Surface Double Layer on (001) Surfaces of Alkali Halide Crystals: A Scanning Force Microscopy Study

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In this Letter we consider the surface double layer on (001) surfaces of UHV cleaved and annealed alkali halide crystals (KCl, NaCl), which we studied with dynamic scanning force microscopy and Kelvin probe force microscopy. Kelvin images show bright and round patches at corner sites and steps. Images with atomic resolution always show kinks at the latter step sites. Our findings are in perfect agreement with the long-standing picture that, due to the presence of divalent impurity ions, the surface carries a net negative surface charge originating from negative cation vacancies at kinks.

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Because of their insulating character, surfaces of ionic crystals have been frequently used as substrates. They have become important in many research areas of nanotechnology such as in the field of self-organized molecular [1,2] and magnetic nanostructures [3] and catalysis[4].

However, very little attention has been paid to a very important characteristic of ionic materials which concerns the so-called *surface double layer* and which probably plays an important role in the above mentioned surface processes. Already in 1946, Frenkel pointed out that, in thermal equilibrium, pure ionic crystals possess a charged surface and a region of space charge of opposite sign below the surface as soon as the free energies of formation for cation and anion vacancies differ [5,6]. This so-called *intrinsic case* is dominant at elevated temperatures for, e.g., alkali halide crystals because the formation energy is indeed different for cation and anion vacancies [7,8]. However, at relatively low temperatures like at room temperature, the so-called *extrinsic case* predominates [7,8] due to the presence of divalent cation impurities such as Ca^{2+}, which can be found in any normal alkali halide crystal of even highest available purity. The existence of divalent impurities demands a creation of cation vacancies in order to conserve charge neutrality. At thermal equilibrium, a surface double layer is created in that the negative net charge of the cation vacancies on the surface is compensated by the positive impurities below the surface forming a surface dipole [7].

For more than ten years, the surface double layer of silver halides (AgCl and AgBr [9]) and of alkali halides (NaCl [10–14], KCl [13,14], KBr [14]) has been extensively studied with various experimental techniques. Also much theory can be found in literature dealing with the modeling of the surface double layer [6–8,15–18]. It is well known that in the extrinsic case, alkali halides possess a net negative surface charge originating from negative cation vacancies. Because the above mentioned experiments probed the complete surface globally and not locally at nanometer scale, it was believed for a long time without direct proof, that the negative cation vacancies are located at kinks of steps [8,17–19].

Dynamic scanning force microscopy (SFM) is a suitable technique to investigate this net charge in vacuum, locally with nanometer or even with atomic resolution [20]. Recently we reported on UHV cleavage induced charging phenomena, which we observed on (001) surfaces of alkali halides and magnesium oxide by force spectroscopy and Kelvin probe force microscopy (KPFM) [21,22]. A large part of these cleavage induced charges disappeared after a sufficiently long time or after annealing, but we could still observe a strong KPFM contrast especially at cleavage steps. Because of the relatively low resolution of the KPFM contrast we could not attribute the contrast to precise surface sites. We speculated that the contrast was probably due to *residual charges* at atomic sites [22].

We applied KPFM and atomic resolution dynamic SFM imaging in order to study the Kelvin contrast and the corresponding topography more in detail. In this Letter, we show that in KPFM images, only bright and round patches can be observed at corner sites and steps. The latter steps have been imaged with atomic resolution and always kinks at the positions of the bright patches were found. We believe that the kinks are indeed negatively charged as believed since a long time [8,17–19], which might play an important role in many surface processes (see, e.g., Ref. [23]).

All alkali halide crystals were produced in our lab by the Czochralski growth method in a similar way as described in Ref. [24] and had Ca^{2+} ions as the main impurity source. The surfaces were prepared by UHV cleavage at room temperature followed by annealing in an UHV oven at 150–200 °C [21,22]. The crystals were annealed for a couple of hours in order to put them into their equilibrium charge state [22]. Experiments were performed in the low 10^{-10} mbar pressure range and at room temperature with a dynamic SFM (Omicron STM/AFM, digital demodulator from nanoSurf). We used conductive silicon cantilevers (p-Si, 0.015 Ω cm, Nanosensors) which were annealed in an UHV oven at 250 °C for 5–10 h. In KPFM, a dc (U_{dc}) and ac voltage (U_{ac}) are applied between tip and surface [25], in our case the voltage is applied at the rear side of the sample (tip at ground). The electrostatic tip-surface interaction is minimized at each point on the surface yielding the contact potential difference $U_{\mathrm{dc},0}$ between tip and surface. The latter can be, however, strongly modified by charges on the surface in the case of an insulator [22,26]. The setup of our Kelvin force microscope is described in Ref. [22]. Images which show the dc voltage are called *potential images* in the following.

