

# Atomic force microscopic observation of surface processes on salts in humid air

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Atomic force microscopic (AFM) observation of surfaces of alkali halide crystals in air revealed spontaneous motion of monatomic steps depending on the line tension of the steps and the relative humidity (RH). In the case of NaCl, the step motion was noticed at above 47% RH. Further increase in the step speed with RH is related to phase transition of adsorbed water at the surface. Capillary condensation of 3-dimensional (3D) water was observed at the contact of the AFM tip with the surfaces, where salt hillocks were formed. The step motion on NaCl was retarded by the presence of voids at the surface, which contain the 3D water. The structure of NaCl surface in the saturated aqueous solution was also studied.

## 1. INTRODUCTION

In a humid climate like in Japan, caking of salt is a serious problem in households and in storehouses. In order to prevent it, the first thing to do is to know the enemy, or in other words, to analyze the process in the atomic level. Fortunately, we have a new experimental technique called Atomic Force Microscopy (AFM)<sup>1</sup>, with which we can observe *in situ* the transportation processes of atoms at salt surfaces in air, in vacuum, or in liquids without any pre-treatments.

In AFM, a very tiny stylus attached to a flexible cantilever is scanned horizontally over the sample surface as shown in Figure 1. The bent of the cantilever due to attraction and repulsion of the stylus by the surface atoms is detected by deflection of the laser light illuminated on it. The recorded image gives the profile of the surface including regular arrangement of atoms, positions of defects and steps. The technique is especially

sensitive in height measurements.

In the present experiments, NanoScope III AFM of Digital Instruments was used. Commercially available silicon cantilevers with silicon nitride tip were used.

## 2. RESULTS AND DISCUSSION

### 2.1. Step motions in humid air

The AFM images in Figure 2a,b were observed on NaCl(001) with 3 minutes' time

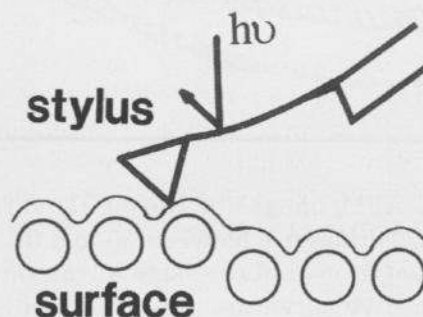


Figure 1. Principle of operation of AFM.

