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Atomic resolution for non-equilibrium structures in the steady state and for structural transformations at the interface between NaCl(c) and water

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Abstract. Observations of both nanoscale and microscale images were carried out on a NaCl(001) surface in water using atomic force microscopy (AFM). The observed higher density of steps and the observed convex and concave steps in water result from the forward motion of monatomic steps and crystal growth of the so-called step-flow mode. The non-equilibrium structure having a unit cell of $C(2 \times 2)$ structure has been observed for the first time on terraces. Since every Na^+ on terraces is located at the same height as Cl^- , each Na^+ as well as each Cl^- have been observed as protrusions by AFM. The metastable configuration at the interface between the NaCl(001) surface and water was transformed, at steps, into the equilibrium structure of NaCl(c), about 3 h after the NaCl(001) surface had been covered with its own saturated water. After about 30 min, however, Na^+ still remains at the same height as Cl^- at steps, or sodium ions leave the surface at steps. The reason why the forward motion of monatomic steps takes place at the interface between the NaCl(001) surface and water is the decrease of about 0.05 nm in the distance of like nearest neighbours in the non-equilibrium structure having a unit cell of $C(2 \times 2)$ structure on terraces after its structural transformation to the equilibrium structure of NaCl(c) with the aid of water molecules.

1. Introduction

Despite the considerable theoretical and experimental activity on crystal growth over the years [1, 2], little is known about the two-dimensional structure of the metastable layer and the motion of ions at the interface between NaCl(c) and water. On the other hand, the well known terrace–ledge–kink model [3], which is understood as the essence of crystal growth and dislocations, describes the surface morphology in terms of terraces, steps or ledges, kinks, and adatoms and vacancies.

When atoms or ions on surfaces (in particular those covered with water) move by overcoming the potential barriers, they wander on the surfaces and find the optimum crystal sites. The structural dynamics at the interface between NaCl(c) and water have been an area of continuing interest for scientists, not only because the motion reflects the nature of barriers caused by interaction potentials between the ions and between ions and the upper water molecules but also because their two-dimensional translation is one of the essential parameters controlling crystal growth.

Atomic force microscopy (AFM) as well as scanning tunnelling microscopy (STM) have given a step-function impetus to the investigation of the motion of atoms or ions on the

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interface between an ionic crystal and water and the nanoscale structure of crystal growth [4]. Since atomic force and scanning tunnelling microscopes allow observation of a wide range up to $10\ \mu\text{m}$ in spatial resolution and also individual atoms by extending the range up to a few nanometres, they are powerful tools for elucidating the crystal growth mechanism at the atomic level [4]. Atomically resolved images of ionic crystals have been observed since 1990 [5–9] and also in water or another liquid [10–12] using AFM. The real-space observation of individual ions on the cleavage plane of ionic crystals in air has made no contribution to crystal growth studies. Real-time observation has demonstrated the crystal growth which occurred in a layer-by-layer fashion by the forward motion of monatomic steps [13]. No one has observed the atomically resolved images of ions on terraces and at steps in water and of non-equilibrium structure at the interface between NaCl(c) and water.

This work presents the *in situ* observation not only of aqueous crystal growth on NaCl(001) surfaces of $5\ \mu\text{m} \times 5\ \mu\text{m}$ spatial resolution, maintaining the height sensitivity of a fraction of one atomic layer, but also for the atomically resolved images for non-equilibrium structure at the interface between NaCl(001) surface and water.

2. Experimental details

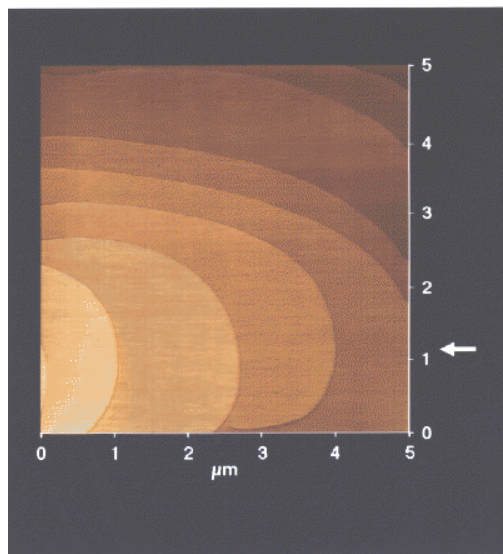
All the AFM images in the present work were measured in the constant-force mode [14, 15]. The sample surface was imaged by mechanically tracing its topography using a microfabricated cantilever with an integrated pyramidal Si_3N_4 tip. Here, the cantilever's force constant is $k = 0.58\ \text{N m}^{-1}$. The deflections of the cantilever were caused by surface features and detected via a laser beam reflected off the back of the cantilever into a two-segment photodiode for position sensing. A feedback loop moves the z -translator as necessary to keep the beam position constant or to maintain a constant force between the surface of samples and the tip. The z -axis displacement is read as the height of the surface features but maintaining the height sensitivity of a fraction of one atomic layer. In our experiments the scanning force over the surfaces of samples was $F = 10\ \text{nN}$ in air and $F = 1\ \text{nN}$ in water; the image acquisition time was less than 10 s. The forces correspond to attractive overall forces showing negative values in the observed force curve plots, where the zero force point is measured for large tip-sample separations [11].

The NaCl crystal can be cleaved easily along the (001) faces. No further surface treatment has been applied. The sample epoxied into a stainless-steel cup mount was sealed by a O-ring against a glass fluid cell [13] filled with the saturated NaCl aqueous solution; the sample should be in thermal equilibrium with the saturated NaCl aqueous solution. Since the whole cantilever probe was immersed in water, capillary forces should be mostly eliminated.

