Characterization of the NaCl Suzuki structure by scanning force microscopy

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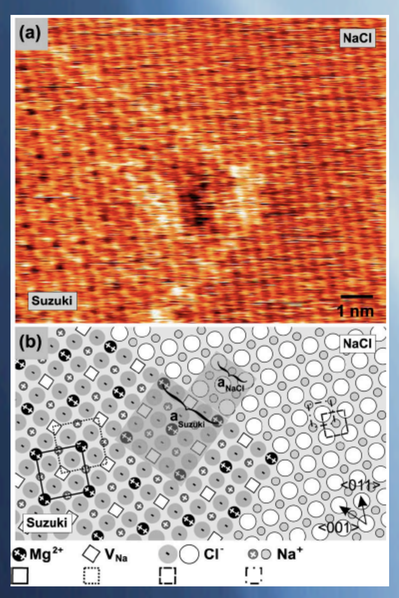
Introduction

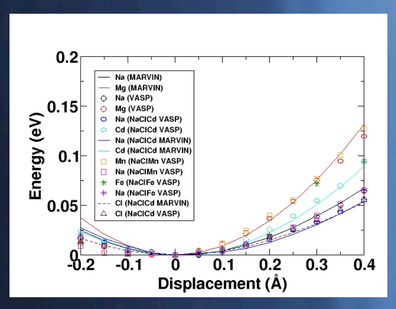
Due to their insulating character, the (001) surfaces of bulk alkali halide crystals are emerging as important substrates in many nanosystems. Particular focuses are supported metal nanoclusters for the study of **catalytic properties** and the adsorption of molecules to the surface for applications in **nanoelectronics**. For simultaneous characterization of both the substrate and nano-object at the atomic scale, Scanning Force Microscopy (SFM) remains the tool of choice, but on the highly symmetric alkali halide surfaces, unambiguous interpretation of contrast is difficult. Possible solutions, such as using force spectroscopy, are extremely challenging both experimentally and theoretically, and do not offer a routine approach to the problem. It is clear that a much more desirable setup would provide interpretation directly from images alone.



Recently, it was proposed to **dope NaCl crystals** with divalent **impurity cations** as part of a combined SFM and Kelvin probe microscopy study [1]. Above a certain divalent impurity content, the doped NaCl system creates precipitates in their well-known **Suzuki phase** [2] on the surface. The precipitates are embedded in the NaCl(001) matrix, so that two different types of surfaces regions, which are well separated, can be found.

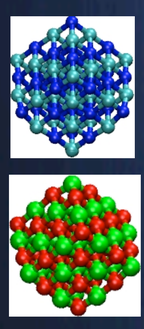
Methods

• *ab initio (PAW-PBE-VASP)* calculations of bulk and surface used as benchmark for fitting of atomistic potentials.



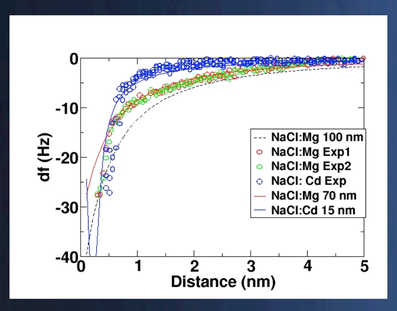
• Structure matches experiments and *ab initio*.

• Atomic displacement profiles also match.



• Considered several tip models, including NaCl:Mg and NaCl:Cd based models.

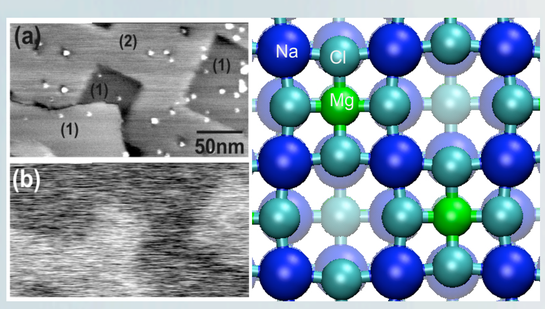
• Upper third of tips and lowest layer of surface frozen, all other atoms allowed to relax fully.



• Long-range forces fitted to experimental frequency change curves and distance dependence images.

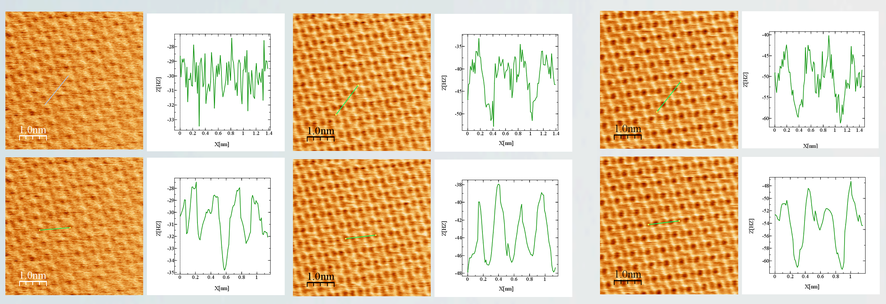
• Images simulated using experimental parameters.

NaCl:Mg



• NaCl doped with Mg^{2+} ions, resulting in characteristic Suzuki islands on the surface.

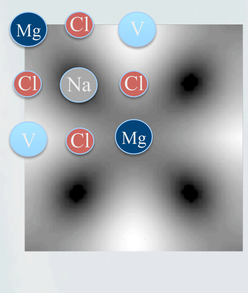
• Contrast plotted such that **bright is lower frequency change** i.e. weaker attraction.



