Site-specific force-distance characteristics on NaCl(001): Measurements versus atomistic simulations

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A scanning force microscope was used to measure the frequency shift above various atomic sites on a NaCl(001) surface at 7 K. The data was converted to force and compared to the results of atomistic simulations using model NaCl and MgO tips. We find that the NaCl tip demonstrates better agreement in the magnitude of the forces in experiments, supporting the observation that the tip first came into contact with the sample. Using the MgO tip as a model of the originally oxidized silicon tip, we further demonstrate a possible mechanism for tip contamination at low temperatures.

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I. INTRODUCTION

Over the past decade the scanning force microscope (SFM) has developed into a powerful tool for surface science.[1,2] In particular, by employing the noncontact dynamic mode in ultrahigh vacuum (UHV), Si adatoms and rest-atoms on the reconstructed Si(111)7×7 surface[3,4] have been located in atomically resolved images. Moreover, the tip-surface interaction force could be measured as a function of tip-sample distance above specific lattice positions.[5] By comparing drift-free measurements above different sites, the short-range component of the force could be determined and related to the formation of a single chemical bond. Since then, site-specific surface forces have been studied in detail on a few other samples, including KBr(001),[6,7] NiO(001),[8,9] CaF_2(111),[10] a carbon nanotube,[11] and graphite.[12] Such measurements are useful for understanding SFM resolution and contrast mechanisms and are more generally of interest for gauging interactions at surfaces. A determination of short-range forces, which allow resolution of atomic-scale features, can also help design controlled vertical, as well as lateral manipulation experiments, e.g., of native adatoms on the Si(111)7×7 surface[13] or Sn substitutional adatoms on the Ge(111) $c(2\times8)$ surface.[14]

However, in contrast to the Si(111) 7×7 surface, in most cases the separation of long-range forces is not straightforward, making the determination of short-range forces difficult. One approach to this problem is to compare the measured data to model calculations of the tip-surface interaction. Such calculations themselves pose a challenge because in most experiments little is known about the details of the geometry and chemical nature of the tip apex. The latter may even change during the course of an experiment by picking up material from the surface. In the above-mentioned study of KBr(001),[7] a KBr cluster was used to model the tip apex with good results, further supporting the idea that the tip is often contaminated with material from the surface. Such studies represent significant progress in understanding tip-surface interactions in SFM, but the validation of the assumed model tips requires extensive computations.

In this work, we study the interaction between a silicon SFM tip and a NaCl(001) surface. Previous noncontact SFM studies of this system demonstrated atomic resolution,[15–17] but here we present site-specific force curves over the two sublattices and compare them to simulations for several plausible model tips. We first describe atomically resolved images and site-specific frequency versus distance measurements. In order to gain insight into the forces extracted from those experiments, we then discuss atomistic simulations designed to model our force-distance curves and compare the results to our experimental data. The main goal of this investigation is to use the accurate quantitative information provided by low-temperature experiments combined with simulations to learn more about the nature of the tip apex and the resulting short-range tip-surface interaction.

II. METHODOLOGY

A. Experiment

The experiments were performed on the (001) face of a NaCl single crystal using a commercial (Nanosensors) silicon cantilever with a bending spring constant of c_b =48 N/m and a custom-built, low-temperature SFM operated in an ultrahigh vacuum (UHV) environment.[18] The NaCl sample was cleaved in ambient laboratory conditions and then quickly transferred into the vacuum system. Prior to performing the experiments, both cantilever and sample were cleaned by heating them to approximately 150 °C for 1 h in UHV. Immediately after the heat treatment, the cantilever and sample were transferred into the microscope chamber which was then cooled to approximately 7 K. The lateral temperature drift in this instrument is estimated to be at most 0.1 nm/h. The magnitude of the piezoelectric creep effect depends on the conditions of operation. Special care has been taken in order to minimize creep; for more details see Ref. 5.

After cooling, imaging of the NaCl sample was performed in the dynamic mode using a digital phase-locked loop frequency detection and cantilever excitation scheme.[19] In this

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mode of operation, forces acting on the tip at the free end of the cantilever as it swings close to the sample surface perturb the cantilever oscillation, giving rise to a small shift Δf of the resonance frequency from its unperturbed value $f_0 = 174\,836.91$ Hz. A feedback loop is used to control the tip-sample distance in order to maintain a constant shift, yielding images that correspond to contours of constant Δf. For all the experiments described here, the tip was driven at a constant oscillation amplitude $A = 6.1$ nm.

B. Theoretical

The calculations were performed using atomistic simulation as implemented in the codes SCI-FI[20] and MARVIN.[21] The interatomic forces are computed from a sum of pairwise Buckingham potentials acting between ions. 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. 22–24. Unless specified, all cores and shells were allowed to relax completely with respect to interatomic forces.

The properties of the NaCl (001) surface are well-understood, and can be well-represented by a slab of six layers containing 10×10 ions. Those in the bottom layer were kept fixed, while those on the sides were also fixed in the SCI-FI simulations, but subject to periodic boundary conditions in the MARVIN simulations. The atomic details at the tip apex are to a large extent unknown. In our experiments we expect that the apex of the silicon tip was initially covered by native oxide formed in the course of the fabrication process. However, as mentioned previously, in the course of an experiment material can be picked up by the tip. Therefore the question arises as to whether we should choose a tip model that describes silicon dioxide (SiO_2) or the sample material. In order to provide a comprehensive study we consider both possibilities.

Previously, it has been shown that a magnesium oxide (MgO) cluster describes well the electrostatic field just outside a partially oxidized silicon cluster.[25] This tip model has been widely used to simulate SFM imaging and provided good qualitative agreement with experiments on other ionic surfaces.[26] For this work, calculations were performed using both MgO and NaCl tips, each consisting of a cubic cluster of 32 cations and 32 anions with stable {100} facets oriented such that ⟨111⟩ direction is perpendicular to the sample surface. Ions in the top half of the cluster were kept fixed. For each material, calculations were performed for the cases where an anion or a cation is located at the tip apex facing the sample.