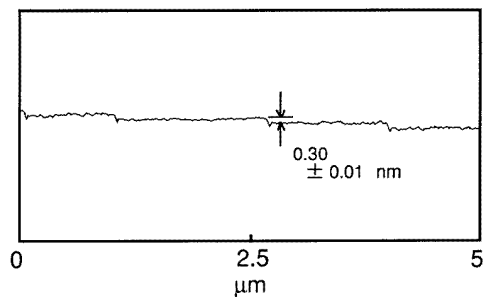
3. Results

3.1. Observations of terraces and steps on a NaCl(001) surface in air and in water

Figure 1(a) shows a high-resolution AFM image of a NaCl(001) surface of $5\ \mu\text{m} \times 5\ \mu\text{m}$ area in air while still maintaining the height sensitivity of a fraction of one atomic layer as shown in figure 1(b) for the cross section profile. Some terraces and steps in fields of view are as large as several micrometres; the terrace width along the arrow in figure 1(a) is equal to about 250 nm and the step height of $0.30 \pm 0.01\ \text{nm}$ (see figure 1(b)) corresponds to the monatomic distance. The observed surface of NaCl(001), the single crystal of which was prepared by crystal growth from its own melt, suggests the emergence of a screw dislocation; each step in the spiral is monatomic in height [16]. Figure 2 shows atomic resolution of its



(a)



(b)

Figure 1. (a) AFM image of the NaCl(001) surface in air. The brighter regions are higher. (b) Cross section profile as indicated by the arrow in figure 1(a). As the height of the steps corresponds to half the unit-cell length (0.284 nm), the terraces are one atomic layer deep.

5 nm \times 5 nm image in air. The cross section profile along the three cell axes [100], [010] and [001] (see figure 2(b)) almost reproduced the ionic crystal structure of NaCl; from the x-ray structure determination the length of the unit cell is equal to 0.5628 nm and the difference between the ionic radii of chloride and sodium ions is equal to 0.086 nm. The observed AFM image of the NaCl(001) surface and the corrugation amplitude reproduced the same image obtained in ultrahigh vacuum using an optical-beam-deflection force microscope [6]. The bright spots in figure 2(b) correspond to the protrusions which are attributed to the chloride ions [5, 7, 8]. The atomic-resolution images on the NaCl(001) surface were observed both at the centre of terraces and at steps.

An AFM image (5 μm \times 5 μm area) of the terrace and step structures of the NaCl(001) surface exposed to its own saturated aqueous solution (SAS) is shown in figure 3. The observed higher density of steps and a number of observed convex and concave steps are characteristic of the constricted growth at the restricted region of the surface of NaCl(c) in water, while the height of the steps still remains equal to a monatomic distance (see figure 3(b)).

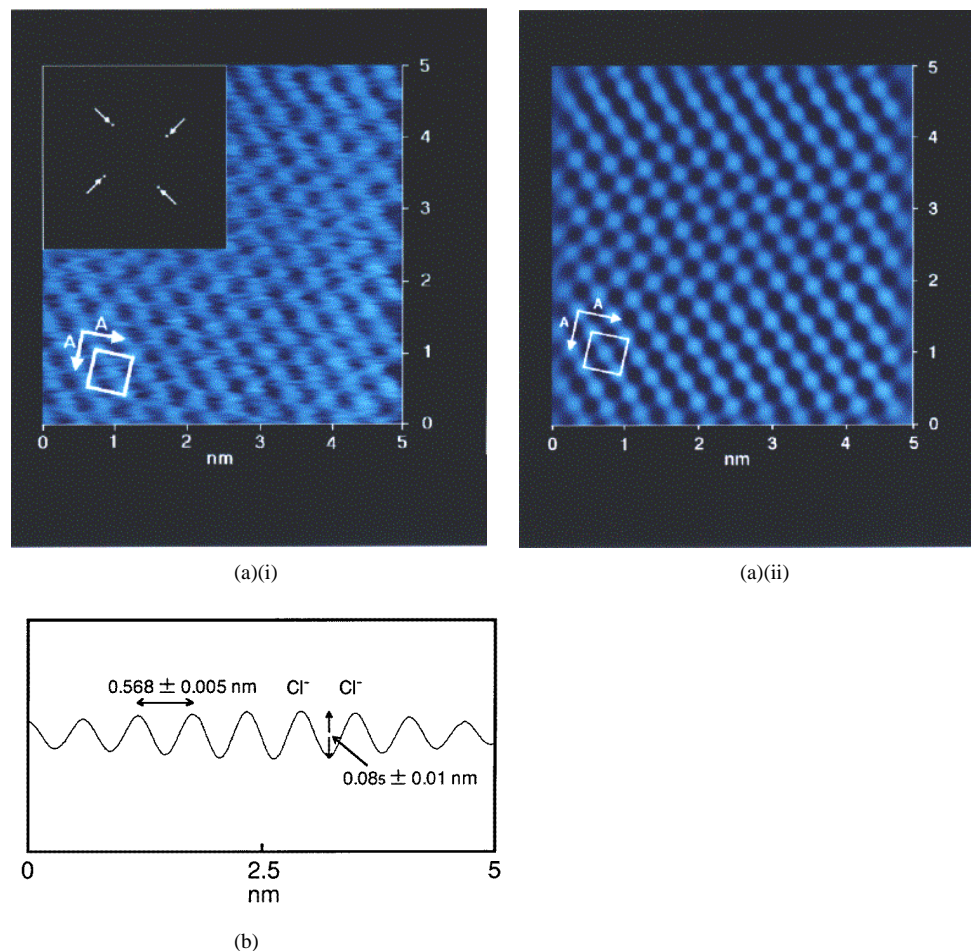
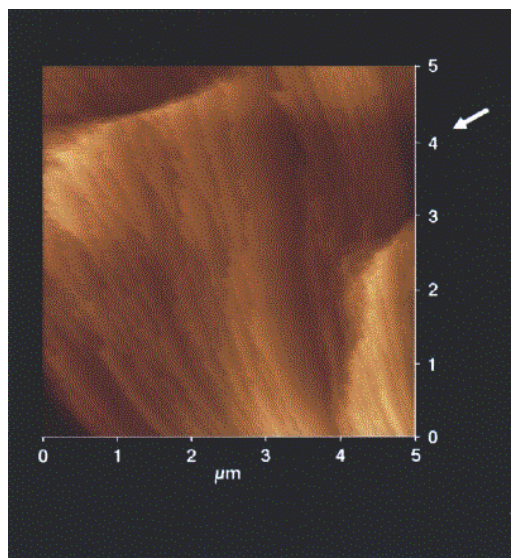


