

## Fluorinated aluminium bulk structures and surfaces

### First principle investigations of $\text{AlO}_x(\text{OH})_y\text{F}_z$ bulk and surfaces and their interaction with water

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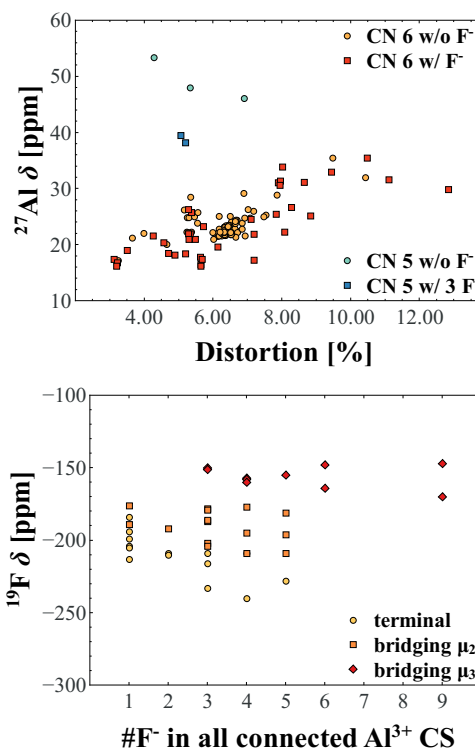
#### In Short

- Studying the interaction of water on fluorinated aluminium oxides and hydroxides
- Determine NMR shifts of crystal structures, especially of  $\text{AlO}_x(\text{OH})_y\text{F}_z$  mixtures with low concentration of fluorine
- Analysis of the fluorination of the  $\alpha\text{-Al}_2\text{O}_3$  surfaces and their water adsorption properties
- Bulk crystal structures and surface effects are intended to be investigated by employing periodic density functional theory calculations
- Compare the found structure motifs of adsorbed water with structure motifs in different ice phases

Our main goal is to understand the corrosion effects of water in aluminium oxides and hydroxides, the solvation of corresponding nanocrystals and the influence of defects on those processes. Since we know that the inclusion of fluorine into aluminium compounds is not only experimentally known[1], but also influences the solubility and the reactivity with water, we already investigated fluorinated bulk structures[2] and finished the study of fluorinated surfaces and their water adsorption capabilities using the Vienna *ab-initio* Simulation Package (VASP)[3–6]. In order to make our results more comparable with experimental data, we also calculated  $^{27}\text{Al}$  and  $^{19}\text{F}$  NMR shifts, which enhances the mutual verification and analysis of the obtained results.

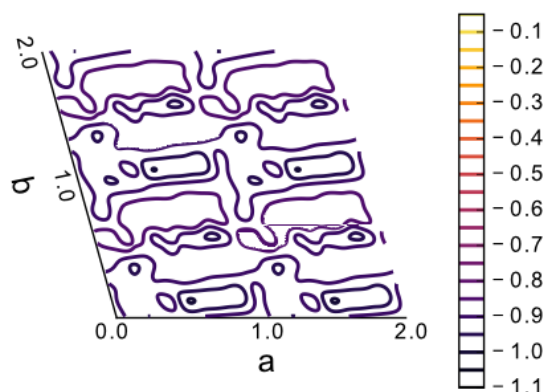
Our results for the NMR shifts of  $^{27}\text{Al}$  and  $^{19}\text{F}$  in the differently fluorinated  $\alpha\text{-Al}_2\text{O}_3$  surfaces (see Figure 1) were again able to help and confirm assumptions of the experimental group of Prof. Dr. Kemnitz and PD Dr. Scholz. Thus, the bulk and surface NMR shifts were both able to enhance the analyses of experimental NMR data.