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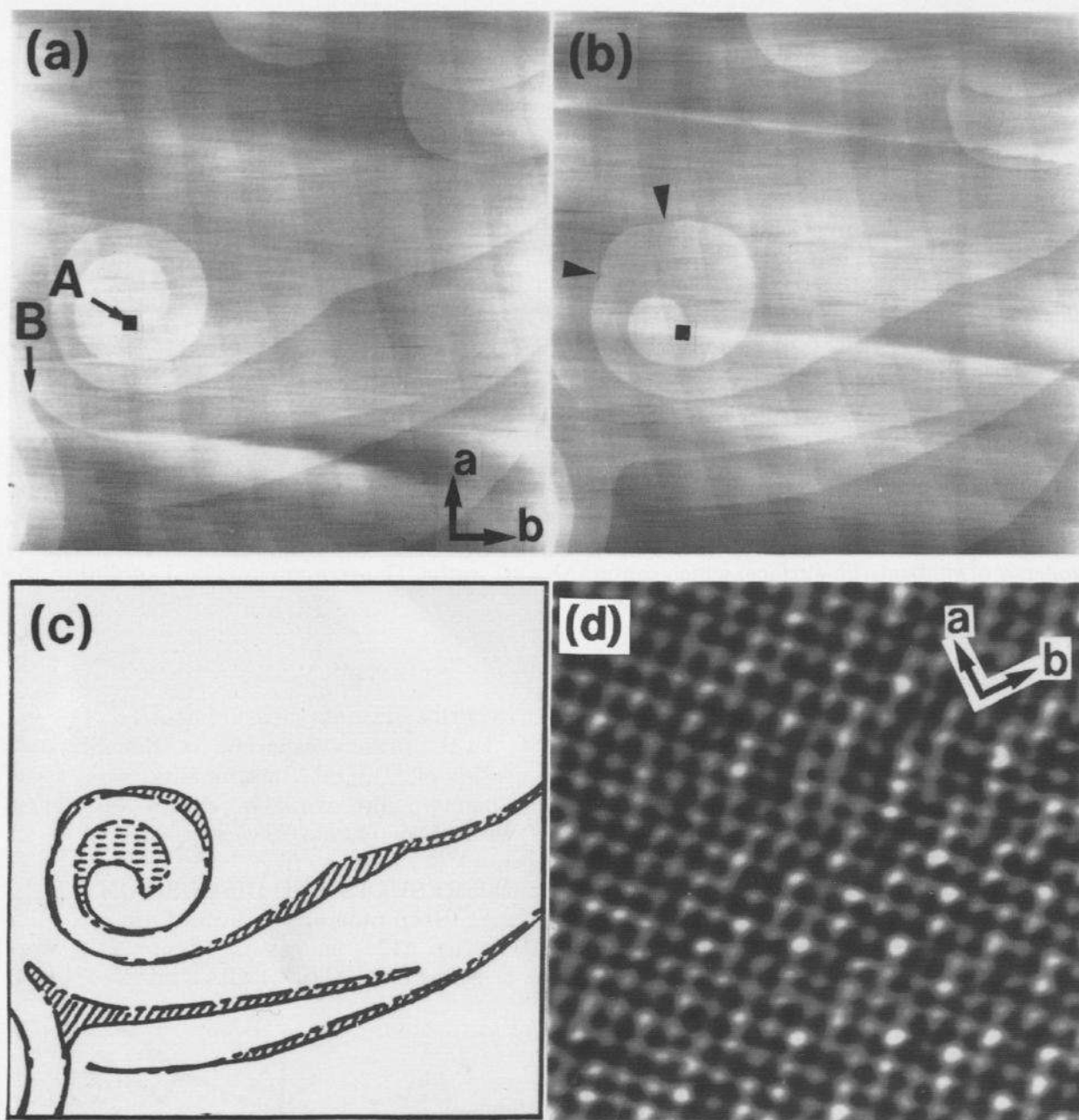


Figure 2. AFM images of NaCl(001) surface. (a,b)  $8\ \mu\text{m} \times 8\ \mu\text{m}$  images recorded with 3 min. interval. (c) difference between (a) and (b). The area with minus signs indicates step retreat, while the hatched areas indicate step advancement. The spiral step originating at screw dislocation A with a positive curvature is retreating due to the line tension, while the part B with a negative curvature is advancing quickly. (d) While the step motion is observed, periodic structure of the surface atoms are observed ( $7\ \text{nm} \times 7\ \text{nm}$ ). The bright spots are considered to be given by the larger Cl ions. The dents as indicated by the wedges in (b) were formed by the anisotropy in the step motion.

interval. Brighter parts are located at higher levels. The curves are monatomic steps which move spontaneously. The difference between the two images are shown in Figure 2c. Thermal drift of the images was compensated for by the positions of cores of screw dislocations which do not move. The spiral step originating at the dislocation A and having a large positive curvature is retreating, while the step having a negative curvature at around B is advancing very quickly. This is quite reasonable considering line tension, or one-dimensional surface Gibbs energy.