III. RESULTS

A. Experimental images and force-distance curves

After acquiring a large-scale image which revealed terraces and steps on the NaCl surface, the tip-sample spacing was reduced until frequency jumps due to atomic instabilities occurred while imaging an area with apparent defects. Upon modification of the frequency set-point and continued imaging of the surface, stable operation was recovered. We interpret the underlying instability in the tip-sample interaction as likely resulting from the transfer of material from the sample to the tip, as discussed in detail later. We have estimated the change of the tip mass based on the magnitude of the frequency changes and stress that the underlying jump processes are incompatible with a change in overall tip shape. Furthermore, the overall surface structure appeared unchanged indicating that the tip change involved only a few atoms. Following this initial tip change, all further images and all of the frequency versus distance measurements discussed here were obtained without further apparent modification of the tip or instabilities in the imaging process. We could then again reduce the tip-sample spacing until high-resolution imaging of the atomic lattice was achieved. We then used these images to locate surface features and performed frequency versus distance measurements above a maximum and a neighboring minimum of the observed atomic-scale corrugation, i.e., positions 1 and 2 indicated by labeled crosses in Fig. 1.

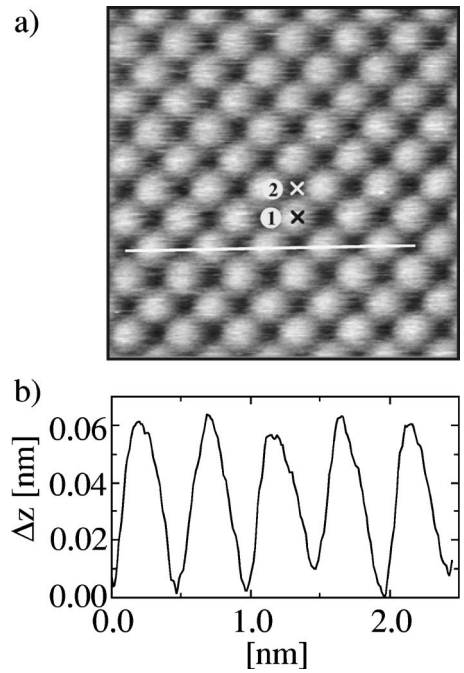

FIG. 1. (a) Atomic resolution image obtained on the NaCl (001) surface with a frequency shift $\Delta f = -14$ Hz $[\gamma = (\Delta f / f_0) c_b A^{3/2} = -1.8 \times 10^{-15}\ \mathrm{N\ m^{0.5}}]$ and (b) line cut through image (a).

As long as the maximum cantilever restoring force $c_b A$ considerably exceeds the force $F(z)$ on the tip, the frequency shift is given by the following integral over the oscillation period $T = 1/f$:[27]

$$\Delta f(s) = -\frac{f_0}{c_b A} \int_0^T F(\bar{z} + A \cos \omega t) \cos \omega t \frac{dt}{T}, \qquad (1)$$

where $\omega = 2\pi/T$, A is the oscillation amplitude, c_b the bending spring constant of the cantilever, $\bar{z}$ the time-averaged position of the tip, and $s = \bar{z} - A$ is the nominal tip-sample distance at the lower turning point of the oscillation.

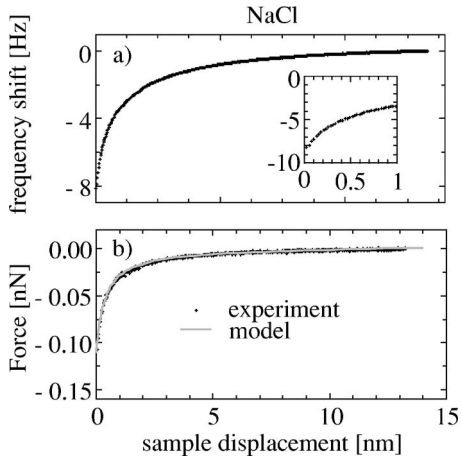

FIG. 2. (a) Frequency shift with a zoom into the region from 0 to 1 nm (inset) and (b) force on the tip as a function of tip-sample distance in the range 0.5–13 nm. At these distances the force arises mainly from the van der Waals and electrostatic interactions with a relatively large part of the tip. The best fit to a model describing these two forces for a conical tip terminated by a spherical cap against a flat sample is shown.

In order to convert the frequency shift versus distance data to force versus distance data, we used the method briefly described in Ref. 28 which was inspired by that proposed in Ref. 29. The frequency shift in our experiments results from a combination of long-range forces due to van der Waals and electrostatic interactions as well as from a short-range contribution that is responsible for the atomic-scale contrast observed at small enough tip-sample spacings. We are primarily interested in the short-range force and therefore attempted to separate it from the long-range forces. To do this, we fitted the force extracted in the tip-sample distance range from 0.5 to 13.0 nm to an analytic model for the long-range contributions. Below 0.5 nm the frequency shifts measured above the positions 1 and 2 begin to deviate noticeably from each other. We then subtracted this fit from the force extracted over the full distance range of 0.2 to 13.0 nm (the procedure used to set the zero point on the distance scale is described later). Note that the superposition principle is not strictly valid for forces in SFM because relaxation of the atomic positions may be nonlinear, and each force contribution depends on the relaxation. However, this is a higher order effect, and the different contributions are assumed to be additive.

