

## Bulk Terminated NaCl(111) on Aluminum: A Polar Surface of an Ionic Crystal?

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Atomically resolved scanning tunneling microscopy reveals the existence of triangular (111) bulk terminated NaCl islands. The islands can be grown by subsequent adsorption of Na and Cl<sub>2</sub> on Al(111) and Al(100) or by conversion of stoichiometric NaCl(100) islands to NaCl(111) via additional Na adsorption. The NaCl(111) islands have Na-Cl-Na sandwich structure. *Ab initio* calculations of the electronic structure of these islands show that each of the Na atoms carries half a positive elementary charge, leaving the islands neutral and explaining the existence of an otherwise unstable surface.

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The shape of some crystals in nature, e.g., the almost perfect cubes formed by NaCl, has fascinated mankind long before anything about crystallography was known. It was realized much later that the shape of many ionic crystals is governed by the fact that only very few facets, such as NaCl{100}, are electrically neutral and, thus, stable, whereas others, such as NaCl{111}, would have a charged surface, where the uppermost layer would consist of either Na<sup>+</sup> or Cl<sup>-</sup> ions only (*polar surfaces*). As the whole crystal must remain neutral, this implies opposite electrical charges elsewhere, e.g., on some other surfaces. Therefore, a huge electric field would build up, with an energy diverging with crystal size (see Fig. 1a). In other words, the surface energy of polar surfaces such as bulk-terminated (111) surfaces of NaCl-type ionic crystals is formally infinite, and such surfaces are unstable and do not occur in nature (see, e.g., Ref. [1]).

On the other hand, (111) surfaces of NaCl-type ionic crystals have been very attractive to surface science studies, as the first layer would consist of one type of ions only, and one would expect, e.g., very unusual adsorption properties. It was hence tried several times to create crystals or thin films with this surface orientation, especially for metal oxides. For an NiO(111) single crystal it was found that an unreconstructed surface is stabilized by adsorption of light elements [2]. In the case of NiO(111) films on Ni substrates the unreconstructed surface is stabilized by OH groups [3,4]. Another way of stabilizing an otherwise polar surface is surface reconstruction, as shown schematically in Fig. 1b. For an NaCl-type (111) surface theoretical studies propose a  $p(2 \times 2)$  reconstruction to be stable [5]. Such a reconstruction was indeed found for thin NiO(111) films [6–8]. Also MgO(111) shows several different reconstructions [9], but no unreconstructed adsorbate-free (111) surface for this or other NaCl-type crystals was found until now. In this Letter we present the successful growth of unreconstructed adsorbate-free islands with NaCl(111) structure on aluminum surfaces.

Density functional theory calculations are used to determine the electronic structure of these films.

All measurements were performed with a scanning tunneling microscope (customized Omicron Micro STM) at room temperature in a two-chamber UHV system with a base pressure below  $10^{-10}$  mbar (see also Ref. [10]). Na was evaporated by using well outgassed dispensers [11]. The amount of Na on the surface was determined by STM, taking advantage of the well-known superstructures [12,13], and Auger electron spectroscopy (AES). Cl<sub>2</sub> was dosed from an electrochemical AgCl cell. Although Cl could be detected with AES, quantification was not possible by this method due to strong electron stimulated desorption. Therefore, the Cl flux was calibrated by monitoring the formation of different Cl superstructures on Cu(111) [14] by LEED. NaCl was evaporated by heating NaCl powder in a Mo crucible. The evaporation rate

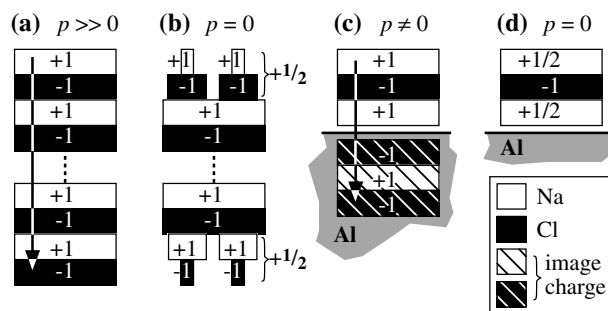


FIG. 1. Charge distribution and resulting dipole moments  $p$  for different NaCl(111) configurations discussed. The numbers in the layers refer to the charge per atom. (a) Thick NaCl crystal with (111) surface orientation. The resulting dipole moment, and, hence, electrostatic energy diverges with crystal size. (b) Reconstructed surface, only  $\frac{1}{4}$  and  $\frac{3}{4}$  of the lattice positions are occupied for the first and the second layers, respectively. (c) Triple Na-Cl-Na layer on an Al substrate neutralized by image charges. (d) Neutral triple Na<sup>+1/2</sup>-Cl<sup>-1</sup>-Na<sup>+1/2</sup> layer as found in the present work.