While the steps are moving, atom-resolved AFM image was observed at terraces as shown in Figure 2d, indicating that the surface is still in solid state. Presence of dents on the spiral step, as indicated by the wedges in Figure 2b, also shows the solid-like nature of the surface. While the  $\text{Na}^+$  and  $\text{Cl}^-$  ions are supplied from the upper terrace, more of them are used in the advancement of the step in  $\langle 110 \rangle$  directions rather than in  $\langle 100 \rangle$  direction. It is due to the stability of electrically neutral steps along the crystal

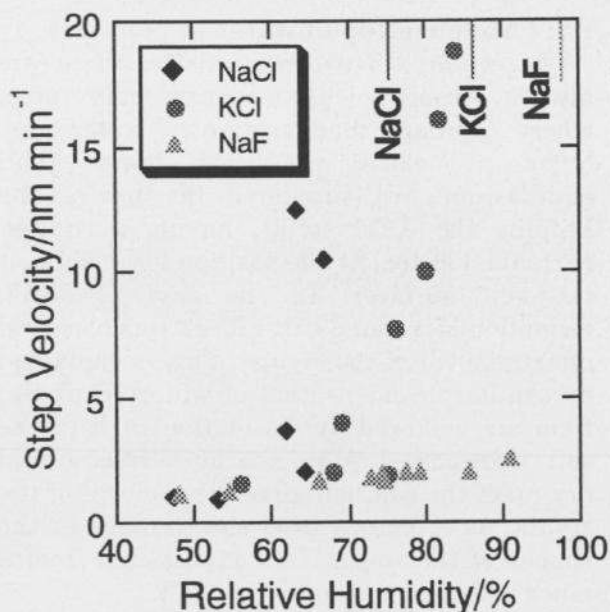


Figure 3. Dependence on relative humidity of the step mobility on alkali halide surfaces. The ticks at the top indicate deliquescence points. The data for NaF are for step retreat.

axes compared to polar steps.

As will be discussed in 2.3, the same phenomenon was observed in an experiment in saturated aqueous solution of  $\text{NaCl}^2$ .

At room temperature, the ions cannot move without the help of adsorbed water. We have, then, checked the dependence upon relative humidity (RH), of the speed of the step motions on various salt surfaces.

Step speeds can be measured by comparing AFM images recorded with appropriate time intervals while keeping the RH constant. In order to avoid the effect of curvature, the step speeds were measured at straight parts. Slower speeds, however, cannot be measured very accurately since small displacements are measured.

The results are shown in Figure 3. In the case of  $\text{NaCl}$ , step motion was first detected at 47% RH. From 63% to 70% RH, rapid increase was observed in the step speed<sup>3,4</sup>. The increase is most probably related to the phase transition of adsorbed water.

Such phase transitions were proposed through adsorption experiments of water with powder samples<sup>5-7</sup>. As illustrated in

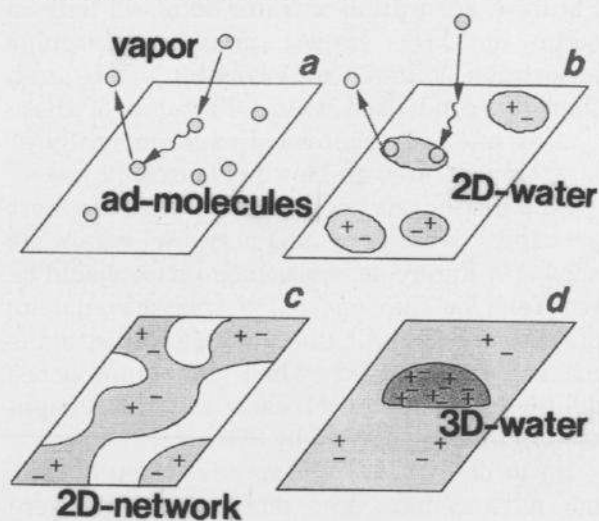


Figure 4. Various phases of adsorbed water on salt surfaces.

(a) molecular adsorption, (b) 2D-condensed phase, (c) 2D-network, (d) 3D-condensed phase. At least 2D-network is required for the ions to be transported long distances.