To fit the long-range forces we have chosen a model that describes the van der Waals force plus the electrostatic force of a conical tip terminated by a spherical cap interacting with a flat sample surface.[30] The measured force and the best fit to the data are shown in Fig. 2. Assuming a Hamaker constant $H=6.5\times10^{-20}$ J (Ref. 31) and a total cone angle of 20°, the best fit was obtained with a voltage difference of $\Delta V=1.2$ V and a cap radius of $R=1.5$ nm.

The fitted radius is rather small considering the specifications given by the manufacturer ($R<10$ nm). However, similar radii have been obtained with this method on different samples[32] and have also been observed in high resolution transmission electron microscope images of commercial silicon tips by our own measurements as well as by the manufacturer (see, for example, www.nanosensors.com). In addition, mild indentation experiments performed with fresh Nanosensors tips on the KBr(001) surface have shown that it is possible to create depressions of the size of a few nanometers. In one particular experiment a hole of 3.8 nm diameter and 2 nm depth was thus created.[33] Although it is likely that the tip did not reach the bottom of the hole during subsequent imaging and that displaced material rearranged after the indentation prior to imaging,[34] these observations provide additional support that a tip radius of $R=1.5$ nm is not unrealistic.

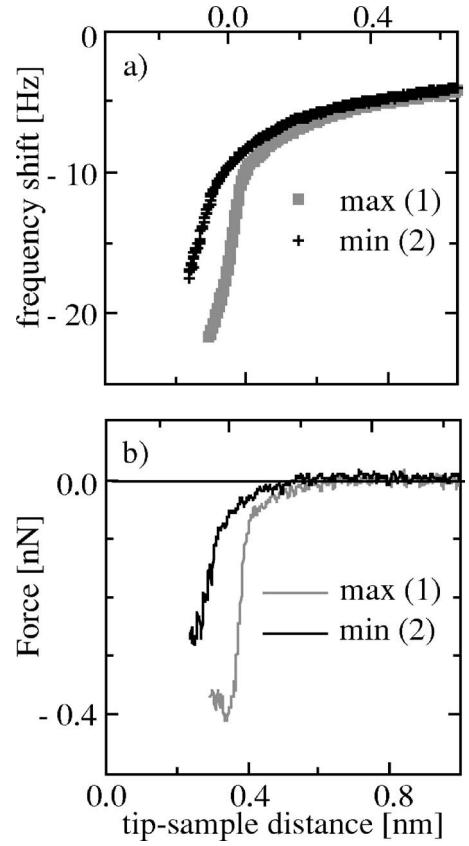

FIG. 3. (a) Total frequency shift and (b) short-range forces obtained in the distance range between 0.2 and 1 nm to the sample surface above the positions indicated in Fig. 1. The distance to the surface was calibrated using the calculated data using a procedure described in the discussion of Fig. 6(a) while the upper distance scale corresponds to the experimental one used in Fig. 2.

In Fig. 3 we plot the short-range forces measured above the two lattice positions after subtracting the fitted long-range force. Note first that the magnitude of the short-range force is relatively small, less than 0.5 nN, e.g., about five times weaker than above Si adatoms on the Si(111) 7×7 surface.[5] Second, somewhat surprisingly, the measured short-range forces are attractive both above the local maximum (1) and minimum (2) positions.

B. Computations

The insets in Figs. 4 and 5 show the three surface sites over which the tip-surface interaction was calculated for the

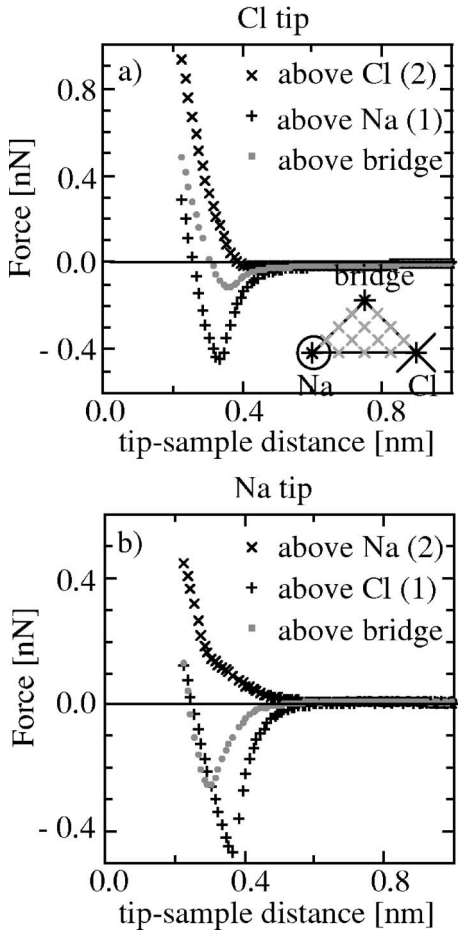

FIG. 4. Calculated forces for the NaCl tip at three inequivalent atomic sites; the tip is oriented such that in (a) a Cl^- ion is at the tip apex and in (b) a Na^+ ion is at the tip apex.

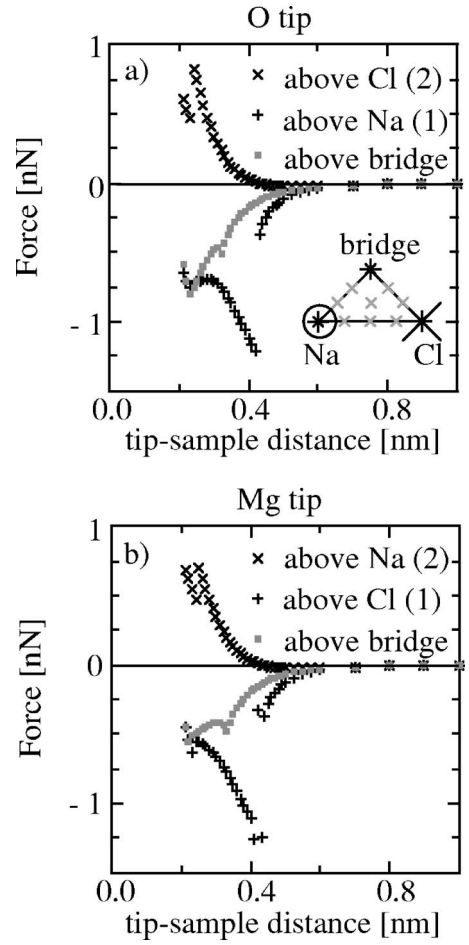

FIG. 5. Calculated forces for the MgO tip at three inequivalent atomic sites; the tip is oriented such that in (a) an O^{2-} ion is at the tip apex and in (b) a Mg^{2+} ion is at the tip apex.