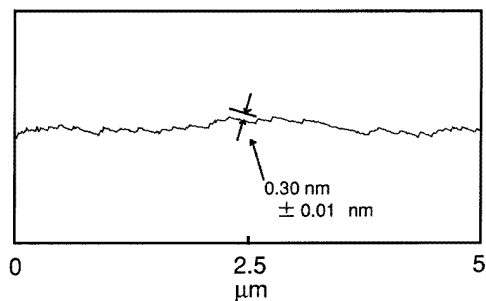
Figure 2. (a)(i) Unfiltered and (ii) filtered atomic-resolution AFM images of the NaCl(001) surface in air. The bright spots correspond to the protrusions which are attributed to the chloride ions. The white square in the image indicates a unit cell of NaCl(c). The inset shows fast Fourier transforms of the real-space unfiltered image (ii). The filtered image (ii) was obtained from the fast Fourier transforms of fast Fourier transform spots denoted by arrows. (b) Cross section profile in the direction of the two arrows in (a). The separation between two peaks corresponds to the lattice constant and the corrugation amplitude is equal to the difference between the ionic radii of chloride and sodium ions at the NaCl(001) surface.

3.2. Atomic-resolution images at the centre of terraces and at steps in water

At the centre of terraces the atomic-resolution images of $5 \text{ nm} \times 5 \text{ nm}$ area in SAS are shown in figure 4(a). The AFM images have the non-equilibrium structure of the $C(2 \times 2)$ reconstruction as a unit cell (labelled A) at the interface between the (001) layer of NaCl(c) and water. The sodium ions are at the same vertical height as the chloride ions, as shown in the cross section profile in figure 4(b). If the alignment along the axis labelled B in figure 4(a) consists of sodium ions, another alignment along the axis labelled C consists of chloride ions. Since a two-dimensional unit cell is of area $0.62 \text{ nm} \times 0.62 \text{ nm}$ (see figure 4(b)), the two-dimensional number density n_s of the metastable layer is equal to 5.5 nm^{-2} . The above distance between like ions becomes longer by about 0.05 nm ,



(a)



(b)

Figure 3. (a) AFM image of the NaCl surface covered with its own (SAS). (b) Cross section profile in the direction of the arrow in (a). The height of the steps, the number of which is greater than that in air (see figure 1), is one atomic layer. The observed steps are convex as well as concave.

compared with the lattice constant of NaCl(c) and the above magnitude of n_s is small in comparison with that (6.3 nm^{-2}) of the NaCl(001) surface. It is worthwhile to show that the nearest-neighbour distance along the axis indicated by B or C is equal to 0.37 nm which corresponds to the sum of the ionic radii of chloride ions.

The AFM measurements were carried out at steps after about 30 min and just after the NaCl(001) surface was covered with SAS; 30 min was the shortest time required to reach the atomic resolution of AFM images at steps exposed to water. Figures 5 and 6 show the non-equilibrium structures at the interface between the (001) surface and SAS; their ionic configurations are similar to the NaCl(001) surface except that firstly the sodium ions are still located at the vertical height of chloride ions (see figure 5) without any change from the height of sodium ions at the centre of terraces, or secondly there exists a layer having no sodium ions at the interface between the NaCl(001) surface and water molecules (see figure 6). Since figures 6(b) and 6(c) show that in unit cells labelled A and B there exist vacancies of 0.20 nm in depth between bright spots along their axes, the sodium ions do

