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Sublattice identification in noncontact atomic force microscopy of the NaCl(001) surfaceR. Hoffmann,¹ D. Weiner,^{2,3,*} A. Schirmeisen,^{2,3} and A. S. Foster^{4,5}¹*Physikalisches Institut and DFG Center for Functional Nanostructures (CFN), Universität Karlsruhe, D-76128 Karlsruhe, Germany*²*Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany*³*Center for Nanotechnology (CeNTech), Heisenbergstraße 11, 48149 Münster, Germany*⁴*Department of Applied Physics, Helsinki University of Technology, P.O. Box 1100, Helsinki 02015, Finland*⁵*Department of Physics, Tampere University of Technology, P.O. Box 692, Tampere 33101, Finland*

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We compare the three-dimensional force field obtained from frequency-distance measurements above the NaCl(001) surface to atomistic calculations using various tip models. In the experiments, long-range forces cause a total attractive force even on the similarly charged site. Taking force differences between two sites minimizes the influence of such long-range forces. The magnitude of the measured force differences are by a factor of 6.5–10 smaller than the calculated forces. This is an indication that for the particular tip used in this experiment several atoms of the tip interact with the surface atoms at close tip-sample distances. The interaction of these additional atoms with the surface is small at the imaging distance, because symmetric images are obtained. The force distance characteristics resemble those of a negative tip apex ion which could be explained, e.g., by a neutral Si tip.

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I. INTRODUCTION

A scanning force microscope (SFM) operated in the dynamic mode, where severe tip damage due to hard contact between tip and sample can be avoided, cannot only be used to image surfaces with atomic resolution, but also the force as a function of tip-sample distance on specific atomic sites can be measured.^{1–3} The method has first been demonstrated on the (111) surface of the semiconductor Si,^{4,5} and has then been applied to ionic crystalline^{6,7} and oxide surfaces.^{8,9} It has been shown that identification of atomic species on semiconducting surfaces is possible through a careful study of the force as a function of tip-sample distance.¹⁰ On many insulating surfaces with a distribution of positive and negative charge, identification of the positively and negatively charged atomic sublattices is difficult, since the charge of the imaging ion on the tip is unknown. For the CaF₂ (111) surface composed of one positively charged Ca²⁺ and two negatively charged F⁻, the different arrangement of the positively and the negatively charged ions and of the resulting forces allows the identification of the Ca²⁺ and F⁻ sublattices from SFM images,^{11,12} and this makes an analysis of the force as a function of distance easier.⁷ On NaCl-type (001) surfaces, however, the arrangement of positively and negatively charged ions is similar, and consequently the Na⁺ and Cl⁻ sublattices cannot be identified from SFM images alone. Recently, a comparison between calculated and measured data has shown that on the (001) surface of KBr, site-specific force-distance data can be used to identify the charge of the imaging ion on the tip.^{6,13} Calculating force differences between two sites allow to eliminate long-range forces due to residual surface charge¹⁴ and due to the van der Waals interaction. Similarly, it has been proposed that an analysis of the force as a function of distance should allow to identify the charge of the imaging ion on the tip for the (001) surface of NaCl,¹⁵ a surface that has been recently studied with three-dimensional force measurements.¹⁶ The goal of this paper is

to investigate whether the charge of the imaging ion on the tip can indeed be determined from force-distance data for the case of NaCl(001). To do this, the force as a function of distance on the maximum, the minimum and on the bridge site is measured and compared to calculations. Long-range forces are eliminated by calculating force differences between two atomic sites. We show that even for tips where several atoms of the tip interact with the surface, it is possible to determine the charge of the main imaging ion. In the case of a neutral Si imaging atom, the characteristics of the tip-sample interaction still allow to determine the position of the positively and negatively charged surface sublattices.

II. METHODS**A. Experiment**

For the measurements, clean NaCl(001) surfaces have been prepared by cleaving in air and subsequently annealing to 520 K in ultrahigh vacuum for one hour a commercial NaCl crystal (Mateck GmbH, Germany) under ultrahigh vacuum conditions (about 2×10^{-10} mbar). The crystal was then moved to the SFM chamber without breaking the vacuum and investigated using a commercial Nanosensors Si cantilever with a force constant of 21 N/m and a resonance frequency of 280407 Hz equipped with a supersharp Si tip of a nominal radius of 2 nm. The cantilever was oscillated with an amplitude of 4.5 nm determined from stepwise changing of the excitation voltage during imaging. After finishing the measurements, the oscillation amplitude was checked again—no change was detected. First, in order to cover the tip apex with NaCl, the tip was brought into soft contact with the sample surface by slowly decreasing the tip-sample distance until the excitation amplitude reached the upper limit of its output range. Then symmetric atomic resolution images were obtained at a frequency shift of -144.9 Hz (Fig. 1). The assumption that the tip could indeed be covered with