NaCl and MgO cluster tips, respectively. For each position, the force on the tip was calculated at incrementally decreased tip-sample distances. The calculated short-range forces obtained during such approaches are shown in Figs. 4 and 5. Note that the tip-sample interaction between the MgO tip and the sample is about 2 to 3 times stronger than the interaction between the NaCl tip and the sample. The reason is mainly that Mg^{2+} and O^{2-} are doubly charged while Na^+ and Cl^- are singly charged. However, the former cation and anion are also smaller, so that the MgO tip is much stiffer and therefore relaxes less than the NaCl tip.

The larger interaction forces observed with the MgO tip give rise to instabilities, which are manifested as jumps in the calculated approach curves. Initially, as the MgO tip is approached to the surface, the closest surface ion of opposite polarity to the tip apex is strongly pulled out and then jumps to the tip as the spacing is further reduced. Such instabilities in the force versus distance data are observed for both tip terminations of the MgO tip at all lattice positions studied here at distances ranging between 0.44 and 0.24 nm. Further instabilities involving collective jumps of several ions are expected at closer distances, but were not investigated. However, as discussed below and in Sec. III C, already the first instability upon approach gives rise to a modified force vs distance dependence upon retraction.

In contrast, when the NaCl tip is approached, the displacements of the nearest sample and tip ions stay to a good approximation proportional to the force, and no instabilities are observed in the distance range studied. Compared to the Cl^- terminated tip, the results for the Na^+ terminated tip show a somewhat stronger attraction and repulsion above a surface ion of the opposite and of the same sign, respectively. Movies illustrating calculated displacements of nearby ion cores for the Na^+ terminated tip at the three positions indicated in the inset of Fig. 4(a) can be viewed as supplementary material.[35] Upon approach above a Na^+ ion, that cation is first pushed into the sample; then the tip end is deflected sideways as two of the anions behind the apex cation become attracted to two nearby cations of the sample. All displacements are nevertheless continuous and reversible. Above a Cl^- ion, that ion and the apex cation are first pulled towards each other; then both are pushed back into the sample and the tip end, respectively. Above the bridge site displacements become noticeable only at shorter distances; the two nearest sample anions are attracted to the apex cation, whereas the two nearest sample cations are pushed sideways.

It is instructive at this stage to compare the present results with independent computations performed with the MARVIN code for several cuboid NaCl model tips oriented in different

ways with respect to a NaCl(001) sample.[36] The computed force curve (Fig. 11 in that work) is only slightly different from that in Fig. 4(b) for a smaller Na^+ terminated tip oriented like ours (same maximal attraction, albeit at 0.38 nm, above Cl^-; slightly weaker repulsion above Na^+). Only a mild disagreement is expected because in the distance range studied (0.36–0.60 nm), only the tip apex and a few adjacent nearest neighbors are appreciably interacting with the sample. On the other hand, model NaCl tips oriented such that an edge exposing two or three ions was parallel to the sample surface led to a significantly stronger maximal attraction at position 1 (between 0.75 and 1.1 nN, respectively). The corresponding force-distance curves also showed a stronger dependence on the size of the assumed model tip, owing to appreciable relaxation of a larger number of ions. An interesting finding was that the small model tip which produced the maximum attraction at position 1 generated a short-range force with a somewhat stronger maximum attraction at position 2 (rather than repulsion, as in all other cases, including ours). This peculiar behavior arose from a rotation of the corresponding tip which ultimately exposed a 6-ion facet instead of a 3-ion edge at close approach. Such a rotation is prevented in model tips with a fixed base layer of atoms, however. Another surprising finding was that all model tips produced similarly looking simulated images at comparable tip-sample distances, except for lateral shifts of maxima and minima from ideal lattice positions. Nevertheless, it appears that the nature of the tip apex and its orientation could be determined by comparing computed corrugation amplitudes and force vs distance characteristics with those extracted from the measurements.

C. Comparison of experimental and computed short-range forces

Experimentally, no discontinuities are observed in the frequency versus distance measurements. The approach and retraction data look very similar, i.e., identical and continuous within the limit of experimental noise. In addition, repeated measurements above the same and above equivalent sites were also very similar. A frequency jump would be expected if, for instance, a forward and backward atomic-scale jump or tip change occurred in each oscillation cycle. Indeed, the resulting force hysteresis between approach and retraction would manifest itself as a drop in the frequency shift at the distance where the jump occurs upon approach.[37–40]

It is important to note that in the experiments the tip is oscillated with a large amplitude and high frequency relative to the time scale of the frequency versus distance measurement. Each data point is actually the average of many oscillation cycles. Therefore if overall reversible jumps or tip changes occur irregularly but at a rate faster than the measurement time at each data point (between 19 and 39 ms in the frequency versus distance measurements), they would still cause a frequency discontinuity on average. The term reversibility is used here in the sense that the atomic configuration is recovered in each cycle. This does not imply that the system evolves continuously; indeed the underlying force hysteresis causes dissipation.[37–40] Stable imaging appears impossible at distances below the maximum one for which a force hysteresis appears. One possible exception arises if the underlying instability leads to a more stable tip configuration which is preserved in subsequent approach-retraction cycles.