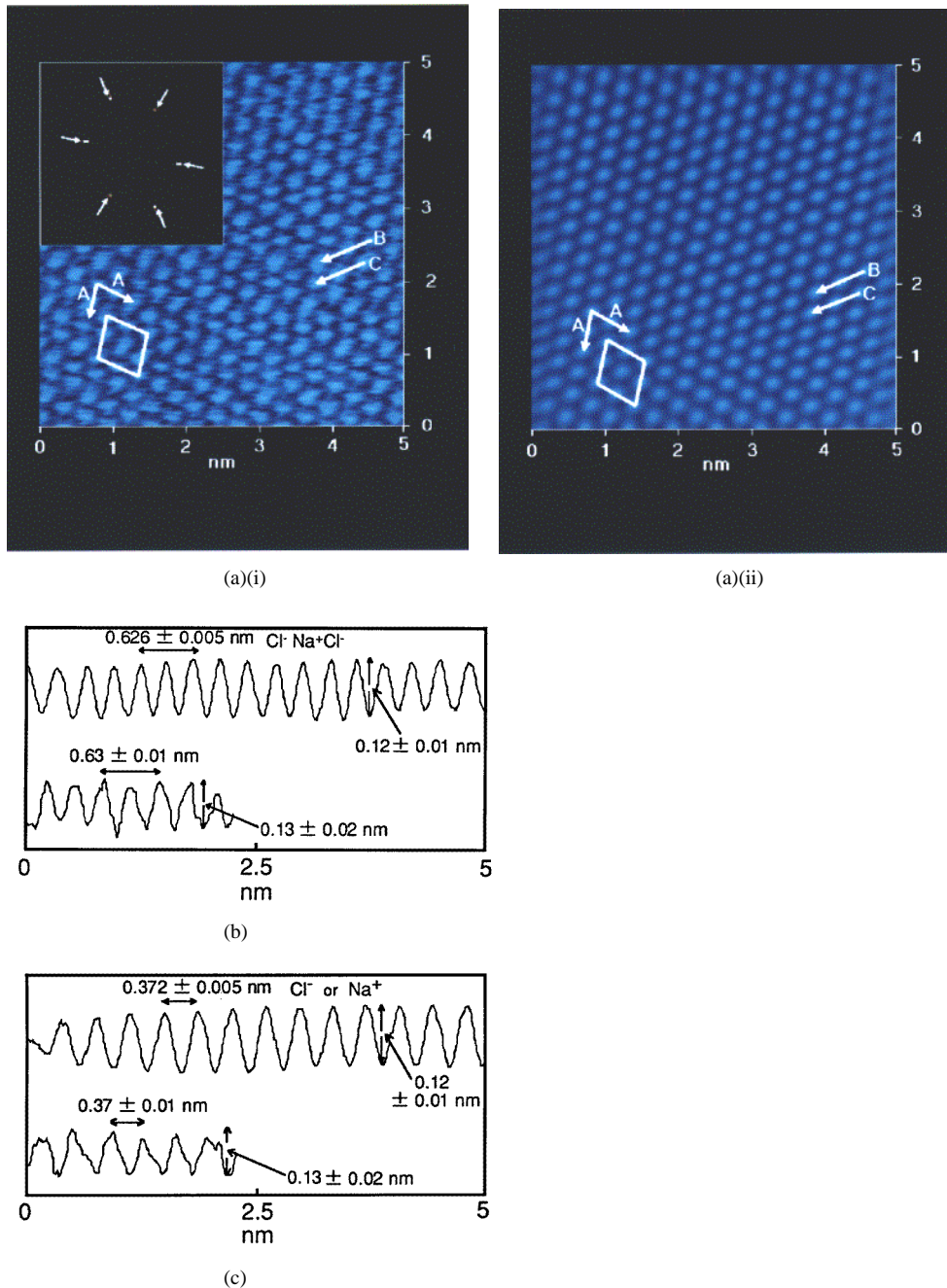


Figure 4. (a)(i) Unfiltered and (ii) filtered AFM images of the NaCl surface at the centre of a terrace in SAS. A rhombus in the images indicates a $C(2 \times 2)$ unit cell. Half of the protrusions correspond to chloride ions and half to sodium ions. The caption of figure 2(a) helps us to understand this figure. (b) Cross section profile (upper curve) in the direction of the two arrows A in the filtered AFM image in (a)(ii). Chloride and sodium ions are aligned alternately and each sodium ion is located at the same vertical height as the chloride ions. (c) Cross section profile (upper curve) in the direction of the arrows B and C in the filtered AFM image in (a)(ii). If sodium ions are aligned along arrow B, chloride ions are aligned along the other arrow C. The lower curves in (b) and (c) were obtained from the unfiltered AFM image in (a)(i).