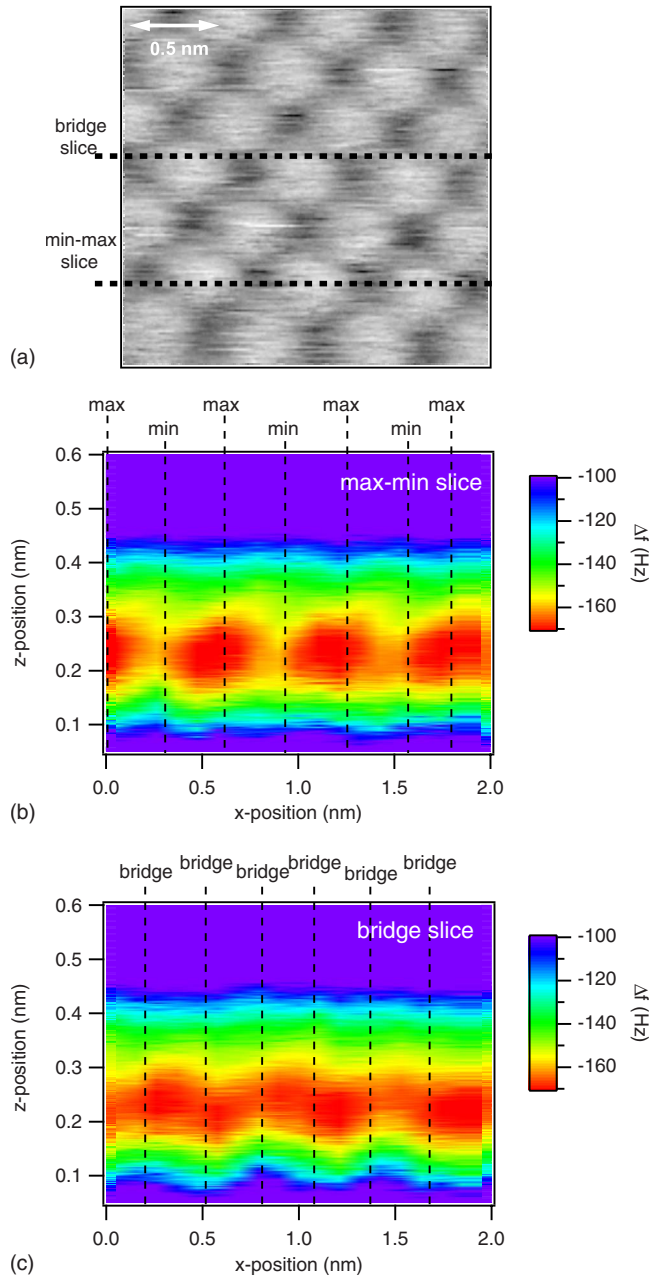


FIG. 1. (Color online) (a) Atomic resolution image obtained on the NaCl(001) surface at $\Delta f = -144.9$ Hz. (b) Slice of the three-dimensional frequency-shift data across the position of the topographic maximum and minimum. (c) Slice of the three-dimensional frequency-shift data across the bridge positions.

sample material is supported both experimentally and theoretically: in experiments, instabilities have been observed when an oxide covered Si tip is brought to the vicinity of an NaCl surface.¹⁵ In calculations, hopping of Na⁺ and Cl⁻ surface ions to the apex of a MgO tip representing the oxidized Si tip have been observed.¹⁵ However, since the effect of the tip-sample contact cannot be checked experimentally, a number of materials are considered for the tip in this paper.

To obtain the three-dimensional force field we measured 400 frequency shift versus distance curves on a 20×20 grid of equidistant points covering a total area of 2×2 nm² using