Both model NaCl-tips (Fig. 4) reproduce the general shape of the short-range force obtained (Fig. 3) above the local maximum in the image (position 1), i.e., increasing attractive (negative) force, maximum attraction, then decreasing attraction followed by repulsion, are observed with decreasing tip-sample distance. The maximal absolute value of the force calculated using the NaCl-tip is only slightly larger than that obtained from the experimental data. Note, however, that while short-range attractive forces are also obtained above the local minimum in the experimental data (position 2), essentially repulsive forces are found for both model tips in the calculations. Possible reasons for this discrepancy are discussed below.

Considering both the lack of discontinuities in the measured frequency shifts versus distance and the magnitude of the extracted forces, we conclude that it is unlikely that the SFM tip apex was terminated by an oxide. We therefore focus next on a comparison of the experimental force-distance data with the NaCl-tip calculations in more detail.

For the model NaCl tip, the force measured at the maximum (position 1) agrees reasonably well with the calculation for either tip termination when the tip apex faces a sample ion of opposite sign. However, at the minimum (position 2) there is an apparent discrepancy. Deviations between the actual long-range force and the model assumed in order to separate that contribution to the total force could give rise to a systematic error in the remaining short-range force. In similar work on KBr(001) (Ref. 7) the proposal was made to circumvent this problem by comparing differences between forces measured above pairs of easily recognizable positions rather than considering the sites individually. In this way site-independent contributions are naturally removed. The site-dependent part, i.e., the difference between forces measured above two sites, can then be directly compared to the force difference obtained from the calculations. We have adopted this approach here and present the results in Fig. 6.

The experiments described here were performed before it was realized that a determination of the force vs distance above a bridge site could provide a useful independent check.[7] For this reason the desired comparison can only be made for the force differences between the minimum (2) and the maximum (1) in the image [Fig. 6(a)]. The calculated force differences between the minimum (2) and the brige site [Fig. 6(b)], as well as between the bridge site and the maximum (1) [Fig. 6(c)], are included for the sake of completeness. From the calculated force differences and a thorough comparison to carefully measured experimental data, identification of the positively and negatively charged sublattices is possible following the method described in Ref. 7.

The measured force difference is indeed short-ranged. Comparing the experimental data to the calculated force differences in Fig. 6(a), we find that the latter is still larger than the former, although the computed points for the Na^+ terminated tip lie closer to the data. Requiring the rather sharp onsets of the corresponding differences to match allows us to define the absolute tip-sample distance scale adopted in Figs.

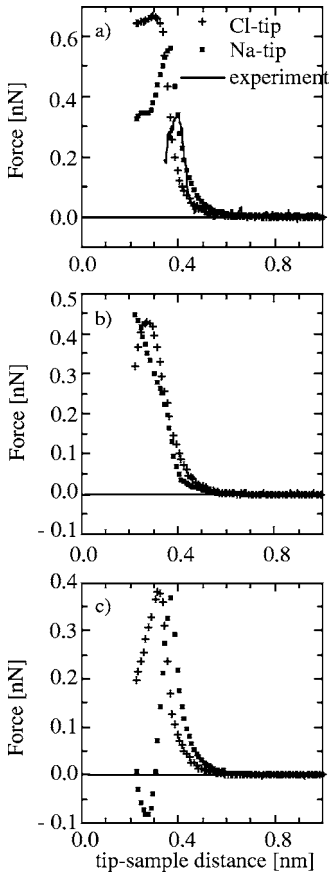

FIG. 6. Comparison of the calculated force differences: (a) minimum (2) -maximum (1), (b) minimum (2) -bridge, and (c) bridge -maximum (1). Panel (a) shows a comparison with the experimentally determined difference, which was also used to define the tip-sample distance in Fig. 3.

3 and 6(a). We estimate a possible systematic error in the determination of the force from the measured frequency shift up to 30%, resulting from the uncertainty in the calibration of the oscillation amplitude. However, even this significant experimental error cannot account for the deviation between experiment and calculation. Most of this deviation arises because of the previously mentioned discrepancy between experiment and calculations at the minimum position (2). We therefore conclude that improper modeling of the long-range forces together with experimental errors cannot be the only reasons for the observed differences between experiment and theory.

Another possible source of the discrepancy is symmetry-breaking relaxation. As observed in the movies, at the minimum (2) the tip end deflects to the side, and several atomic layers behind the apex ion tip take part in that deformation. A large part of the tip is involved in that process, in contrast to the other sites, where only the frontmost ion and, on the maximum (position 1), one further layer relax significantly, while the tip symmetry is preserved. As discussed in Sec. III B, short-range forces are more sensitive to the size of the assumed tip cluster if more ions relax significantly. Considering the likelihood that the silicon tip was contaminated by just a few ions from the NaCl sample, the present model of a

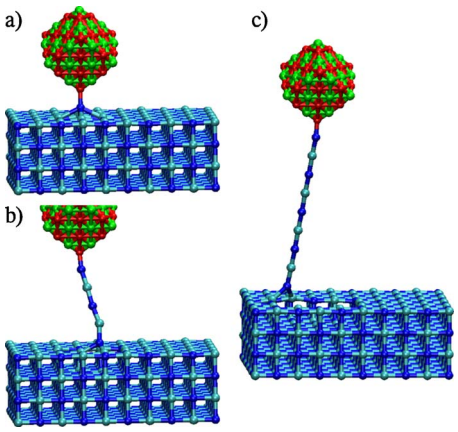

FIG. 7. (Color online) Snapshots from the simulations with an oxygen-terminated MgO tip starting above a Na^+ ion and showing several stages of NaCl chain formation at nominal tip-sample distances of (a) 0.44 nm, (b) 1.30 nm, and (c) 2.73 nm.