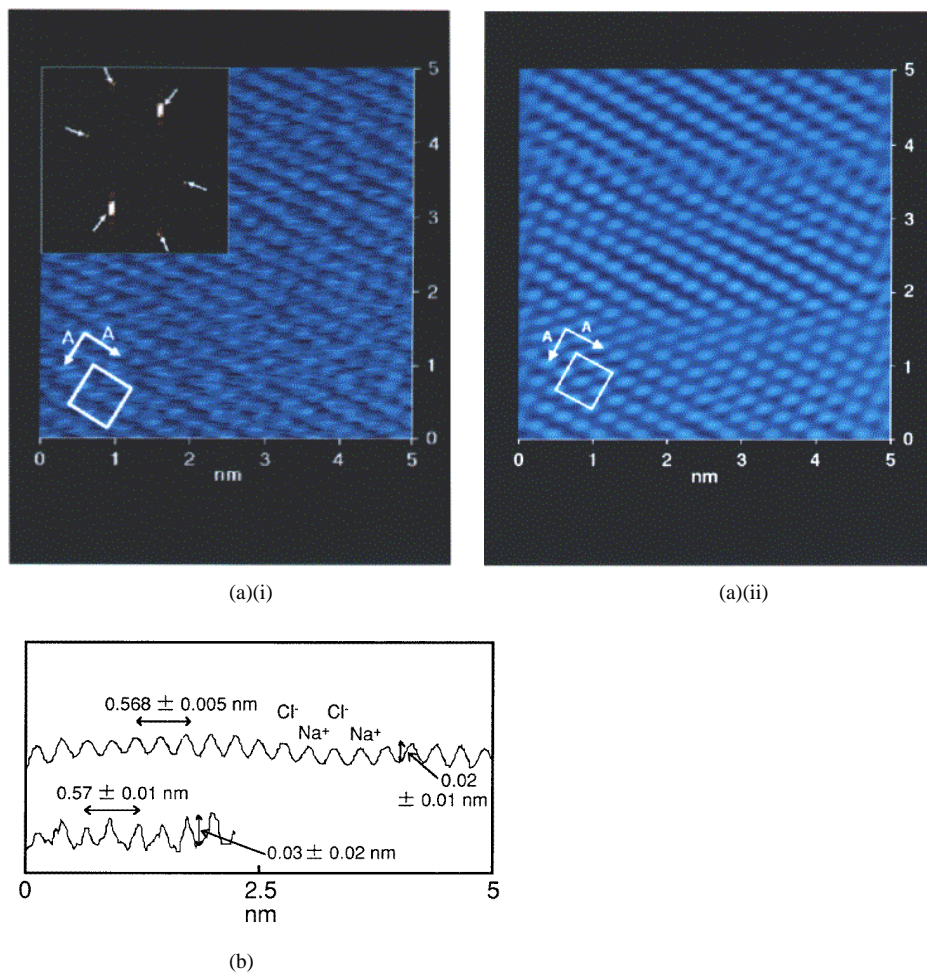


Figure 5. (a)(i) Unfiltered and (ii) filtered atomic-resolution AFM images of NaCl surface at steps in SAS observed about 30 min after the NaCl(001) surface had been covered with SAS. A square ($0.568 \text{ nm} \times 0.568 \text{ nm}$) in the images indicates a unit cell. Half the bright spots corresponds to chloride ions, and half to sodium ions. The caption of figure 2(a) helps us to understand this figure. (b) Cross section profile (upper curve) in the direction of the two arrows A in (a). The distance between sodium ions or chloride ions corresponds to lattice constant of NaCl(c), but sodium ions still exist at the same vertical height as chloride ions. The lower curve in (b) was obtained from unfiltered AFM image in (a)(i).

not stay on the NaCl(001) surface and the intervals between chloride ions along the axis labelled A are equal to the lattice constant of NaCl(c) before and after sodium ions leave the layer at the NaCl(c)–SAS interface.

Since these configurations of ions do not correspond to the equilibrium state, they should depend on real time. After immersion of the NaCl(c) for 3 h, we continued to measure the configurations; figure 7 shows that sodium ions moved to the equilibrium sites of NaCl(001) and the apparent distance of their transfer along the [001] axis was longer than about 0.05 nm, as shown from figures 5(b) and 7(b).

For each filtered atomic-resolution AFM image the nature of the Fourier filtering process has been specified from the spots of fast Fourier transform of each real-space image, as

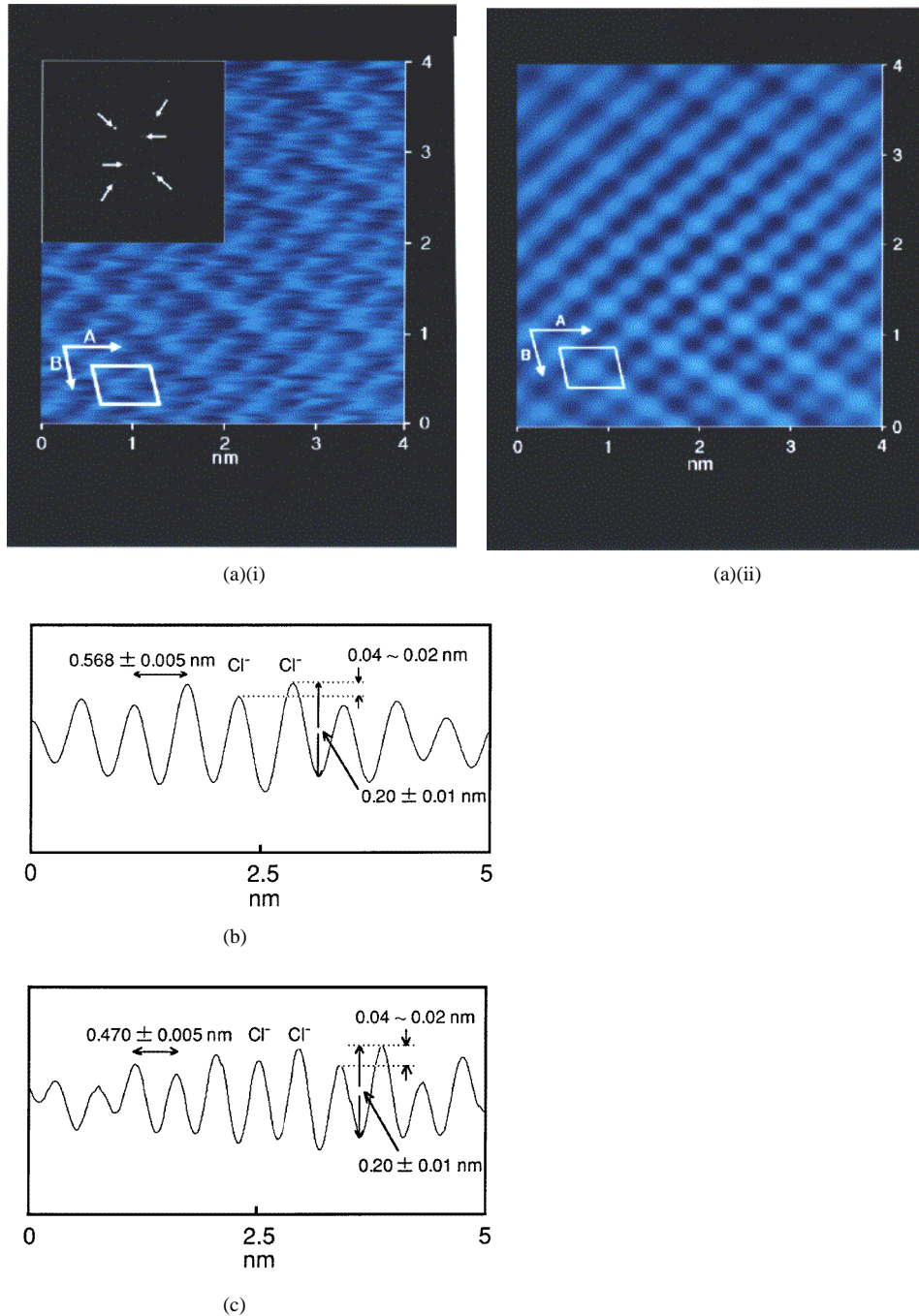


Figure 6. (a)(i) Unfiltered and (ii) filtered AFM images of NaCl surface at steps in SAS observed about 30 min after the NaCl(001) surface had been covered with SAS. The parallelogram in the image indicates a unit cell. All the bright spots may indicate chloride ions and no sodium ions exist on the NaCl(001) surface. The caption of figure 2(a) helps us to understand this figure. (b) Cross section profile in the direction of arrow A in (a). (c) Cross section profile in the direction of arrow B in (a).