was determined with a quartz crystal microbalance. The sample was at room temperature during all adsorption experiments.

The results were obtained on  $\text{Al}_{99}\text{Cu}_1(100)$ ,  $\text{Al}(111)$ , and  $\text{Al}_{99}\text{Cu}_1(111)$  single crystals. The alloy surfaces were found to consist of pure Al, as expected due to the lower surface energy of Al. As we could not see any difference in the NaCl growth behavior between the alloy and the pure crystals we will refer to the alloys as pure Al crystals from here on. Cleaning of the crystals was done by several cycles of sputtering ( $\text{Ar}^+$  1 keV) and annealing (620–670 K) until no contaminations were detectable with AES or STM.

To produce NaCl(111) islands we start with evaporation of Na on the Al substrates. Na forms  $(\sqrt{3} \times \sqrt{3})R30^\circ$  superstructure domains [12] [for coverages up to  $\frac{1}{3}$  monolayer (ML)] and a  $c(2 \times 2)$  [13] reconstruction on Al(111) and Al(100), respectively. After subsequently dosing  $\text{Cl}_2$  on the Na covered Al surfaces we find triangular islands, which are growing with increasing  $\text{Cl}_2$  dose while the Na domains are shrinking. The islands are preferentially located at the lower side of substrate step edges (Fig. 2a). The edges of the islands are parallel to the close packed directions on the Al(111) substrate, and randomly oriented

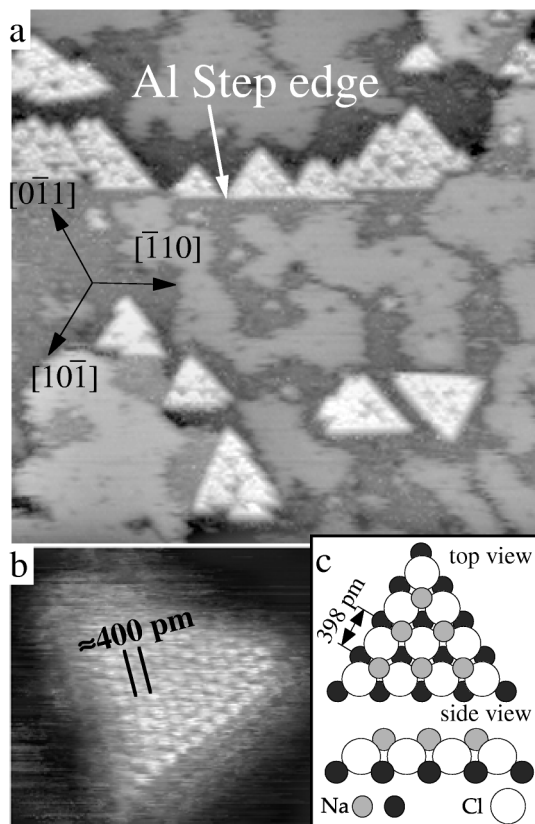


FIG. 2. STM constant current topographs of Al(111) after adsorption of 0.35 ML Na and a dose of  $\text{Cl}_2$  corresponding to 0.2 ML. (a)  $50 \times 50 \text{ nm}^2$ ,  $-1.2 \text{ V}$ ,  $0.06 \text{ nA}$ . (b) NaCl(111) island with atomic resolution ( $7 \times 7 \text{ nm}^2$ ,  $-1.2 \text{ V}$ ,  $0.3 \text{ nA}$ ). (c) Structure model of an NaCl(111) island.

on the (100) substrate. Some of the islands consist of smaller triangles with some defects between them.