64-ion cubic NaCl cluster may be unrealistic. For the smaller, similarly oriented 8-ion cluster investigated in Ref. 36, the repulsion at the minimum (2) is in fact weaker, so that the force difference between minimum (2) and maximum (1) would be closer to the experimental difference. In the same computational study, reduced repulsion (and even attraction) was obtained at the minimum (2) with model tips with an edge parallel to the sample. However, at the maximum (position 1) they produced a maximum attraction significantly stronger than observed in Fig. 3. Taking into account available results computed for different model tips, we tentatively conclude that the oxidized Si tip used to record our site-dependent data was most likely terminated by a small NaCl cluster with stable {100} facets and one edge tilted towards the sample.

Note finally that the lack of instabilities and the appearance of the force-distance curves computed for the NaCl tip suggest that stable imaging with a tip which picked up a cluster from the sample should be possible even in the weakly repulsive regime. As long as requirements for stable distance and oscillation amplitude control are satisfied, images recorded at constant frequency shift should then show inverted contrast.[41,42]

D. Tip contamination scenario

Although it seems probable that the tip picked up sample material during the successive approach and imaging steps required to locate a flat terrace, it is interesting to consider the process of contamination itself. In both experiments and simulations, instabilities were observed with oxide tips upon approaching the sample surface. In this section we focus on further results of calculations with the oxygen-terminated MgO tip as a plausible model of an oxidized silicon tip.

As in our simulations, previous work[24,43] predicted that above a cation a jump towards the MgO tip occurs below a critical distance [0.44 nm in our case: see Fig. 7(a)]. Moreover, they showed that a neighboring sample ion is pulled out if the tip is further retracted. In order to investigate possible contamination scenarios, we performed further calculations

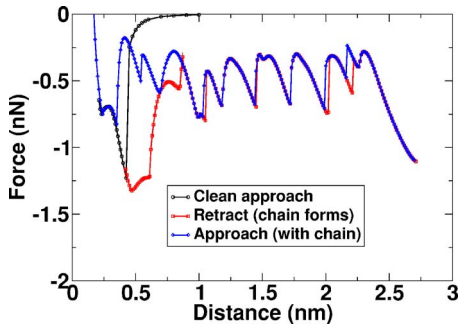

FIG. 8. (Color online) Initial approach, retraction, and reapproach force curves computed for the oxygen-terminated MgO tip.

with the MARVIN code in which the tip was retracted out to a large distance and then reapproached.

As the tip is retracted, a chain consisting of alternating Na^+ and Cl^- ions is formed [see Fig. 7(b)]. The tip pulls out a chain of nine ions [see Fig. 7(c)], leaving a narrow rectangular groove (vacancy cluster), before the groove approaches the edge of the simulation box where periodic boundary conditions are imposed. The calculation then becomes unrealistic due to the finite size of the simulated system. Jumps in the corresponding force curve (see Fig. 8) occur as each subsequent ion of the chain is pulled from the surface. Pulling out the first Cl^- ion requires a tensile force of about 1.25 nN, but the following ions which are then surrounded by less counterions requires only about 0.75 nN. The appearance of the accompanying force variations is reminiscent of those observed while pulling biomolecules with a functionalized SFM tip.[44,45] Nevertheless the underlying physics is rather different. In the latter case, the nonmonotonic evolution of the force has been attributed to, e.g., the successive unfolding of coiled subunits. In our case, the tension stiffens as the bond connecting the last pulled out ion to a nearest neighbor straightens out, then drops as that ion is in turn pulled out. Small irregularities in the force oscillations arise because two adjacent neighbors always compete, as can be seen in the last movie provided as supplementary material.[35]

At finite temperature such a chain will undergo thermal fluctuations; it is expected to break beyond a certain length. The actual breaking point and mechanism could in principle be determined using molecular dynamics computations, which would probably require a much larger simulation box.[46] Such simulations predict that the first Na^+ ion pulled out of the surface returns to its original location already at 100 K, and no chain is formed.

In the present zero temperature relaxation simulations, an almost identical force curve is obtained if the tip is reapproached, as the previously pulled out ions successively move back into place, refilling the groove and essentially following the pull-out sequence in reverse, except for the last few ions. This is not surprising because the vacancy cluster imposes a particular directionality as long as it remains groovelike. Thermal fluctuations should suppress this partial reversibility. Note also that the experimental cantilever oscillation amplitude is much larger than the chain length observed in the calculations, therefore in the experiment described here, if a chain was formed, the reversibility would be lost when the chain breaks at large tip-sample distances.

With the present experimental technique it is not possible to determine whether chains of appreciable length are in fact pulled out of the sample. Nevertheless, it seems likely that a native oxidized Si tip would become contaminated with NaCl due to the initially stronger interaction forces. This may be the origin of the instability observed during the initial imaging of the sample. A possible scenario is that a jump is triggered if the oxidized tip swings close enough to the sample surface and a chain is pulled out and breaks as it swings back (this may require a few cycles). The pieces connected to the tip and the sample will then collapse and eventually form more or less compact clusters. The time required for those processes are difficult to estimate. Once a stable NaCl cluster is formed at the tip apex, stable imaging should be possible, as discussed at the end of Sec. III B.