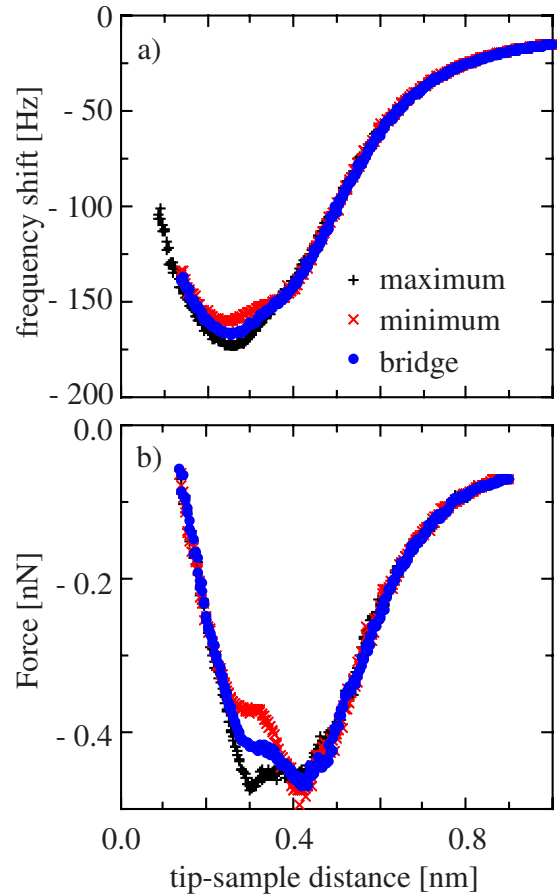


FIG. 2. (Color online) (a) Experimental frequency shift and (b) short-range forces at specific atomic sites (maximum, minimum, and bridge site).

the following protocol. First, frequency distance data were measured on 20 equidistant points along the x axis while the feedback was disabled. After each of these 20 points the feedback was switched on to stabilize the distance of the tip to the surface. Then the surface topography was imaged during 10 scanlines with the feedback enabled and then the procedure was repeated. The comparison of topography and frequency distance data allowed us to locate the position of the curves with respect to the topographic surface sites.

In Figs. 1(b) and 1(c) we show the raw data of the acquired frequency shift versus tip-sample distance along the x axis, represented in two-dimensional frequency-shift slices in x - z space, for two different positions on the y axis, as indicated in Fig. 1(a). Figure 1(b) shows a two-dimensional frequency-shift slice along a line across the topographic minima and maxima of the surface which can be identified with the positions of the two ionic species. Figure 1(c) shows the two-dimensional frequency-shift slices along the line between two atomic rows, i.e., across the bridge positions. The data shows lattice periodicity of the NaCl surface thus demonstrating the high reproducibility of the individual frequency-shift curves. In all frequency versus distance graphs the tip-sample distance (z axis) is taken to be the minimal distance reached during one oscillation cycle. The offset of the z axis is chosen in Figs. 1 and 2 such that the frequency shift is zero at $z=0$. In the following this offset

will be modified as one parameter to find better agreement with the simulations.

For the subsequent quantitative analysis, the frequency shift data over the specific atomic sites was then determined as an average over measurements above 3–4 equivalent sites indicated by dashed lines in Figs. 1(b) and 1(c). The averaged frequency-shift data is represented in Fig. 2(a). The frequency-shift data was converted to force using the method described in Ref. 17 and smoothed over ten data points [Fig. 2(b)]. These conversion methods are well understood and have been used successfully by different groups (see, e.g., Refs. 4, 7, and 10). Several methods give similar results^{17–19} and the dependence of the converted force on the oscillation amplitude has been thoroughly checked.²⁰ The data was cut at small tip-sample distances such that the part where differences between the two equivalent bridge sites occur is eliminated. The average over both bridge sites is used for the analysis. At tip-sample distances of about 0.2–0.4 nm, differences between atomic sites are clearly observed both in the frequency shift and in the force. In all three force-distance curves, a clear minimum at large tip-sample distances is followed by another shoulder at smaller tip-sample distances. Such a behavior has been observed before,¹⁶ and the first minimum has been interpreted as the interaction of the front-most tip atom with the surface while the shoulder has been attributed to the interaction of several atoms of the tip with the surface at distances closer than the imaging distance.⁸

B. Theory

The calculations were performed using atomistic simulations as implemented in the codes SCI-FI (Ref. 21) and MARVIN.²² The interatomic forces are computed from a sum of pairwise Buckingham potentials acting between ions treated atomistically. Ions are treated in a shell model with coupled oppositely charged cores and shells in order to describe their polarizabilities. Parameters for the species considered were taken from Refs. 23–25. Unless specified, all cores and shells were allowed to relax completely with respect to interatomic forces. Full details of the general methodology of simulating dynamic mode SFM images and force-distance data can be found in Refs. 26 and 27.