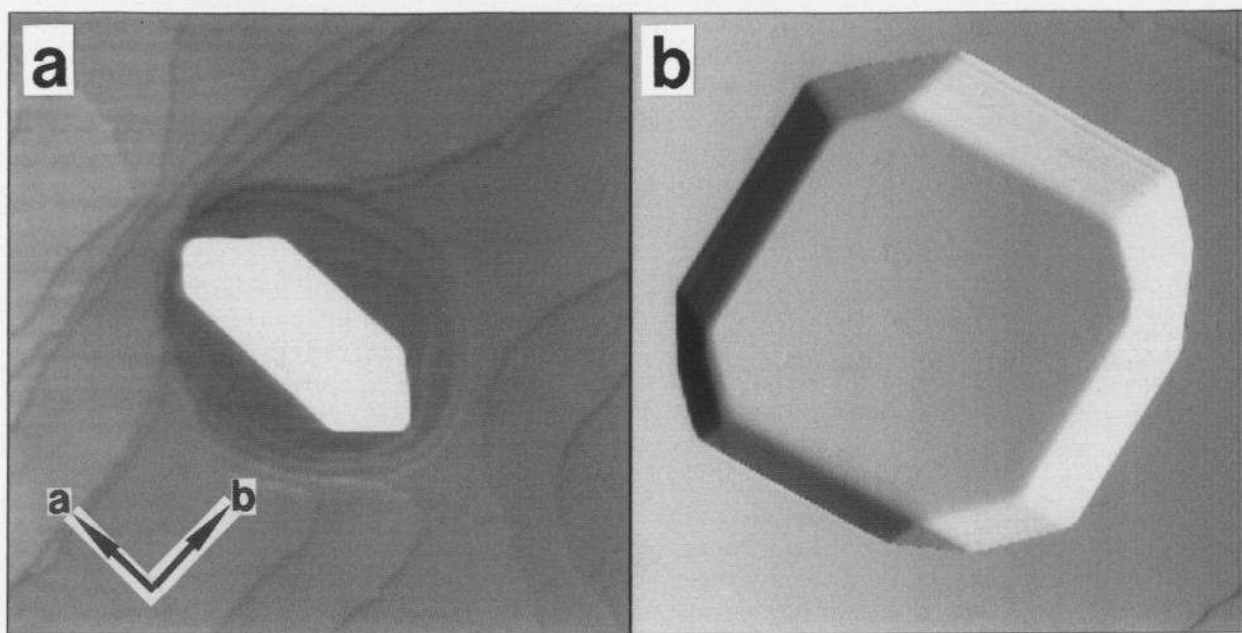


Figure 5. AFM images of micro-crystals spontaneously growing on NaF surface after prolonged contact with the stylus. (a) Topographic image ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of an epitaxially growing micro-crystal (32.6 nm thick). The salt is pumped up from the substrate to the top of the crystal by water. (b) Deflection image ( $1.7\ \mu\text{m} \times 1.7\ \mu\text{m}$ ) of another micro-crystal.

Figure 4, adsorption of water on alkali halides occur in three stages, namely, molecular adsorption, followed by formation of 2D- and, then, 3D-condensed water. Presence of those phases has been confirmed experimentally at low temperatures and low pressures.<sup>8-10</sup>

Step motions at lower RH in Figure 3 is most probably caused by 2D-network water as shown in Figure 4c, since such phase would be required for the ions to be transported long distances. For NaCl and KCl, the step speed is markedly increased when RH approaches deliquescence point of each salt. The rapid motion must be caused by 3D-water.

In the case of NaF, the speeds of step retreat, not advancement was measured. We were unable to raise RH high enough to cause rapid increase of the step speed at flat terraces. Those parts are deprived of the 3D water. Presence of 3D water around NaF micro-crystals will be discussed in the next section<sup>4</sup>.

## 2.2. Condensation of water at contacts

At contacts between particles, there are always surfaces with negative curvatures, where capillary condensation of water may occur at vapor pressures lower than equilibrium. We simulated the process by keeping the AFM stylus, having a square-pyramidal shape, at one position for a while at the salt surfaces. In the case of NaCl, formation of a round salt hillock was observed after removal of the stylus<sup>3</sup>. This is explained by capillary condensation of water (3D-phase) from air, followed by dissolution in it of the salt transported from nearby terraces, and dry-up of the solution after the removal of the stylus. As is known from the changes in the shapes of the steps, NaCl is collected from a much wider area compared to KCl.