IV. CONCLUSIONS AND OUTLOOK

We used a low-temperature SFM operated in the constant-amplitude dynamic mode to study the interaction between an initially oxidized silicon SFM tip and a NaCl(001) surface. Force-distance curves extracted from the measurements are compared to theoretical ones obtained from simulations which assumed a MgO as well as a NaCl cluster as models for the tip. Although one cannot unambiguously identify the polarity of the tip apex from the experiments alone, calculations show that the model oxide tip induces jumps, in contrast to our calculations for the model NaCl tip and in contrast to our measurements. Moreover, the calculated short-range attractive forces are much larger for the oxide tip than in the experiment. Therefore a stable NaCl cluster is a better model for the actual tip in our experiments. As the SFM tip probably came into contact with the sample surface before the data presented here were recorded, it is also quite likely that the tip picked up a cluster of NaCl. The fact that no repulsion was observed in the experimental site-specific forces curves, in contrast to the present computations, also suggests that the real NaCl cluster is smaller and not so symmetric as assumed here.

Going beyond a qualitative analysis of the tip apex, a determination of its polarity and hence of the correspondence between the anion and cation sublattices on one hand, and the contrast in lattice-resolved images on the other hand, has proven difficult in this study. In similar work on the KBr(001) surface,[7] a comparison between the force obtained at the maximum (position 1) and that obtained at the saddle point located between two neighboring cations and two neighboring anions (the bridge site in the insets of Figs. 4 and 5) was used to determine the tip polarity, assuming a KBr model tip like our NaCl tip. In the case of the K^+ terminated tip, the two force curves crossed, while they did not in the case of the Br terminated tip. A similar, albeit less pronounced crossing is found here for the Na^+ terminated model tip facing a NaCl(001) surface. On KBr, as well as NaCl(001) samples, the calculated tip relaxation at the saddle point is much smaller than at the maximum (1) or minimum (2) in the images, since the tip apex mainly experiences forces generated by two positively charged ions and two

negatively charged ions at about the same distance. Therefore sample relaxation becomes dominant. The shape of the force curve is affected by the stronger relaxation and polarization of the anions, owing to their somewhat larger size and much greater polarizability. The above-mentioned crossing is expected for any tip which generates an electrostatic field of positive polarity around its apex. This phenomenon can then be used to determine the tip polarity and the sublattices imaged as maxima and minima on the (001) cleavage surfaces of ionic crystals with the rocksalt structure. Future experiments will hopefully provide the data required to check this prediction for a series of such samples.

Computations showing the formation of a chain of alternating ions being pulled out from a NaCl(001) surface by a model oxide tip suggest a plausible scenario leading to the formation of a cluster of sample material at the apex of an oxidized silicon SFM tip.

The site-dependent measurements discussed here relied on the essentially drift-free operation achieved at low temperature. In principle, similar information can be extracted from a series of images recorded at closely spaced constant distances or frequency shifts.[47] At room temperature, unavoidable drifts must be compensated, using, e.g., recognizable features as markers. Recently, a feature-tracking technique[48] was applied at room temperature to compensate drifts between successive frequency-distance measurements.[49] On the Si(111)7×7 surface, the corresponding results came out remarkably close to the pioneering low-temperature measurements.[5] This encouraging development opens the door for the accurate site-dependent study of tip-sample interaction forces at room temperature, as well as variable temperature. Measuring the site-specific frequency shift as a function of distance at variable temperatures should allow one to study jumps and dissipation effects as a function of temperature like those predicted by recent simulations.[46,50]

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[1] *Noncontact Atomic Force Microscopy*, edited by S. Morita, R. Wiesendanger, and E. Meyer (Springer, Berlin, 2002).

[2] F. J. Giessibl, Rev. Mod. Phys. **75**, 949 (2003).

[3] M. A. Lantz, H. J. Hug, P. J. A. van Schendel, R. Hoffmann, S. Martin, A. Baratoff, A. Abdurixit, H.-J. Güntherodt, and Ch. Gerber, Phys. Rev. Lett. **84**, 2642 (2000).

[4] T. Eguchi and Y. Hasegawa, Phys. Rev. Lett. **89**, 266105 (2002).

[5] M. A. Lantz, H. J. Hug, R. Hoffmann, P. J. A. van Schendel, P. Kappenberger, S. Martin, A. Baratoff, and H.-J. Güntherodt, Science **291**, 2580 (2001).

[6] R. Hoffmann, M. A. Lantz, H. J. Hug, P. J. A. van Schendel, P. Kappenberger, S. Martin, A. Baratoff, and H.-J. Güntherodt, Appl. Surf. Sci. **188**, 238 (2002).

[7] R. Hoffmann, L. N. Kantorovich, A. Baratoff, H. J. Hug, and H.-J. Güntherodt, Phys. Rev. Lett. **92**, 146103 (2004).

[8] R. Hoffmann, M. A. Lantz, H. J. Hug, P. J. A. van Schendel, P. Kappenberger, S. Martin, A. Baratoff, and H.-J. Güntherodt, Phys. Rev. B **67**, 085402 (2003).

[9] S. M. Langkat, H. Hölscher, A. Schwarz, and R. Wiesendanger, Surf. Sci. **527**, 12 (2003).

[10] R. Hoffmann, C. Barth, A. S. Foster, A. L. Shluger, H. J. Hug, H.-J. Güntherodt, R. M. Nieminen, and M. Reichling, J. Am. Chem. Soc. **127**, 17863 (2005).

[11] M. Ashino, A. Schwarz, T. Behnke, and R. Wiesendanger, Phys. Rev. Lett. **93**, 136101 (2004).

[12] S. Hembacher, F. J. Giessibl, J. Mannhart, and C. F. Quate, Phys. Rev. Lett. **94**, 056101 (2005).

[13] N. Oyabu, O. Custance, I. Yi, Y. Sugawara, and S. Morita, Phys. Rev. Lett. **90**, 176102 (2003).

[14] Y. Sugimoto, M. Abe, S. Hirayama, N. Oyabu, O. Custance, and S. Morita, Nat. Mater. **4**, 156 (2005).