The properties of the NaCl (001) surface are well understood, and can be well represented by a slab of 4 layers containing 10×10 ions with those in the bottom layer kept fixed [see example setup in Fig. 3(a)]. In contrast, the atomic details of the tip are to a large extent unknown. In our experiments we expect that the apex of the silicon tip was initially covered with native oxide and hydroxyl species due to exposure to the atmosphere. However, it is well known that in the course of an experiment material can be deposited on the tip. In order to provide a comprehensive study we consider several possibilities in this work. To represent an oxidized tip, we use a 64-atom cubic cluster of MgO, which can be oriented such that the (111) direction is perpendicular to the surface with either an Mg or O atom at the apex [Figs. 3(a) and 3(f)]. Previously, it has been shown that a magnesium oxide (MgO) cluster describes well the electrostatic field emitted by a partially oxidized silicon cluster.²⁸ This

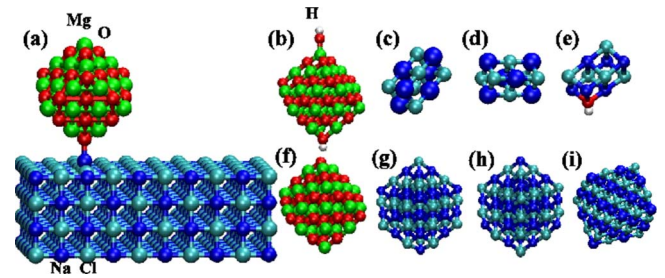


FIG. 3. (Color online) Atomic structures from simulations of (a) NaCl surface and O-terminated MgO tip (MgO-O), (b) OH-terminated MgO tip (MgO-OH), (c) short-edge NaCl cuboid tip (cub-sh), (d) long-edge NaCl cuboid tip (cub-lg), (e) OH-terminated NaCl cuboid tip (cub-OH), (f) Mg-terminated MgO tip (MgO-Mg), (g) Na-terminated NaCl tip (NaCl-Na), (h) Cl-terminated NaCl tip (NaCl-Cl), and (i) Na-terminated NaCl tip tilted by 30° (NaCltilt-Na).

can be modified to include the effects of water contamination by replacing an oxygen at the apex with a hydroxyl group [Fig. 3(b)]. A similar cube can be constructed from NaCl to represent tip contamination from the surface [Figs. 3(g) and 3(h)], but we also consider clean and water contaminated smaller NaCl cuboids [Fig. 3(c)–3(e)], which have been shown previously to provide a variety of different tip-surface interactions.²⁹ For all tip models, roughly the upper one third of atoms were kept frozen to represent the macroscopic part of the tip. The tip-sample distance is defined as the distance between the atomic cores in their unrelaxed positions. This definition has been used to represent the data in Figs. 4 and 5. However, from experiments, the absolute tip-sample distance is often unknown. Therefore in Fig. 6 for the overview comparing all model tips with the experiment, all curves have been normalized such that $z=0$ corresponds to the position of the first maximum in the minimum-maximum curves which is best suitable for a comparison of the shape of the curves.

III. RESULTS

The experiments show an attractive total force on all sites [Fig. 2(b)] while most of the tips used for calculations show small forces or even repulsion on the oppositely charged ion. Although the overall magnitude of the total experimental force is only slightly larger than expected from the calculations, this could be at least partially due to long-range forces. In previous publications (see, e.g., Ref. 15) we have used models to determine the long-range force. Since only the total force is measured, and the precise tip-sample distance and thus the onset of short-range forces is unknown, it is difficult to choose a suitable distance range for fitting. From a careful comparison with theory, one can determine the onset of the short-range forces to within about 0.1 nm. One can then fit the long-range forces with a suitable function in the range above the onset of the long-range forces, 0.1 nm in Fig. 6. However, the region where the correct determination of the long-range forces is crucial is the region below 0.1 nm, where short-range forces are important. In this region,