In Figs. 1(a) and 1(b) a topography and corresponding potential image are shown, respectively, which were recorded simultaneously during one KPFM measurement on a (001) surface of a pure KCl crystal (~99.99% purity). Atomically flat terraces can be seen in the topography image [1(a)] which are separated by monoatomic high steps. At corner sites of crossing steps and at steps with higher indices (e.g., see dotted ellipse), the potential image shows bright patches with a diameter of ~20 nm. At these patches a more positive voltage $U_{\mathrm{dc},0}$ was needed for the compensation of electrostatic forces (bright) in comparison to terrace sites (dark). Most of our measurements show that long and straight sections of ⟨001⟩ steps do not exhibit bright patches in potential images. Only occasionally we observed bright patches also at these steps as it can be seen at the step marked by the dotted circle in Fig. 1(a). At this position, we performed constant height measurements with a larger magnification but without the Kelvin modulation technique. One image of the step with almost atomic resolution is shown in Fig. 1(c). The ⟨001⟩ step changes 2 times its orientation introducing two kinks at position (1) and (2). At, or in the vicinity of the kink sites, two black spots with a lateral size of 0.5 nm can be seen. The image contrast does not allow to follow precisely the atomic structure of the step. However, we strongly anticipate that the black spots are located directly at the two kinks of the step. A similar pronounced contrast at kink sites was also previously observed [27] and explained by calculations [28].

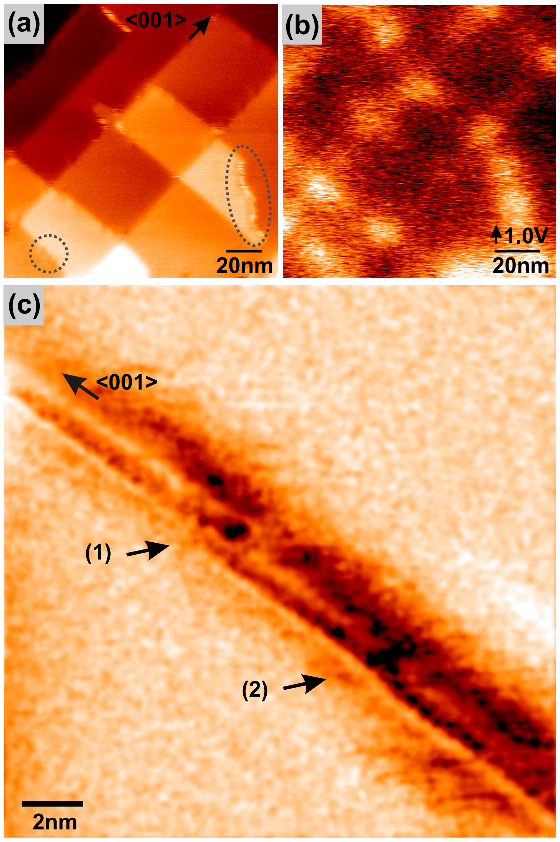

FIG. 1 (color online). Topography (a) and potential image (b) recorded during a KPFM measurement on the KCl(001) surface. (b) Voltage difference between patches and adjacent terrace sites: 0.4 V, absolute value on terraces: 0.6 V. (c) Constant height image recorded in the surface region marked by the dotted circle in (a). A black contrast corresponds to a more negative detuning value. (a),(b) $150 \times 150\ \mathrm{nm}^2$, $f_0 = 69.2$ kHz, $A_{p-p} = 15$ nm, $k = 2.4$ N/m, $\Delta f = -19$ Hz, $U_{\mathrm{ac}} = 1.5$ V, $f_{\mathrm{ac}} = 470$ Hz; (c) $18 \times 18\ \mathrm{nm}^2$, $\Delta f = -52.4$ Hz.

In all of our potential images, we observed bright and round patches only at low coordinated surface sites. We determined a density of 10^{10}–10^{11} patches/cm^2 for our pure KCl and NaCl crystals. Because we observed almost only bright and not dark patches in our potential images [29], we believe that the bright contrast reflects on a net surface charge of one sign. As mentioned above, it is known that KCl and NaCl crystals with positive divalent impurity ions have a net negative charge on the surface at room temperature [7,10–12] due to the surface double layer. The positive divalent impurity ions create negative cation vacancies, which condense on the surface. The impurity ions form a positive space charge layer below the surface. Some recent works show that the negative cation vacancies are expected to be preferentially located at kink sites of steps, rather than on flat terraces [8,10]. As a result, an excess of negative kinks is present on the surface and the surface carries a net negative charge. We strongly anticipate that this long-standing model does indeed explain our observations—the bright patches in our potential images are due to negative corners and kinks.