[15] M. Bammerlin, R. Lüthi, E. Meyer, A. Baratoff, J. Lü, M. Guggisberg, Ch. Gerber, L. Howald, and H.-J. Güntherodt, Probe Microsc. **1**, 3 (1997).

[16] R. Bennewitz, A. S. Foster, L. N. Kantorovich, M. Bammerlin, Ch. Loppacher, S. Schär, M. Guggisberg, E. Meyer, and A. L. Shluger, Phys. Rev. B **62**, 2074 (2000).

[17] R. Bennewitz, S. Schär, V. Barwich, O. Pfeiffer, E. Meyer, F. Krok, B. Such, J. Kolodzej, and M. Szymonski, Surf. Sci. Lett. **474**, L197 (2001).

[18] H. J. Hug, B. Stiefel, P. J. A. van Schendel, A. Moser, S. Martin, and H.-J. Güntherodt, Rev. Sci. Instrum. **70**, 3625 (1999).

[19] C. Loppacher, M. Bammerlin, F. M. Battistion, M. Guggisberg, D. Müller, H. R. Hidber, R. Lüthi, E. Meyer, and H.-J. Güntherodt, Appl. Phys. A: Mater. Sci. Process. **66**, S215 (1998).

[20] L. N. Kantorovich, A. S. Foster, A. L. Shluger, and A. M. Stoneham, Surf. Sci. **445**, 283 (2000).

[21] D. H. Gay and A. L. Rohl, J. Chem. Soc., Faraday Trans. **91**, 925 (1995).

[22] M. J. L. Sangster and R. M. Atwood, J. Phys. C **11**, 1541 (1978).

[23] R. Grimes, C. Catlow, and A. Stoneham, J. Phys.: Condens. Matter **1**, 7367 (1989).

[24] A. L. Shluger, A. L. Rohl, D. H. Gay, and R. T. Williams, J. Phys.: Condens. Matter **6**, 1825 (1994).

[25] A. I. Livshits, A. L. Shluger, A. L. Rohl, and A. S. Foster, Phys. Rev. B **59**, 2436 (1999).

[26] W. Hofer, A. S. Foster, and A. L. Shluger, Rev. Mod. Phys. **75**, 1287 (2003).
[27] F. J. Giessibl, Phys. Rev. B **56**, 16010 (1997).
[28] O. Pfeiffer, R. Bennewitz, A. Baratoff, E. Meyer, and P. Grütter, Phys. Rev. B **65**, 161403(R) (2002).
[29] F. J. Giessibl, Appl. Phys. Lett. **78**, 123 (2001).
[30] M. Guggisberg, M. Bammerlin, Ch. Loppacher, O. Pfeiffer, A. Abdurixit, V. Barwich, R. Bennewitz, A. Baratoff, E. Meyer, and H.-J. Güntherodt, Phys. Rev. B **61**, 11151 (2000).
[31] L. Bergström, Adv. Colloid Interface Sci. **70**, 125 (1997).
[32] M. A. Lantz, H. J. Hug, R. Hoffmann, S. Martin, A. Baratoff, and H.-J. Güntherodt, Phys. Rev. B **68**, 035324 (2003).
[33] J. M. Mativetsky (private communication).
[34] E. Gnecco, R. Bennewitz, and E. Meyer, Phys. Rev. Lett. **88**, 215501 (2002).
[35] See EPAPS Document No. E-PRBMDO-74-060648 for movies showing ion core displacements (exaggerated by a factor of 2.4 for easier visualization) upon the approach and retraction of a Na^+ terminated ⟨111⟩-directed NaCl tip facing a Na^+, a Cl^- ion, and the saddlepoint site in the top layer of a NaCl(001) slab, respectively. A fourth movie illustrates the formation of a chain of alternating anions and cations during the retraction of an O^- terminated ⟨111⟩-directed MgO cluster which had initially pulled out a Na^+ from the top layer of a NaCl(001) slab. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[36] R. Oja and A. S. Foster, Nanotechnology **16**, S7 (2005).
[37] N. Sasaki and M. Tsukada, Jpn. J. Appl. Phys., Part 2 **39**, L1334 (2000).
[38] L. N. Kantorovich, J. Phys.: Condens. Matter **13**, 945 (2001).
[39] H. Hölscher, B. Gotsmann, W. Allers, U. D. Schwarz, H. Fuchs, and R. Wiesendanger, Phys. Rev. B **64**, 075402 (2001).
[40] H. J. Hug and A. Baratoff, Chap. 20 in Ref. 1.
[41] F. J. Giessibl and M. Reichling, Nanotechnology **16**, S118 (2005).
[42] M. Heyde, M. Sterrer, H.-P. Rust, and H.-J. Freund, Appl. Phys. Lett. **87**, 083104 (2005).
[43] A. L. Shluger, L. N. Kantorovich, A. I. Livshits, and M. J. Gillan, Phys. Rev. B **56**, 15332 (1997).
[44] M. Reif, M. Gautel, F. Oesterhelt, J. M. Fernandez, and H. E. Gaub, Science **276**, 1109 (1997).
[45] H. Dietz and M. Reif, Proc. Natl. Acad. Sci. U.S.A. **101**, 16192 (2004).
[46] T. Trevethan and L. Kantorovich, Nanotechnology **16**, S79 (2005).
[47] A. S. Foster, C. Barth, A. L. Shluger, R. M. Nieminen, and M. Reichling, Phys. Rev. B **66**, 235417 (2002).
[48] D. W. Pohl and R. Möller, Rev. Sci. Instrum. **59**, 840 (1988).
[49] M. Abe, Y. Sugimoto, O. Custance, and S. Morita, Appl. Phys. Lett. **87**, 173503 (2005).
[50] L. N. Kantorovich and T. Trevethan, Phys. Rev. Lett. **93**, 236102 (2004).