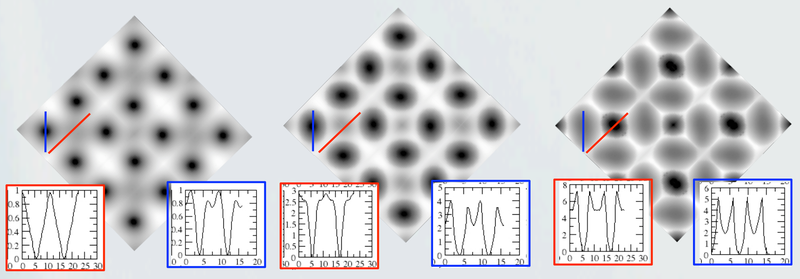
df = 16 Hz
contrast = 2-3 Hz

df = 20 Hz
contrast = 5-7 Hz

df = 24 Hz
contrast = 6-8 Hz



• Simulated images with a Cl-terminated NaCl tip match experimental contrast pattern, frequency change and contrast magnitude as a function of tip-surface separation.



h = 0.45 nm df = 16.8 Hz
ct = 1.8 Hz

h = 0.35 nm df = 20.4 Hz
ct = 5.5 Hz

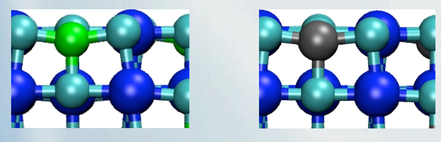
h = 0.275 nm df = 22.7 Hz
ct = 8.2 Hz

• Clear evidence that experiment was imaging the Suzuki structure on the surface with vacancy sites as maximum contrast i.e. minimum attraction. All sublattices are resolved.

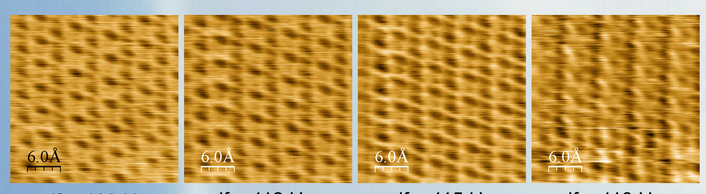
• Other tips produced characteristically different contrast or were much less stable than an NaCl tip.

NaCl:Cd

• NaCl also doped with Cd^{2+}, resulting in the appearance of similar Suzuki islands at the surface.



• Calculated surface geometries are similar, although Cd demonstrates larger displacement from the surface.



df = 109 Hz
df = 112 Hz
df = 115 Hz
df = 118 Hz

• Experimental images show a different contrast pattern, which cannot be seen in simulated images of NaCl:Mg for any tip

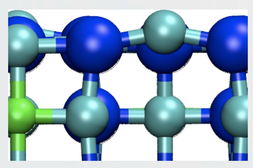
[1] C. Barth and C.R. Henry, Phys. Rev. Lett. 100, 096101 (2008)
[2] K. Suzuki, J. Phys. Soc. Jpn. 10, 794 (1955) and 16, 67 (1961)

Suzuki terminated?

• Despite accurately capturing the differences between NaCl:Mg and NaCl:Cd, the experimental images cannot be explained by any tip model… do we have the right surface?

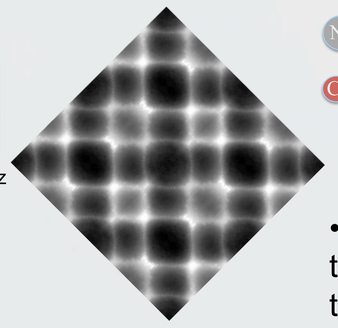
NaCl termination

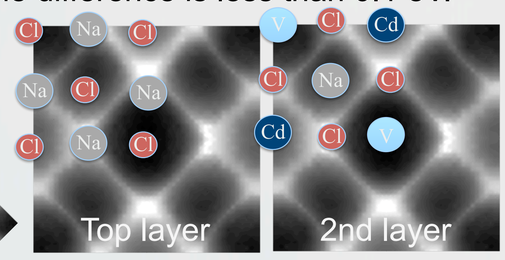
• Termination by an "ideal" NaCl layer has not been considered in earlier works.



• From *ab initio* surface energy calculations, NaCl:Mg Suzuki termination is favoured by 0.3 eV over NaCl termination.

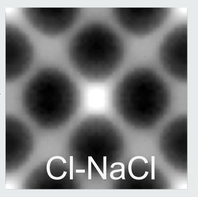
• For NaCl:Cd the difference is less than 0.1 eV.

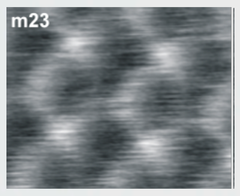


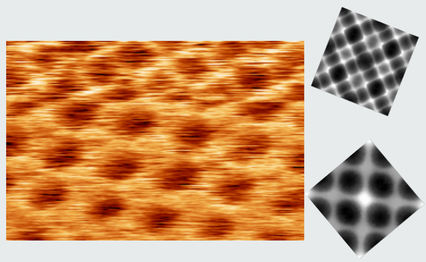


• Simulated images of the NaCl terminated surface with a Na-terminated tip match experiment.

• Agreement with other tips in further experiments…







• Both contrasts seen in a tip change image.

Summary

• A combination of nc-AFM experiments and simulations provides clear evidence for **surface termination** of two different Suzuki materials - reveals surface structure that would be **invisible** to other surface techniques.

• Suzuki phases can also be formed from **magnetic impurities** and with **oxides** - MgO:Mn, NiO:Mn, NaCl:Fe and NaCl:Mn.

• **Ongoing studies** to take advantage of the unusual surface properties in nanocatalysis and molecular electronics.