

## Quantum Description of Geological Twins

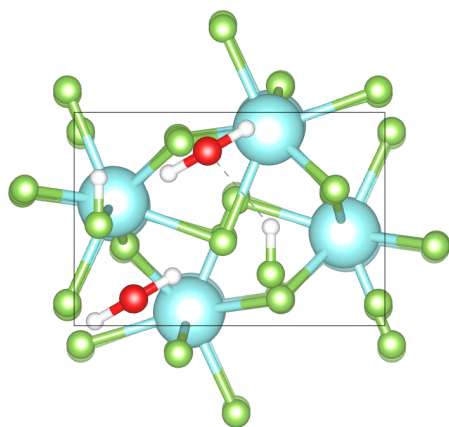
### Quantum Investigation on the Fractioning of Geological Twins by Fluoride

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#### In Short

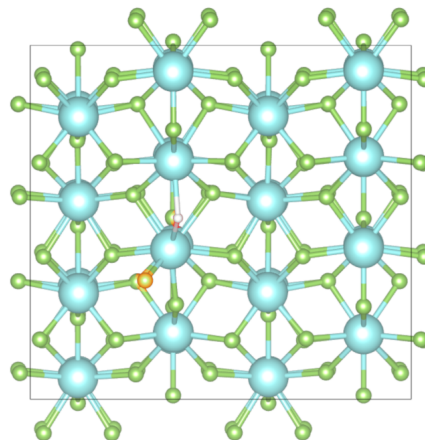
- geological twins
- surface analysis
- rare earth element fluorides
- high field strength elements

The term geological twins refers to the identical geochemical behaviour of two elements caused by the equivalent charges and ionic radii of their most stable oxidation states. Y and Ho are such a pair. By their small ionic radii of 1.075 Å (Y) and 1.072 Å (Ho)[1] and only stable oxidation state of +III, both belong to the interesting group of high field strength elements (HFSE). As a lanthanide (Ln), Ho also belongs to the rare earth elements (REE). Due to their twin character, Y is also generally associated with that group as REE+Y. The whole series of middle and late REE (Sm–Lu) trifluorides exhibits the same low temperature phase of  $\beta$ -YF<sub>3</sub> structure (Pnma symmetry).[2-10] As a consequence, the mineral waimirite-(Y), mainly consisting of  $\beta$ -YF<sub>3</sub>, possesses relatively high concentrations of those co-crystallizing REE.[11]



**Figure 1:** full coverage example:  $(1 \times 1 \times 5)$  YF<sub>3</sub> (010) surface with HF:H<sub>2</sub>O monolayer mixed 1:1.

From the classical point charge of view, Y<sup>III</sup> and Ho<sup>III</sup> are practically equivalent. However, quantum mechanically, they are of course very different in their electronic structure. YF<sub>3</sub> can already be reasonably well treated by density functional theory (DFT) methods. For LnF<sub>3</sub> with partially filled 4f-orbitals,



**Figure 2:** isolated adsorption example:  $(2 \times 2 \times 2)$  YF<sub>3</sub> (101) surface with 1 single HF (highlighted in orange) which dissociated during relaxation.

DFT+U is the least demanding method to achieve good results. However, no published benchmarking on the empirical parameter U exists for the series of LnF<sub>3</sub>. Thus, we will perform a DFT+U benchmark for the series of isostructural middle and late LnF<sub>3</sub> with the help of new experimental band gap data of our experimental colleagues at AG John, FU Berlin.

In solubility experiments of YF<sub>3</sub> and HoF<sub>3</sub> in aq. HF, these colleagues have already shown that the geological twins Y and Ho are separable by their different affinity to F<sup>-</sup>. [12] Within the first HLRN funding period, we have performed a surface stability analysis for both geological twin fluorides, YF<sub>3</sub>(PBE) and HoF<sub>3</sub>(PBE+U) for all seven low-lying Miller indices using symmetric 2D-slab models. In our study, we included any possible termination giving a stoichiometric slab, or one with a small F-deficit of max. 2 per surface. We now use the determined most stable surface terminations to analyze their interaction with solvents and ions present in hydrothermal fluids. Within those fluids, the current model proposes that Cl<sup>-</sup> takes the major part in REE+Y transport and F<sup>-</sup> in fixation.[12-15] To quantify the underlying quantum mechanical differences in solvent/ion to surface interactions, we apply pEDA-NOCV[16] on isolated (fig. 2), as well as full coverage (fig. 1) adsorptions. Within pEDA, the bond of two fragments is separated into the attractive orbital, electrostatic and dispersion interactions and the Pauli repulsion. NOCV allows to split the orbital term into separate orbital-orbital interactions. For each such pair, it can be analyzed how electron density changes upon bond formation - where it accumulates or decreases.

## WWW

<https://www.bcp.fu-berlin.de/en/chemie/chemie/forschung/PhysTheoChem/agpaulus/index.html>

## More Information

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