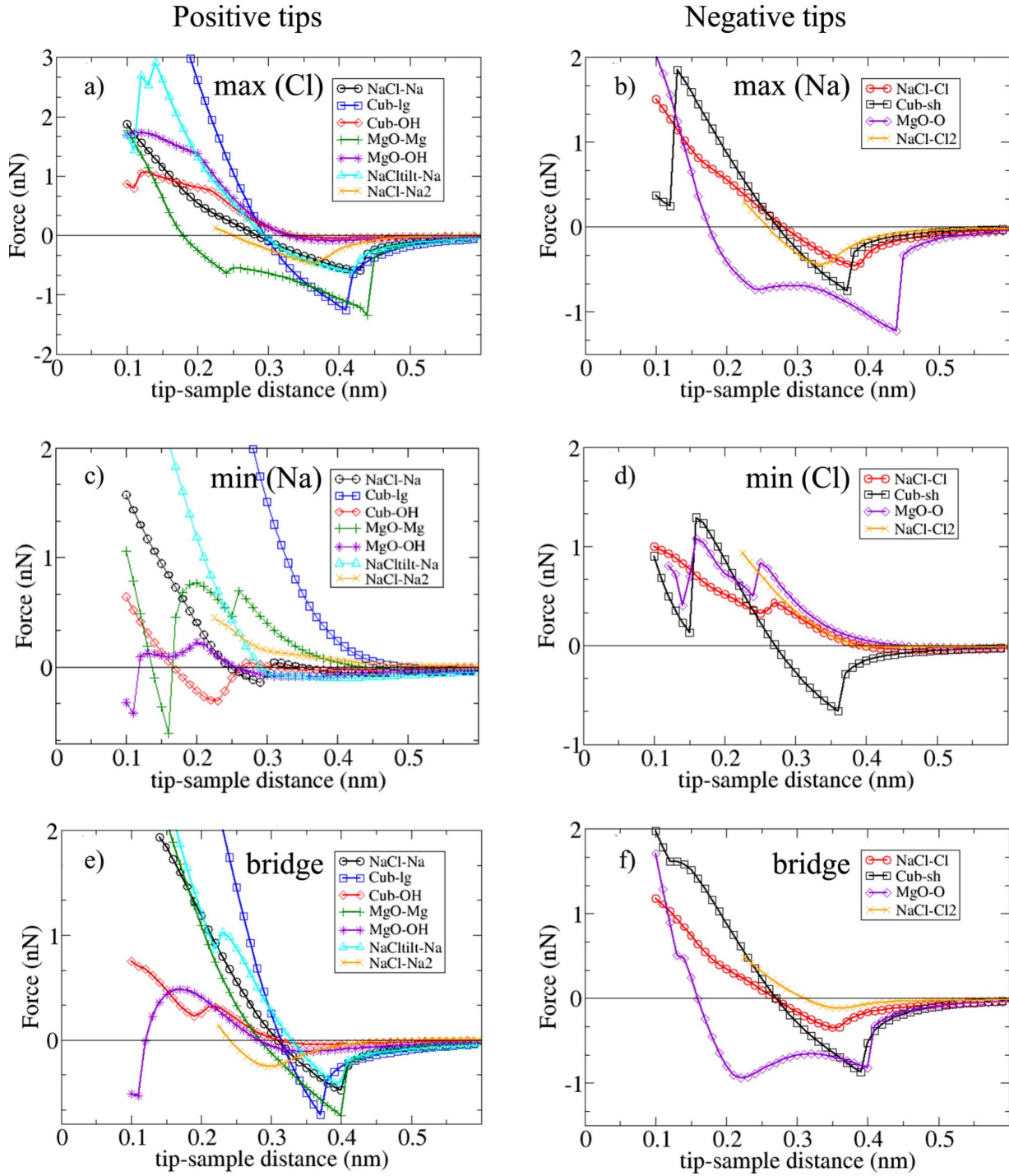


FIG. 4. (Color online) Calculated forces: maximum for tips with strongest attraction to (a) surface anions and (b) surface cations; minimum for tips with strongest attraction to (c) surface anions and (d) surface cations; bridge for tips with strongest attraction to (e) surface anions and (f) surface cations. All x axes of the curves have been taken directly from the calculations.

the long-range contribution is obtained by extrapolation and the reliability of the assumptions cannot rigorously be tested. To circumvent these difficulties, similar to the method proposed in Ref. 6, we calculate the force differences between two atomic sites (Fig. 5).

As a first model for understanding the measured experimental curves, we consider a tip contaminated by NaCl from the surface.³⁰ In Fig. 5 we compare the experimental force

difference curves with those for NaCl-Na and NaCl-Cl tips.⁶ For all force differences, the calculated values are about a factor of 6.5–10 larger than the measured ones. In comparison with Ref. 15 the measured force differences are about a factor of 6 smaller. We first carefully checked whether this could be explained by systematic experimental errors. The total systematic experimental error in the calibration factor for the frequency to force conversion amounts to $\pm 50\%$, and