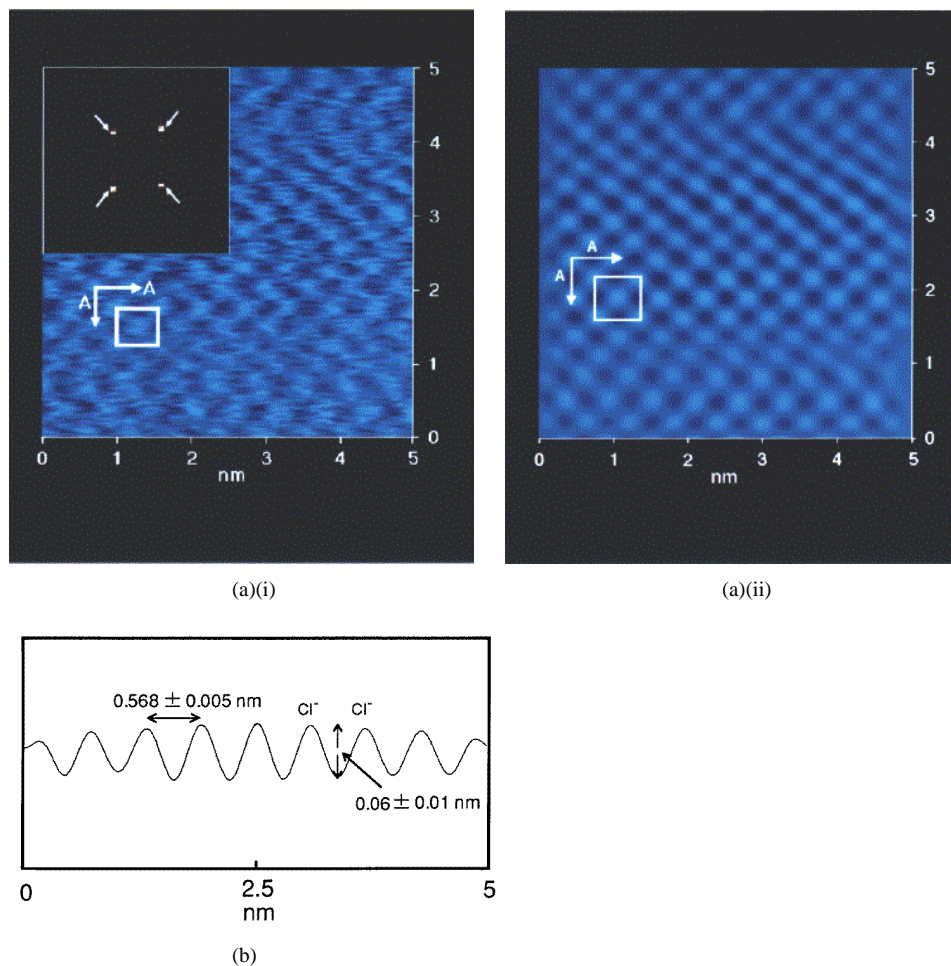


Figure 7. (a)(i) Unfiltered and (ii) filtered atomic-resolution AFM image of NaCl surface at steps in SAS observed about 3 h after the NaCl(001) surface had been covered with SAS. The square in the image indicates a unit cell of NaCl(c) (see the caption of figure 2(a)). (b) Cross section profile in the direction of the two arrows A in (a).

shown in figures 2, 4 and 5–7. The comparison between unfiltered and filtered atomic-resolution AFM images has shown that no Fourier filtering process has ever significantly altered the periodicity and amplitude of atomic corrugations to a different image. Certainly, the lower curves in figures 4(b), 4(c) and 5(b) show reasonable agreement with respect to both the periodicity and the amplitude of atomic corrugation between the observed image without any Fourier filtering process and the Fourier-filtered image.

4. Discussion

The interface between the NaCl(001) surface and water should be individually discussed from the viewpoint of the two categories of atomic structure and microstructure on terraces and at steps in water. The atomic structures on terraces and at steps also should be discussed in order to elucidate the structural transformation associated with the motion of ions at the interface.

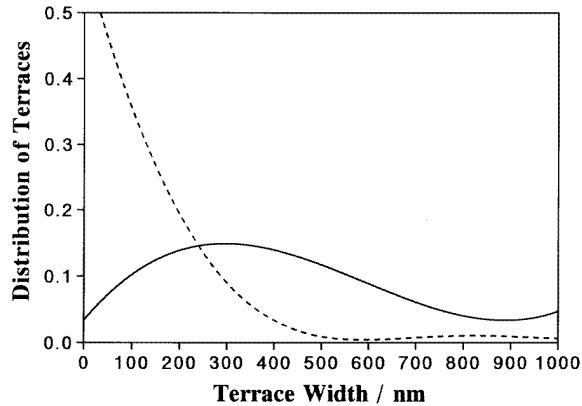


Figure 8. Distribution of terraces versus terrace width. The solid and broken curves indicate the terraces in air and SAS, respectively.