Atomically resolved images of these islands exhibit a lattice with sixfold symmetry and a lattice constant of  $\approx 400 \text{ pm}$  (Fig. 2b). This corresponds to a (111) surface of an NaCl crystal. No other known Al-Na-Cl compound has a structure which could explain this geometry.

AES measurements before and after dosing  $\text{Cl}_2$  confirm that no significant amount of Na has left the surface during Cl adsorption and island formation. The ratio between the  $\text{Na}-(\sqrt{3} \times \sqrt{3})R30^\circ$  area consumed by the process and the total NaCl(111) island areas on the Al(111) substrate, measured in several STM images, is  $3.7 \pm 0.7$ . The Na consumption allows us to determine the amount of Na in the NaCl(111) islands, i.e., the number of Na layers.

The density of Na atoms (calculated from NaCl and Al bulk lattice constants) in one NaCl(111) layer and in the  $\text{Na}-(\sqrt{3} \times \sqrt{3})R30^\circ$  superstructure is  $7.3 \times 10^{14} \text{ cm}^{-2}$  and  $4.7 \times 10^{14} \text{ cm}^{-2}$ , respectively. The ratio of these densities is 1.54. The measured area ratio of  $\text{Na}-(\sqrt{3} \times \sqrt{3})R30^\circ$  consumption and NaCl(111) islands of  $3.7 \pm 0.7$  is consistent with only the value 3.08 calculated for two Na layers in NaCl(111), not with that of one (1.54) or three (4.62) Na layers in the NaCl(111) layer. Assuming a sticking probability of one, the  $\text{Cl}_2$  dose applied would be sufficient for two layers of Cl in the islands. As the sticking coefficient of electronegative molecules on Al, e.g.,  $\text{O}_2$  and  $\text{Cl}_2$ , is much smaller than unity [15], the  $\text{Cl}_2$  dose cannot be used to determine the amount of Cl present on the surface or in the islands. This leaves the possibilities for either three-layer (Na-Cl-Na) or four-layer (Na-Cl-Na-Cl) islands.

The apparent height of the islands is approximately 480 pm, which coincides with the thickness of three bulk NaCl(111) layers. This can be considered a weak indication for a sandwich structure of two Na layers with one Cl layer in between (Figs. 1c and 1d), though it must be kept in mind that electronic effects can significantly affect the apparent height of nonmetal layers in STM (see, e.g., Ref. [10]).

A confirmation of this structure model of the NaCl(111) islands was found by the conversion of NaCl(100) into NaCl(111). After deposition of NaCl on Al(111) or Al(100) we find rectangular NaCl(100) islands [10]. Subsequent adsorption of Na transforms the NaCl(100) islands partially into islands with the NaCl(111) structure (Fig. 3). Since the newly formed (111) oriented islands are formed by adding Na to stoichiometric NaCl and the total number of Na layers in the NaCl(111) islands is two, the number of Cl layers in NaCl(111) must be less than two, i.e., one.

In view of future possibilities of employing the NaCl(111) islands for, e.g., adsorption studies, we have to note that we have not been able to come close to or reach a full monolayer of NaCl(111). Conversion of NaCl(100) to NaCl(111) is not a viable method for this purpose as

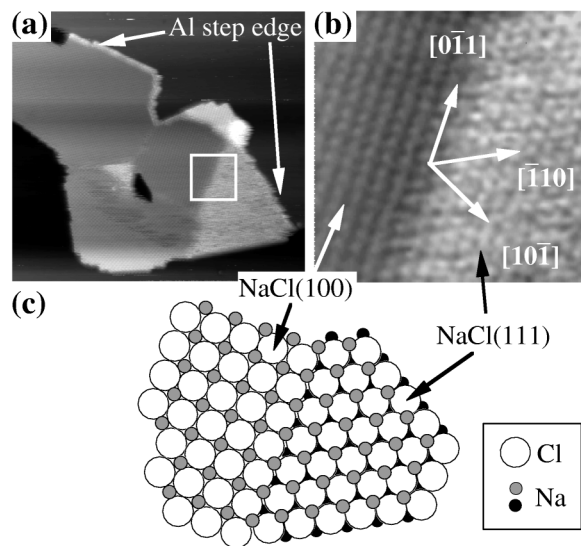


FIG. 3. STM constant current topographs of an island partially consisting of NaCl(100) and NaCl(111). (a)  $50 \times 50 \text{ nm}^2$ ,  $-1.8 \text{ V}$ ,  $0.46 \text{ nA}$ . (b) Magnified domain boundary area between NaCl(100) and NaCl(111);  $7 \times 7 \text{ nm}^2$ ,  $-2.5 \text{ V}$ ,  $0.45 \text{ nA}$ . (c) Model for the domain boundary. The NaCl(100) and (111) phases coincide along their  $[0\bar{1}1]$  directions.