In a similar experiment with NaF, which has a larger lattice energy and a lower solubility in water, a single crystal was formed at the contact as shown in Figure 5. It kept growing spontaneously even after the removal of the stylus<sup>4</sup>. Water pumps the salt from the

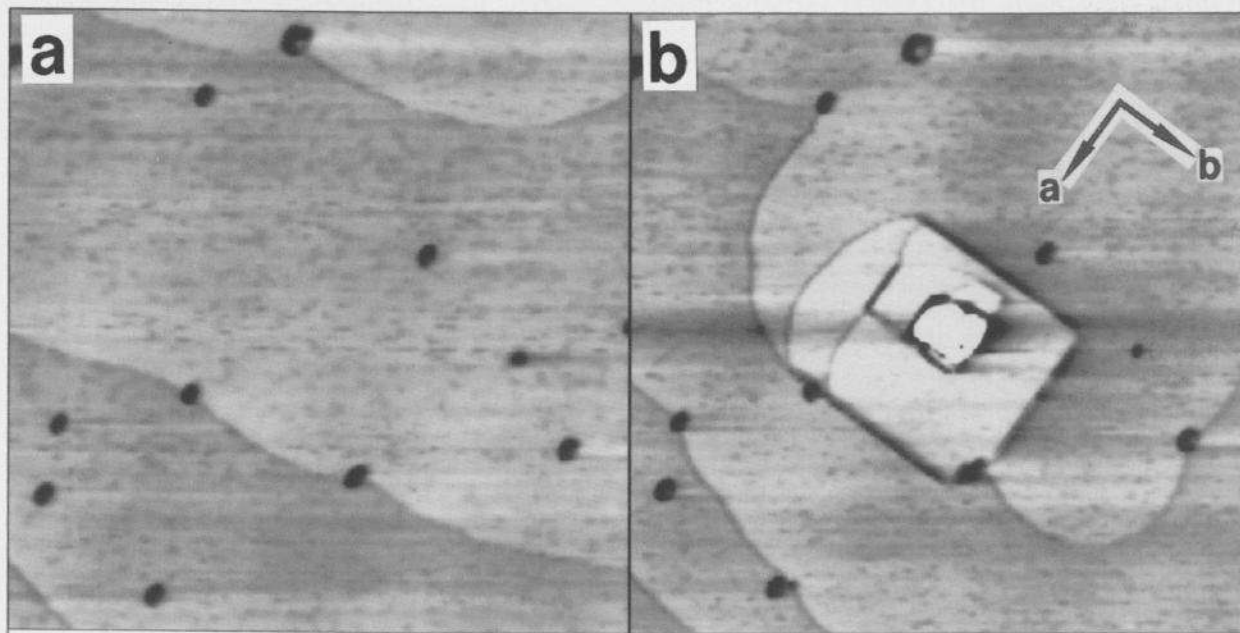


Figure 6. AFM images ( $3\ \mu\text{m} \times 3\ \mu\text{m}$ ) before and after formation of a micro-crystal at NaCl surface having lots of voids (296.5 K, RH=58.5%). (a) Before contact. (b) After placing the stylus for 55 min at the center of the imaged area. The square shape of the hillock (29.5 nm high) indicates that it was grown epitaxially by restricted supply of salt from upper terraces.

lower terrace to the upper face of the micro-crystal. Formation of a ditch around the micro-crystal is explained by the presence of 3D-water there.

The growth of the hillock occurs without scanning the surface with the probe. However, the growth is accelerated several times by the scanning of the surface with the stylus. The probe is transporting some of the salt.

Although the capillary condensation of water at contacts are inevitable, we can decelerate the caking process, if we can suppress mobility of the steps. We have observed such cases with NaCl<sup>4</sup>.