4.1. Microstructures on surfaces in water

The marked increase in steps (see figures 1 and 3) associated with the noticeable decrease in terrace width on surfaces in water makes it clear that the essence of crystal growth proceeds by atom agglomeration at steps and by the forward motion of monatomic steps. Here, the distribution of terraces shows the broad maximum near 250 nm for the cleavage plane (001) of NaCl(c) in air and the terraces in water favour their own much narrower width of less than 100 nm, as shown in figure 8. The fact that many steps are packed closer to each other can be interpreted in terms of the so-called step-flow mode. These results support the fact that the crystal growth occurs in a layer-by-layer fashion by the forward motion of monatomic steps. The forward motion of consecutive steps and the fluctuation in the morphology of monatomic steps may be enhanced by the two-dimensional and cooperative diffusivity of the motion of atoms on terraces, and the impingement rate of ions onto steps as well as terraces from the water phase. The step fluctuation controlled by diffusion kinetics and thermal noise is defined by the non-equilibrium correlation function of the coordinate, which is perpendicular to steps along the x axis, in the steady state [17]. This fluctuation has been observed as the rectangular extensions Δy perpendicular to steps. Figure 3 demonstrates that Δy is equal to about 50 nm and their width to about 25 nm. The advancing step fluctuation is enhanced on surfaces covered with SAS.

4.2. Non-equilibrium structures on terraces at the interface between NaCl(001) and water

The decrease in n_s was observed as mentioned in section 3 and local electric neutrality should occur on the terraces. The moment that the NaCl(001) surface cleaved in air came for the first time into contact with the SAS, the same numbers of Na^+ and Cl^- were dissolved into the liquid phase in an irreversible process. The displacement of ions on terraces took place within their own ionic radii or diameters after they had been dissolved. Their displacements were well regulated by two-dimensional and cooperative motion under the control of the underlying NaCl(001) surface. The sodium ions shifted from their own places to the vacancies of chloride ions in a distance equal to approximately their diameter; both cations and anions were displaced in the same direction. Thus, the surface translation caused a non-equilibrium configuration in a stationary state. The $\text{C}(2 \times 2)$ structure observed

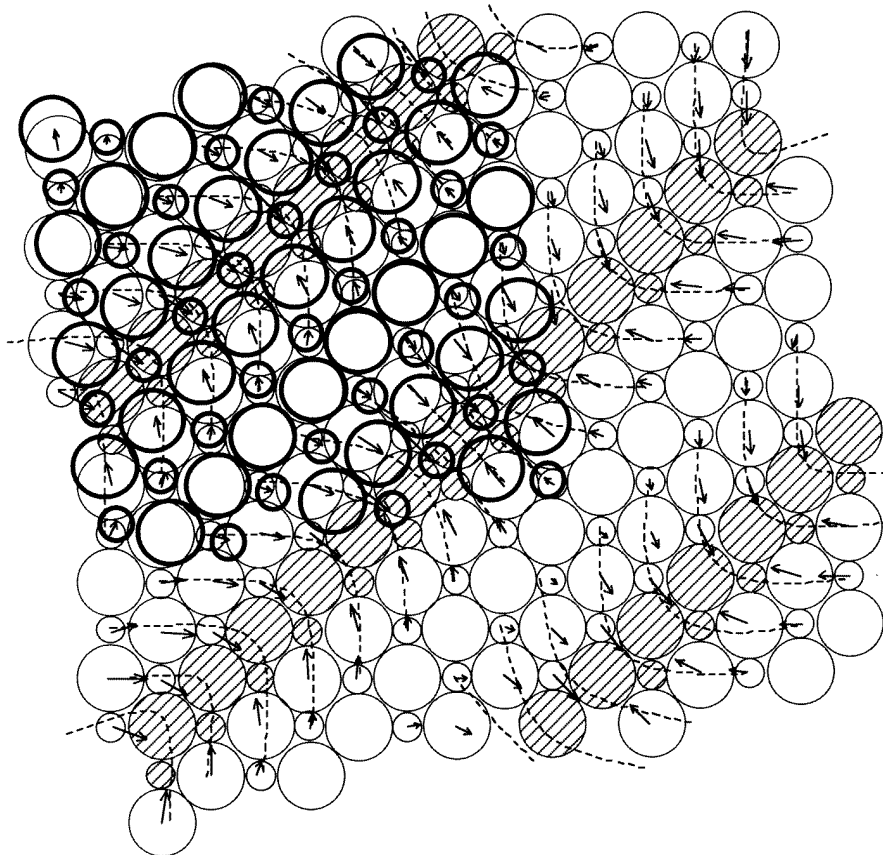


Figure 9. The proposed model for the two-dimensional displacement of ions at the interface between the NaCl(001) surface and water; the relative directions and relative lengths of their surface transformation vectors are demonstrated by the arrow for each ion. The chloride ions (larger circles) and sodium ions (smaller circles) denoted by shaded circles were dissolved in water. The metastable layer established by the above translation corresponds to the two-dimensional configuration of the bold circles (partially shown in this figure); the two-dimensional configuration reproduced the non-equilibrium structure of figure 4(a) observed at the centre of terraces exposed to water.

at the centre of the terraces was independent of real time for the AFM measurements and was characteristic of a metastable layer (see figure 4). Figure 9 shows the proposed model for their relative displacements and for the metastable $C(2 \times 2)$ structure on the centre of terraces exposed to water. Since the distances of unlike and like nearest neighbours in a unit cell of $C(2 \times 2)$ structure became longer (see figures 4(b) and 4(c)), the water molecules have a chance to be brought into contact with Na^+ on terraces and as a result of the interaction with each other the sodium ions stay at the same height as the chloride ions, as shown in figure 4(b).