If the tip is placed above a negative kink at a distance of ~1–2 nm, which is the normal working distance in KPFM, then the tip apex feels an electrostatic force due to the uncompensated charge of the kink [27]. If we assume the latter, the sign of this *charge* can be determined only from our Kelvin measurements. Terris *et al.* proposed a model for the interaction between a tip and a point charge [30], which is drawn in Fig. 2(a). A surface point charge with negative charge (q^-) induces an image charge of opposite sign in the tip (q^+) producing an attractive electrostatic force on the tip [30]. In order to compensate the electrostatic force, a negative charge (q_t^-) must be put into the tip, which is realized by a positive voltage ($U_{\mathrm{dc}} > 0$) with

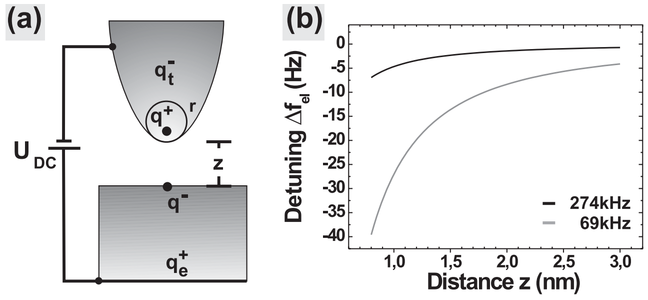

FIG. 2. Interaction between the tip with a point charge. (a) Model of Terris *et al.* [30], (b) calculated detunings for the $f_0 = 69$ kHz ($k = 2.4$ N/m, $A_{p-p} = 15$ nm) and $f_0 = 318$ kHz ($k = 37$ N/m, $A_{p-p} = 23$ nm) tip with a radius r of 10 nm.

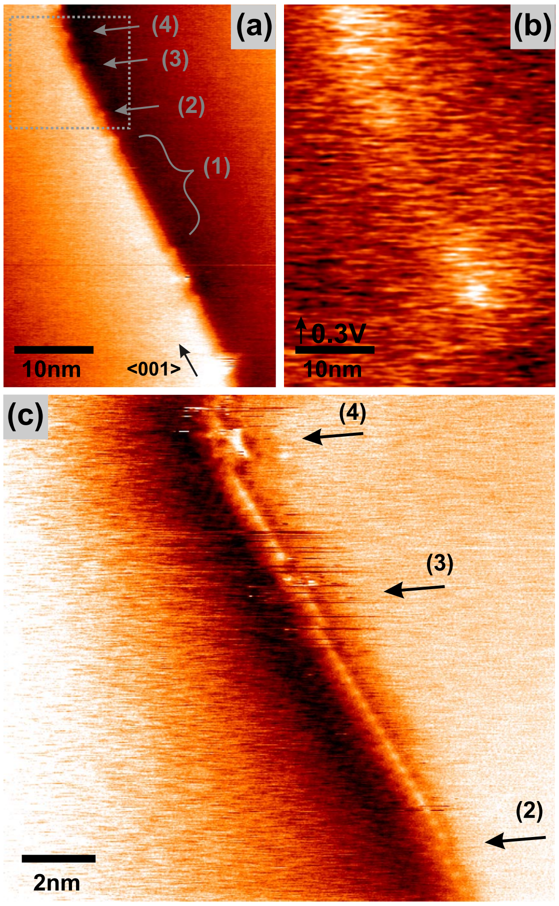

FIG. 3 (color online). Topography (a) and potential image (b) recorded during a KPFM measurement on a doped NaCl(001) surface. (b) Voltage difference between brightest patches and adjacent terrace sites: 0.3 V, absolute value on terraces: -0.1 V. (c) Constant height image recorded in the surface region marked by the dotted square in (a). (a),(b) 34×48 nm^2, $f_0 = 318$ kHz, $A_{p-p} = 23$ nm, $k = 37$ N/m, $\Delta f = -9$ Hz, $U_{ac} = 2.0$ V, $f_{ac} = 470$ Hz; (c) 14×15 nm^2, $\Delta f = -12.1$ Hz.

charge q_e^+ at the rear side of the sample. This is in perfect agreement with the bright patches we observed in our potential images—a more positive bias voltage $U_{dc,0}$ was needed for the compensation than in comparison to voltages of terrace sites.

