Density Functional Theory calculations of nitrogen adsorption features on Fe(111) surfaces
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ABSTRACT
In this work, we present an exhaustive calculations of the interaction of nitrogen atoms and molecules with the Fe(111) surface. These calculations set the basis for subsequent analysis of the N₂ dissociation dynamics. We perform Density functional Theory spin-polarized calculations. We first study the relaxation of the Fe(111) surface, which was a matter of controversy in the past. From here, we calculate the interaction energy of nitrogen atoms and molecules when approaching the Fe(111) surface. Our results show the preferred adsorption paths and sites for nitrogen adsorption, as well as the adsorption energies.

THEORETICAL METHODS

• All DFT calculations were performed using VASP (plane-wave basis set).
• The exchange-correlation energy is calculated with GGSA and the energy functional (PW91).
• The electron-core interaction is described by PAW pseudopotentials.
• The calculation of adsorption energy of N₂/Fe(111) is performed using a (2 x 2) supercell and keeping the geometry of the slab frozen.
• The Brillouin-zone integration is performed with a For lattice parameter (2 x 2 x 1)
• For surface layers relaxation (8 x 8 x 1)
• For Nitrogen (atoms/molecules) adsorption (6 x 6 x 1)
• Monkhorst-Pack grid of spacial K-points.

RESULTS

Adorption Energy for N₂/Fe(111) System

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Z (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top-HCP</td>
<td>-294.00</td>
</tr>
<tr>
<td>Top-FCC</td>
<td>-293.65</td>
</tr>
<tr>
<td>bridge</td>
<td>-293.30</td>
</tr>
<tr>
<td>Top-Fe</td>
<td>-292.95</td>
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</tbody>
</table>

Calculations of Adsorption Energy for N₂/Fe(111)

<table>
<thead>
<tr>
<th>Adsorption Energy (eV)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>0.33</td>
<td>Experiment [1]</td>
</tr>
<tr>
<td>0.32</td>
<td>Experiment [2]</td>
</tr>
<tr>
<td>0.39</td>
<td>Theory [3]</td>
</tr>
<tr>
<td>0.27</td>
<td>Theory [4]</td>
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</tbody>
</table>

CONCLUSIONS

• The magnitude of the interlayer spacing of the surface relaxations are qualitatively close to the LEED values, but do not actually lie within the same range of measurements.
• The interlayer spacing does not depend much on the number of layers in the slab.
• The adsorption energy of N₂ on Fe(111) does not depend much on the number of slab layers.
• For N₂/Fe(111) system, the molecule prefers to accommodate at the surface perpendicularly.
• Calculations of adsorption energy of atomic nitrogen have been performed, for 15 different adsorption sites: The preferred adsorption site for the nitrogen atom is the bridge site.

REFERENCES