For the investigation of nanocrystals and their interactions with water, we are in need of a very good understanding of how water adsorbs and what kinds of interactions occur on aluminium oxide surfaces, because those serve very well as a model for the shells of nanocrystals. To understand which conditions and structural motifs influence the water adsorption and, more importantly, how strong those



**Figure 1:** NMR shifts of (top)  $^{27}\text{Al}$  in dependence on the its CN & the distortion of its first CS and (bottom)  $^{19}\text{F}$  in dependence on their CN and the amount of F in their second CS.

influences are, we investigated the fluorination of various  $\alpha\text{-Al}_2\text{O}_3$  surfaces. We could detect and quantify several points that influence not only the position of the adsorbing water molecules but also how strong they are bound to the surface. This includes the range of the supportive effect of already adsorbed water molecules, insights in the steric demands of adsorbing water molecules, how added fluoride ions enhance the Brønsted acidity of remaining surface hydroxide groups, and of course how the important hydrogen bonds are influenced by the CNs of the donating and accepting partners. The latter, for example, could explain why the adsorption on the fully fluorinated (11 $\bar{2}$ 3) surface were so strong, although, the other surfaces indicated a weakened adsorption with the progressive addition of fluoride ions (see Figure 2). Because on this surface no initial hydrogen bonds have to be broken or weakened to enable the water molecule's adsorption, so there is no compensatory effect on the adsorption energy. Additionally, the terminal fluoride ions provide a much better capability to accept hydrogen bonds than higher coordinated ones. Thus, the adsorption becomes



**Figure 2:**  $2 \times 2$  supercell representations of the adsorption energy surface [eV] of the first water molecule on the sevenfold fluorinated (1123) surface  $1 \times 1$  surface (water laterally fixed, last twelve atomic layers fixed to resemble underlying bulk).

significantly stronger.

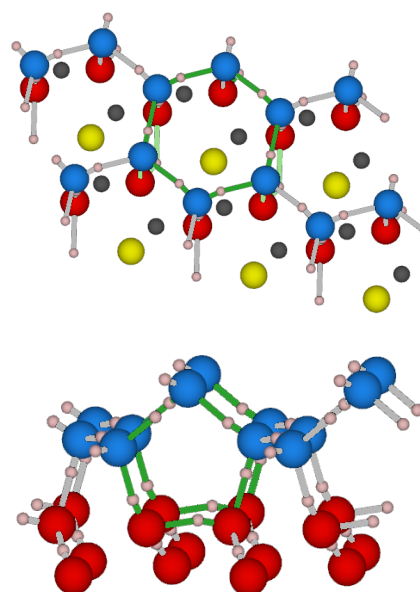
During this investigation of the water adsorption on the different  $\alpha$ - $\text{Al}_2\text{O}_3$  surfaces, several interesting structure motifs are formed from the adsorbing water molecules. The most prominent of such motifs is the formation of zigzag chains of water molecules and water molecules with surface ligands. Those chains can cross each other in different angles and, by association, lead to different net-like structures on the surface. In some cases honeycomb-like structures were observed, in others  $\beta$ -sheet-like shaped chains of small rings occurred and even helices were observable (see Figure 3).

This led us to the structural comparison of the 18 different ice phases with those structure motifs of the adsorbed water molecules, hoping that it might be possible to grow a specific ice phase on one of the studied surfaces. And indeed, several ice phases provide net-like layers of water molecules, the most common among them: a net made from hexagons. Even chains of small rings and helical substructures can be found in the ice phases. Thus, it might be possible to use a certain modified  $\alpha$ - $\text{Al}_2\text{O}_3$  surface to favourably grow one specific ice phase.

That is why we are going to verify the found structure motifs of adsorbed water molecules by distorting them and let them relax again on a bigger supercell. Thus, we can overcome the symmetric restrictions imposed by the use of smaller unit cells and the periodicity within the calculations. Afterwards, we can make much more profound assumptions whether or not certain surfaces can be used to grow specific ice phases.

## WWW

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**Figure 3:** Structure depictions of multiple unit cells with adsorbed water molecules and highlighted structure motifs; (top) two water molecules on the singly fluorinated (0001) surface and (bottom) three water molecules on the hydrated (1102) surface - gray = aluminium, red = oxygen, yellow = fluorine, white = hydrogen, blue = water molecule's oxygen, green/light green = highlighted hydrogen bonds for the structure motif, and light gray = de-emphasised hydrogen bonds.

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## More Information

- [1] Kemnitz, E.; Scholz, G.; Rüdiger, S., *Sol-gel Synthesis of Nano-Scaled Metal Fluorides*, (Ed. Alain Tressaud, Wiley, 1-35, 2010).
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## Project Partners

AG Kemnitz Humboldt Universität zu Berlin

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