this process comes to a standstill before full conversion, leaving NaCl(100) areas surrounded by NaCl(111) even after a high Na dose. We have been able to convert a complete  $\text{Na}-(\sqrt{3} \times \sqrt{3})R30^\circ$  superstructure into NaCl(111) islands, resulting in a coverage of approximately 1/3. Higher starting Na coverages or repetitive Na and Cl dosing cycles could in principle produce higher NaCl(111) coverages. As the tunneling process is very unstable on top of the islands, it was, however, not possible to get clear STM images for higher NaCl(111) coverages. A practical limitation also came from the fact that the formation of the NaCl(111) islands is very sensitive to the presence of additional adsorbates (e.g., oxygen), which leads to more complicated structures not understood yet.

Having established the existence of NaCl(111) islands, we have to ask ourselves why this structure is stable in spite of the previously mentioned arguments on instability of polar surfaces of an ionic crystal. In case of a polar island with opposite charges on the top and the bottom (Fig. 1a) one could argue that the electrostatic energy is proportional to the thickness, and, hence, does not reach exorbitant values for a small thickness of the island. A further reduction of energy could come from the image charge building up in the supporting metal surface. This case does not apply to the islands under consideration here, as the symmetric Na-Cl-Na structure found here has no dipole moment as such. The question we have to ask is rather whether (i) the ion charges of bulk NaCl are retained in the structure observed, yielding highly positive  $\text{Na}^+-\text{Cl}^--\text{Na}^+$  islands, or (ii) the islands are neutral, with the Na atoms carrying only 1/2 of a positive elementary charge each. Model (i) would require shielding of the

positive islands by image charges in the substrate, leading to a net dipole moment associated with high, but (due to the small thickness) finite electrostatic energy (see Fig. 1c). In case of (ii) the dipole moment vanishes (Fig. 1d), but we have to determine the stability of  $\text{Na}^{+1/2}-\text{Cl}^--\text{Na}^{+1/2}$ , a structure differing from bulk NaCl by the altered charge of the Na islands.

To decide between the models (i) and (ii) we have performed density functional theory calculations using the generalized gradient approximation (GGA) of Perdew and Wang [16] and the full potential linearized augmented plane wave method [17,18] including force calculations [19] facilitating the search for the equilibrium structure. As a starting point, a freestanding Na-Cl-Na trilayer with NaCl(111) geometry was assumed. The calculations of this NaCl(111) film show that it is stable with respect to in-plane or out-of-plane expansion and contraction, with a shallow minimum of the energy at a lateral contraction of 1.5% (with respect to the GGA-calculated NaCl bulk lattice,  $a_{\text{lat}} = 569 \text{ pm}$ ). The vertical distance between the central Cl layer and the Na layers is expanded by 4.2%. Thus, the structure of bulk NaCl(111) is well reproduced even though the stoichiometry of the islands is  $\text{Na}_2\text{Cl}$  and not NaCl, and charge neutrality forces the Na ions to carry only half a positive elementary charge. The lateral contraction lies between that of freestanding one- and three-layer NaCl(100) slabs calculated by the same method. The vertical expansion can be explained by the reduced positive charge of the Na ions, reducing the ionic bonding to the central Cl. Nevertheless, the deviations from the NaCl bulk structure are in the usual range for surface relaxations, allowing us to keep the designation “NaCl(111)” in spite of the different overall stoichiometry.