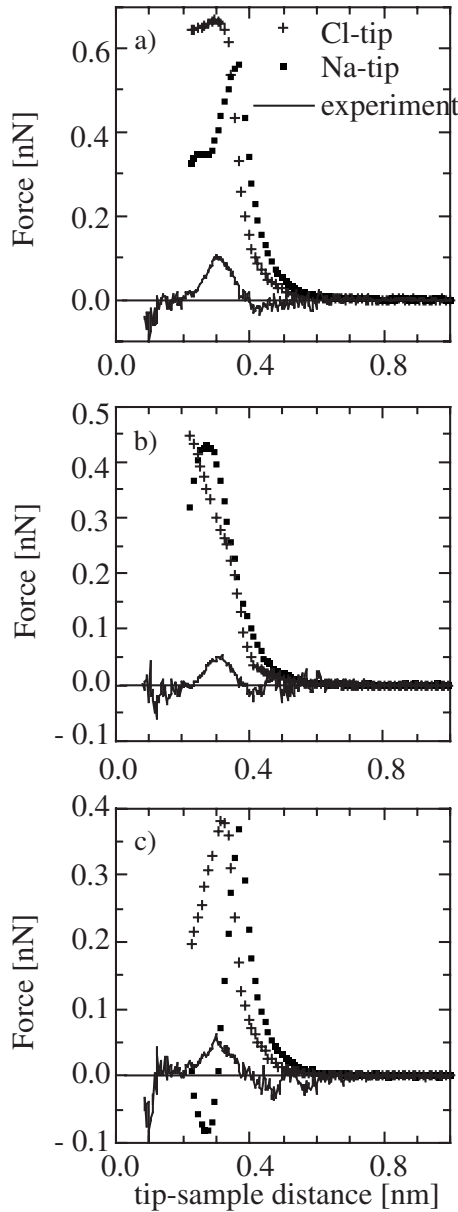


FIG. 5. Measured force differences (black line): (a) $F_B - F_A$, (b) $F_B - F_C$, and (c) $F_C - F_A$, where A is the topographical maximum, B the minimum and C the bridge site. For comparison the results of the atomistic simulations for the NaCl tips have been included in this graph (square and cross symbols).

therefore it cannot explain the quantitative differences between experimental and calculated results. In addition, we estimate that the drift was smaller than 0.003 nm/s and can also not explain the quantitative differences between experiment and calculations.

Since experimental errors cannot explain the difference between measured and simulated force differences, it is important to check the applicability of the model for the tip-surface interaction. Calculated forces depend on the interatomic potentials, known with good accuracy, and on the relaxations of the individual atoms which in turn depend on the interatomic forces, but also on the microscopic structure of the tip.^{12,29} For KBr, for the negatively terminated tip,

density-functional theory (DFT)-based calculations yield forces of about a factor of 2 smaller than atomistic simulations, while for the positively terminated tip forces of a similar magnitude are obtained.³¹ This could be due to a better modeling of electronic interactions. However, due to the larger calculation times needed for DFT-based calculations, the tip in Ref. 31 comprised only 12 atoms and thus the relaxation could have been underestimated. Our data shows that the relaxation, in particular on the minimum site, concerns atomic layers that are not represented in the 12-atom tip. It is reassuring that despite the different methods used, the overall features of the force, in particular the position and relative magnitude of the force minima at the basis of the sublattice determination, compare well in both approaches.

One important aspect of tip modeling is to understand whether the observed relaxations are typical for one particular atomic configuration or whether similar behavior is expected for other atomic configurations. We have pointed out previously (Ref. 6) that while the relaxations are symmetry conserving on the maximum and on the bridge sites, the tip relaxes sideways on the minimum site, because the frontmost tip atom is attracted by the nearest neighbor ions of opposite sign. The magnitude of this effect could strongly depend on the microscopic tip structure and its relative orientation to the substrate. In order to consider this possibility we calculated force difference curves for all the tips shown in Fig. 3 and they are plotted in Fig. 6. Positively terminated tips, i.e., tips with strongest attraction to surface anions are shown on the left side [Figs. 6(a), 6(c), and 6(e)] while negatively terminated tips with strongest attraction to surface cations are shown on the right side [Figs. 6(b), 6(d), and 6(f)]. The Cub-sh tip that does not really fit into this classification is represented in Figs. 6(b), 6(d), and 6(f). Indeed we observe that, despite the variety of tip structures considered compared with Ref. 6, positively and negatively charged tips show characteristic differences if one excludes OH-terminated tips which show force differences much smaller than the ones observed experimentally. All tips, positively and negatively terminated ones show a nearly linear region at tip-sample distances smaller than -0.05 nm up to about -0.18 nm. For the positively terminated tips, the slope of the force difference is mostly negative with increasing tip-sample distance, while it is mostly positive for negatively terminated tips. The Cub-sh tip exposes one positively charged ion and one negatively charged ion to the sample, and shows vanishing slope of the force difference in this distance regime. The Cub-1g tip exposes two positively charged ions and one negatively charged ion to the sample, and shows a negative slope smaller than other positively terminated tips.

Although we now have a large variety of behavior in the force difference curves, the quantitative mismatch of the measured and calculated force differences remains. We also considered various nonsymmetric orientations of these tips, but it made no significant quantitative difference in the results (compare NaCl-Na and NaCltilt-Na in Fig. 6(a)).

