab layers. The cleavage energy of the unrelaxed surface created by the cleavage planes 001, 010, 100, and 110 was calculated. It was observed that the surfaces formed by the 001 plane have the lowest average cleavage energy, 1.607 J/m^2, indicating that these surfaces are more easily formed. Among all the surfaces created by the 001-cleavage plane, it was observed that the most energetically favorable surface showed a cleavage energy of 0.728 j/m^2 and exhibited intense reconstruction with the sulfur atoms moving from the second layer to the first layer. This is like what was observed for chalcopyrite [2].

The adsorption of oxygen on the 001 surface of monoclinic pyrrhotite was followed by the cleavage of the oxygen molecule and the formation of Fe-O bonds with a bond length of 1.94 Å and S-O-Fe bonds with bond lengths of 1.57 Å for S-O and 1,97 Å for Fe-O. The adsorption energy for the individual oxygen molecule was found to be -438,71 KJ/mol, indicating a strong interaction between the surface and the oxygen molecule and also the oxidation of iron and sulfur on the surface. The projected density of states (PDOS) and the electron localization function (ELF) calculations, performed over the oxygen, sulfur, and iron atoms, also highlight the strong interactions between the molecule adsorbed and the monoclinic pyrrhotite surface. These results are significant for understanding the reactivity and environmental impact of pyrrhotite oxidation.

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