The density of states (DOS; Fig. 4) of this NaCl(111) trilayer film is closely related to that of a NaCl(100) film, which we calculated for comparison. The Cl 3s and 3p bands of the Na-Cl-Na film are shifted by 1.8 eV to higher binding energies. The main difference between stoichiometric NaCl(100) and nonstoichiometric NaCl(111) is the

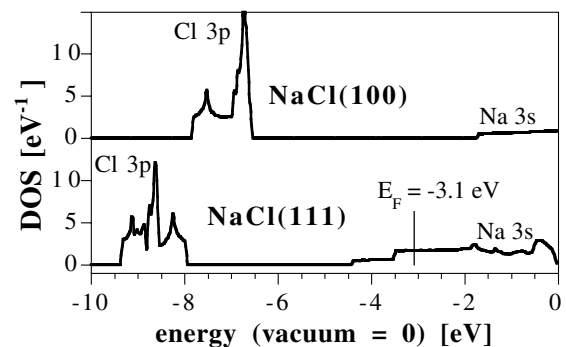


FIG. 4. Comparison of calculated density of states of a 1 ML NaCl(100) film and a NaCl(111) film consisting of two Na layers with one Cl layer in between. The Fermi level of NaCl(100) is in the band gap between the Cl 3p and Na 3s bands, while that of a NaCl(111) trilayer is in the Na 3s band.

position of the Fermi level  $E_F$ . As expected for an insulator the Fermi level is in the band gap of NaCl(100), whereas it is in the Na 3s band for the (111) film. Since filling the Cl 3p band needs only one electron from the two surrounding Na atoms, the two Na atoms are in the ionization state of  $+\frac{1}{2}$ , as mentioned previously. Therefore, the Na 3s band is partially filled, which moves the Fermi level to this band.

An *ab initio* study of the NaCl(111) film adsorbed on Al(111) or Al(100) would require a very large coincidence cell due to the different unit cells of the islands and the substrate. As the experiments did not reveal any influence of the substrate orientation on the structure of the islands, we have decided to use a modified substrate fitting the islands' unit cell, namely a five-layer Al(111) slab stretched in-plane by roughly  $\sqrt{2}$  to fit the NaCl(111) lattice. The interlayer distance of Al was reduced by 50% to compensate for the in-plane expansion, resulting in a structure similar to a body-centered-cubic lattice. The most important outcome of the calculations is the fact that the charge transfer between the NaCl(111) film and the substrate is small ( $<0.2e$  per  $\text{Na}_2\text{Cl}$  unit) and the DOS remains similar to that of the freestanding Na-Cl-Na film, vindicating the model of essentially neutral islands (Fig. 1d). This model also indicates that the islands do not heavily depend on the substrate, in agreement with the fact that we observe them on both Al(111) and Al(100), and we consider it likely that such islands could be grown on other metal surfaces as well.

Partially charged cations are therefore—besides stabilization by adsorbates [3,4] or reconstruction [6–9]—the third way to create an NaCl-type (111) surface, at least in the case of an ultrathin film. Up to now, it is the only way to create such a surface in its bulk terminated form.

Whereas partial ionization of the Na atoms obviously leads to a stable structure in case of the trilayer film discussed here, such a mechanism is less favorable for thick crystals. For a macroscopic crystal one has to expect band bending, i.e., the Na 3s level gradually shifts towards lower energies with increasing depth, and finally above  $E_F$ . This will lead to partial ionization of many Na layers. Similar to the polar surfaces discussed previously, this would cause a significant electrostatic field between an excess of positive charge at the surface and a negative space charge of  $\text{Na}^{(1-\rho)+}\text{Cl}^-$  below, associated with a large (though in this case finite) electrostatic energy. This explains why (111) surfaces of thick NaCl type crystals do not exhibit partially charged cations, but rather a reconstruction (Fig. 1b) [5,6,8] as mentioned previously.

To summarize, we have shown for the first time that it is possible to produce an unreconstructed and adsorbate-free

NaCl(111) surface. The NaCl(111) islands can be grown by adsorption of Na and Cl on Al(111) and Al(100) with an excess of Na. As conversion from NaCl(100) islands to NaCl(111) by Na adsorption shows, the NaCl(111) islands are nonstoichiometric. *Ab initio* calculations show that the islands consist of two  $+\frac{1}{2}$  charged Na layers with one  $\text{Cl}^-$  layer in between; i.e., the islands are charge neutral and the Fermi level is located within the Na 3s band.

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