We can roughly estimate, if a charge with an equivalent amount of one electron ($q^- = e$), can indeed produce a sufficiently large contrast for the force microscope. For simplicity, we assume that the tip can be modeled by a metallic sphere with radius r positioned in a distance z above the charge, so that the force is given by $F_{el} = 1/(4\pi\varepsilon_0)[(q^-)^2 r(z + r)]/[(z^2 + 2zr)^2]$ [31]. In dynamic SFM, the detuning of the cantilever oscillation Δf is measured, which can be calculated with help of the following equation [32]: $\Delta f_{el} = (2f_0^2/kA_{p-p}) \int_0^{1/f_0} F_{el}(z') \times \cos(2\pi f_0 t)dt$, $z' = z + \frac{A_{p-p}}{2}(1 + \cos(2\pi f_0 t))$. The parameters k, f_0, Δf, and A_{p-p} denote the spring constant, cantilever resonance frequency, detuning, and the peak-to-peak amplitude. Numerical integration of the force F_{el} for our two types of tips shows, indeed, that the detuning curves exhibit values of several Hz for distances below 2 nm [Fig. 2(b)], which is in agreement with results of similar calculations [33]. We believe that this is sufficient to be detected by the Kelvin microscope. Because the complete spherical tip apex gets polarized by the surface charge, the lateral resolution is roughly given by the tip radius—this is in agreement with the bright patches which all have same sizes within an image. The size of approximately ~20 nm is indeed comparable to real tip diameters.

In order to test our interpretation further, alkali halide crystals with a known amount of divalent impurity cations can be used. The presence of positive divalent impurity ions demands a creation of cation vacancies [7]. Both form a surface double layer with a net negative surface charge [7]. The net charge should then be formed by negative kinks on the surface [8] producing a bright contrast in the potential images. We performed KPFM measurements on NaCl crystals, which were doped with divalent Mg^{2+} impurity ions (99.9% NaCl, 0.1%$MgCl_2$). One of these measurements is shown in Figs. 3(a) and 3(b). The topography image [3(a)] shows a monoatomic high ⟨001⟩ step. At some parts of the step, a bright contrast in the potential image [3(b)] can be seen, which we observed also in many other surface regions—the surface carries a net negative charge indeed. The small scale of the topography image [3(a)] already permits one to see subtle features at the step. In comparison to the long section of the step in region (1), which appears straight and smooth, the step exhibits sometimes small bright dots at other places, e.g., at positions (2), (3), and (4). Around these dots, a bright contrast in the potential image can be seen. Without the Kelvin modulation technique, we acquired a constant height image with atomic resolution in the region of the bright dots. The constant height image [3(c)] shows clearly the ionic arrangement of the ions on the upper terrace but also of the step forming ions. The dots (2), (3), and (4) are in fact kinks of the step where the step changes its ⟨001⟩ direction. Also here we believe that the bright patches in the potential image [3(b)] are due to negative kinks.

The surface double layer on which we comment in this Letter comprises several aspects and messages with different motivations for the future. (i) As stressed before [34], the surface double layer probably explains the discharge of the surface charging, which we observed after cleavage in UHV [22]. The cleavage produces a charging on the surface in a nonequilibrium state which reorganizes by time in that an equilibrium is installed by the formation of a surface double layer. (ii) Dislocations are also assumed to be sources or sinks of charged vacancies [16,35]. The force microscope in its Kelvin mode and with its capability to image surfaces with atomic resolution can largely contribute in the investigation of dislocations. In order to produce dislocations, the crystal has to be put under mechanical stress [35]. However, we believe that it might be sufficient to examine the surface right after the cleavage in UHV without additional annealing because cleavage already produces dislocations. (iii) We believe that the net surface charge probably plays an important role in many surface processes, e.g., in the deposition of molecules or metal. As was shown in our recent study, electronic properties of gold nanoclusters on alkali halide surfaces get modified due to a modification of their work function by a possible charge transfer between clusters and surface [23]. We believe that surfaces of other materials such as MgO(001) also exhibit a surface double layer which can be studied by KPFM. Even in the case of nanometer thick insulating films a surface double layer is expected [36].

In conclusion, the surface double layer of KCl(001) and NaCl(001) was studied for the first time, locally, at nanometer and atomic scale by means of Kelvin probe force microscopy and atomic resolution dynamic SFM. We could verify that a net surface charge of one sign exists producing only bright patches in our Kelvin images which are exclusively located at corner sites and steps. At the latter steps, kinks can always be found as we verified with atomic resolution imaging. Because of the known sign of the surface net charge from literature and due to a simple model that explains contrast formation in KPFM, the corners and kinks are negatively charged as it was assumed for a long time.

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