When a step was passing a void with the diameter of about 50 nm, the step motion was considerably delayed by the void. Most probably, condensed 3D water in the void takes in salt ions migrating on nearby terraces and prevents advancement of the steps.

At a surface having lots of such voids, steps were segmented into arcs, with both ends being pinned by the voids. Practically, the steps could not proceed at all. Making such

voids at the surface would promote capillary condensation. However, it would prevent the caking process as a whole.

The pinning of steps at the voids is seen in the AFM images in Figure 6. Here, the hillock formation was tried on NaCl surface having lots of voids. Since the surface energy of step segments connecting voids are minimized when they are straight, the voids would resist against both advancement and retreat of the segments. The ionic mobility is, then, fairly suppressed at this surface. This is reflected upon the shape of the micro-crystal formed. The square hillock is most probably a single crystal epitaxially grown under restricted supply of salt from upper terraces. If there is quick supply of salt, the resulting hillock will have a round shape as was reported previously<sup>3</sup>.

### 2.3 AFM observation in solution phase.

The AFM image of the NaCl crystal surface in Figure 7 was observed in the saturated aqueous solution of NaCl. Since the

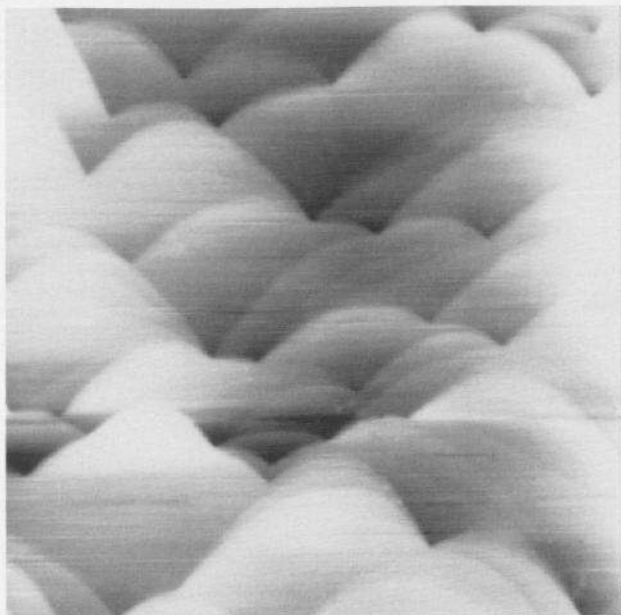


Figure 7. AFM image ( $10\ \mu\text{m} \times 10\ \mu\text{m}$ ) of NaCl surface in the saturated aqueous solution. From six to eight arc steps get bunched at singularities where electrically neutral, stable steps meet at right angles.

cleaved surface is not entirely flat, transportation of the salt occurs from higher to lower parts of the surface. Salt is flowing down from the bottom to the top of the figure.

In that process, monatomic steps are bunched at singularities where electrically neutral steps along the crystal axes intersect at right angles.

The development of this structure was described in our previous report<sup>2</sup>. The advancement of monolayer steps occurs very quickly in the beginning, but the speed depends on their directions. The growth rate is slower at parts closer to the directions of the crystal axes because of their electric neutrality. The monolayer steps, thus, become segmented into arcs connected at corner sites where the two neutral steps intersect at right angles.

The curved parts either cannot proceed

quickly because of their higher line tension due to the positive curvature. The steps are, then, caught up by the next steps coming from behind. Once the corner sites become higher than bilayer, they become extremely stable because of electrostatic protection from adsorption of new ions. In Figure 7, from six to eight monatomic steps are bunched at the corner sites. Step bunching occurs without presence of impurities. The surfaces of growing NaCl crystals must be just like this.

As has been described in this paper, AFM can be used in various conditions and in many different ways. This versatility in addition to the atomic resolution and the real-time capability will make it one of the most powerful tool in studying surface processes of salt crystals.

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