IV. DISCUSSION

When suggesting tip configurations suitable to explain our experimental findings, the main restrictions for possible

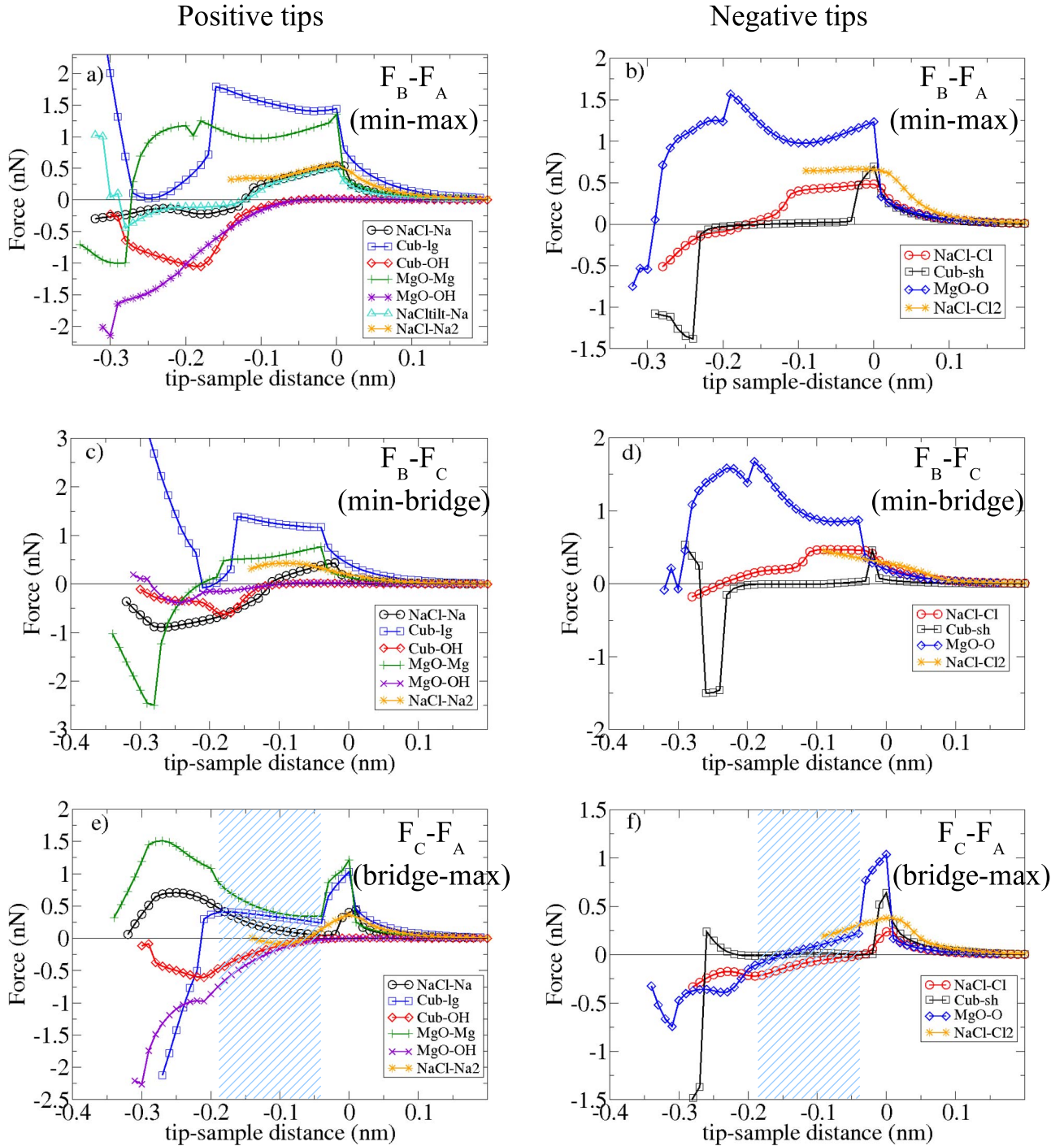


FIG. 6. (Color online) Calculated force difference curves: $F_B - F_A$ for tips with strongest attraction to (a) surface anions and (b) surface cations; $F_B - F_C$ for tips with strongest attraction to (c) surface anions and (d) surface cations; $F_C - F_A$ for tips with strongest attraction to (e) surface anions and (f) surface cations where A is the topographical maximum, B the minimum and C the bridge site. All x axes of the curves have been normalized so that zero is at the position of the first maximum in the minimum-maximum curves. The hatch shows the region where a nearly linear slope is observed. This slope is characteristic for the tip termination for all tips except the OH-terminated tips. The z axes of all models are normalized such that the maxima in the min-max curve match and are set to 0.

models comes from two experimental observations: the symmetry of the atomic resolution images and the magnitude of the measured short-range forces. Symmetric images could be obtained by two general types of tips, tips where the tip material is in registry with the surface, or tips where additional ions contributing to the contrast are relatively far (i.e.,

a significant fraction of the interatomic distance of NaCl) from the tip apex. Models, where the tip material is in registry with the surface, such as Cub-sh and Cub-Ig tips, generally result in comparable or larger forces to atomistically sharp NaCl-Na or NaCl-Cl tips,²⁹ and hence much larger forces than measured here. If we assume an ionic model for

the tip then, in order to account for the symmetric images observed additional tip atoms must be relatively far from the tip-apex ion. Chemical species other than NaCl could be present on the tip at a position far enough from the tip apex to allow symmetric imaging, but close enough to reduce the total tip-sample interaction at the point where maximal attraction is observed. This is actually a similar situation as the one discussed in Ref. 7.