4.3. Atomic structure at the steps of the interface between NaCl(001) surface and water

Since the ions in the metastable configuration diffuse on terraces and reach the steps, a unit cell of $C(2 \times 2)$ observed on terraces (see figure 4) brings about a structural transformation

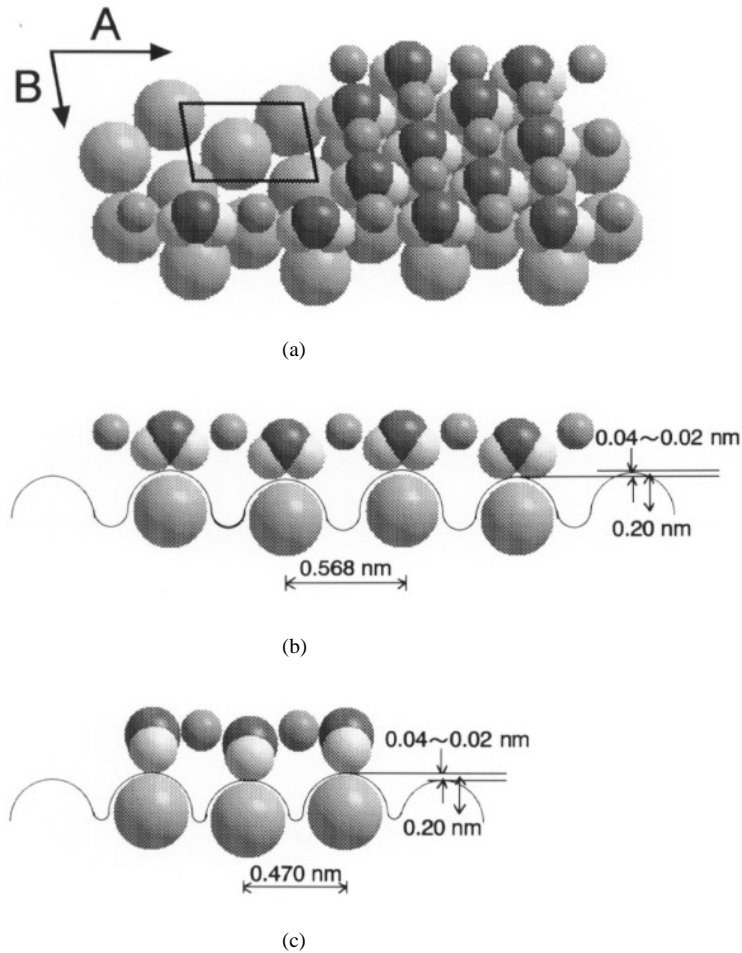


Figure 10. (a) The proposed model for the AFM image of figure 6(a) is as follows: at steps the chloride ions (large spheres) may be covered with sodium ions (small spheres) from the equilibrium sites on NaCl(001) surface and water molecules. Since these sodium ions are surrounded by the water molecules, the sodium ions and water were unable to be imaged by the AFM tip. Here, the configuration of chloride ions on the NaCl surface was given by the AFM image in figure 6(a) and a parallelogram in figure 9(a) corresponds to that in its AFM image. (b) Cross section profile in the direction of arrow A in the proposed model in (a). (c) Cross section profile in the direction of arrow B in the proposed model in (a).

to the closest packing structure of the equilibrium (001) surface (see figure 5), about 30 min after the sample was covered with SAS. This structural transformation at steps, in which the distance of like nearest neighbours became shorter by about 0.05 nm, gives rise to the forward motion of monatomic steps and crystal growth at steps. However, the Na^+ still remains at the same height as Cl^- , after about 30 min. In another metastable configuration at steps (see figure 6), no sodium ions stay on the surfaces under the effect of the interaction with water molecules. Figure 10 shows a schematic representation of the proposed orientation of water molecules and sodium ions which cover the surface at steps; the surface consists of only chloride ions and their configuration is given in figure 6.

These water molecules cause partial hydration of the sodium ions which are located just above the surface; since indirect and direct correlations between unlike ions observed by neutron diffraction measurements show incompletely hydrated ions [18, 19], one can see the super-concentrated electrolyte solutions at the interface between the NaCl(001) surface and water. The cross section profiles of the proposed model (see figure 10(a)) for the observed image of figure 6(a) are shown in figures 10(b) and 10(c); the corrugations along the arrows A and B in figure 10(a) reproduce the experimental results in figures 6(b) and 6(c).

Since the crystal growth at steps is normally sufficiently slow for the diffusion field to relax to the equilibrium state, the atomic structure at steps was measured more than 3 h after they had been covered with SAS. Any observed atomic structures at steps were equivalent to the NaCl(001) surface in an equilibrium state except for the slightly higher positions for sodium ions by about 0.025 nm (see figure 7(b)) because of the interaction with water molecules.

The AFM images observed on terraces and at steps have allowed us to sort out the non-equilibrium atomic structures in each stationary state. One can expect to see progress in the nanofabrication of the non-equilibrium atomic structure of the interface between the ionic crystal and water. The new configuration of a unit cell may be more easily attainable by the surface translation of ions through energetically favourable diffusion paths at the interface associated with the changes in the interionic distances and bond angles than by the formation of new bonds as well as the breaking of old bonds. It can be concluded that the two-dimensional transformation occurs on terraces and at steps; the non-equilibrium $C(2 \times 2)$ structure is established on terraces exposed to water (see figure 4) and is transformed to the equilibrium structure of NaCl(001) at steps (see figure 7). The crystal growth at steps in SAS was sufficiently slow to carry out the quasi real-time measurements using AFM.

Acknowledgment

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