Assuming that these additional atoms only affect the magnitude of the force minimum as well as the shape of the curves at tip-sample distances smaller than about 0.3 nm (the position of maximal attraction), but not its position itself, we proceed with the following comparison between experimental and calculated data. For comparing experimental and calculated results, the respective tip-sample distances must be matched. We first determined the relative tip-sample distance in a way that the agreement for the negatively terminated tip for the force difference $F_B - F_A$ between maximum (A) and minimum (B) sites was good. For this choice of the z -axis offset, we obtain reasonable agreement between calculations and experiment for the z value of the strongest attraction in the force difference $F_C - F_A$ between bridge (C) and maximum (A) sites. Deviations of the force difference $F_B - F_C$ between minimum (B) and bridge (C) sites could be explained by differences of the lateral flexibility between the tips used for the calculations and for the measurements. We then checked whether a similarly fair agreement could be obtained when the offset of the z axis was determined such as to best fit the positively terminated tip for the force difference $F_A - F_B$. In order to obtain such an agreement, the experimental data must be shifted by about 0.15 nm toward positive z values. If this is done, the intersection of the calculated curve with zero force for $F_C - F_A$ is not represented by the experimental data. This intersection had been used in Ref. 7 to determine that the tip charge was positive. Also strongest attraction for $F_B - F_C$ occurs for much too large distances. At these large tip-sample distances the tip does not bend sideways, we do therefore not expect deviations of the calculations from experiment.

This analysis is in agreement with a simple mechanical model, where the ions are treated as hard spheres.³² In such a model, the onset of strong repulsive forces is understood as the contact of hard spheres. Even though the differences in size between cations and anions are rather small, qualitatively, for the smaller positively charged tip, the onset of repulsive forces on the oppositely charged site—the maximum above Cl^- —is expected at larger tip-sample distances than on the similarly charged site—the minimum above Na^+ —i.e., [$z_{\text{rep}}(\text{max}) > z_{\text{rep}}(\text{min})$]. For the larger negatively charged tip, the opposite behavior is expected [$z_{\text{rep}}(\text{min})$

$> z_{\text{rep}}(\text{max})$], because in this case the minimum is measured at the site of the larger similarly charged ion (Cl^-) compared to the oppositely charged ion (Na^+). For the experimental data shown in Fig. 2 this simple consideration also points to a negatively charged tip, if one assumes that at the first minimum in the force-distance curves the frontmost tip atom interacts with the surface.

These simple considerations remain valid if one includes the other positively and negatively terminated tips (see Fig. 4 and Ref. 29 for the force as a function of distance). In addition the analysis of the force differences remains qualitatively valid for these tips. It is not valid for the OH-terminated tips, but the forces from these tips are much smaller than those observed experimentally. The tips that are not atomically sharp (Cub-sh and Cub-lg) also show qualitatively somewhat different behavior. In particular the Cub-sh tip shows a flat slope of the force difference between bridge and maximum at distances between -0.18 and -0.05 nm and therefore best matches the overall shape of the force-difference curves although we expect asymmetric images for such a tip that have not been observed experimentally.

A further possibility is, of course, that the actual tip structure is different from the models considered in this work. The most obvious candidates would be based on a clean silicon tip. Previous calculations have shown that the interaction of a reactive silicon tip³³ with insulating surfaces is strong and unlikely to provide a match.³⁴ However, silicon tips that are terminated by a dimer,³⁵ demonstrate much weaker site-to-site force variation across insulating, cubic surfaces³⁶ and would be a potential candidate to explain the experimental measurements. In addition we expect from preliminary studies that neutral Si tips qualitatively resemble negatively terminated tips. Silicon dimer tips are atomically sharp due to buckling in agreement with the symmetric images observed experimentally.

We conclude that the tip was terminated by several atoms, a considerable fraction of which was probably from a chemical species other than NaCl in spite of the indentation of the tip into the surface prior to the measurements. The dominant interaction with the surface was with a negatively charged tip ion or with a neutral atom resembling these characteristics qualitatively, such as Si.

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