Cleavage of a Layered Compound $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$ in Two Ways[†]

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Cleaved surfaces of $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$, a layered compound with two different interlayer structures, were observed with Atomic force microscope (AFM). Comparison of the atom-resolved images with the crystal structure clearly showed that there are two different ways of cleavage. The more flexible but weaker interlayer was broken in a 'slow' cleavage with application of a very weak tensile force, while the stronger and more rigid interlayer was mainly broken in a 'rapid' cleavage with an excessive force. In estimation of cleavability, dynamic factors must be taken into account in addition to static parameters.

1. Introduction

Obtaining a well-defined and atom-flat substrate is an essential part in constructing two-dimensional assembly of atoms and molecules. Cleaved surfaces of layered compounds such as mica are conveniently used for that purpose. In the case of mica, however, we cannot tell exactly on which face the potassium ions stay upon cleavage.

On the other hand, equal partners are obtained on cleaving the title compound, potassium niobate. In that sense, the cleaved surfaces are well-defined. We have previously reported atom-resolved AFM images of the surface.¹⁾ We also showed that we can use the surface for arranging alkyl ammonium ions by the exchange of K^+ on it.²⁾

As will be explained later in **Fig. 1**, the crystal has two different interlayer structures. It seems reasonable that only cleavage at the weaker, water-containing interlayer has been observed. However, this is not always the case, since cleavage is a dynamic process. We report in this paper, how the other possibility realized.

In our experiments, the single crystals were cleaved in air by peeling off the upper layers with Scotch tape. A Nanoscope II AFM from Digital Instruments was used in observing the atomic arrangement of the cleaved surfaces. Comparison of the AFM images with computer models of the cleaved surfaces shows clearly where the cleavage occurred.

2. Results

The structure of $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$ is shown in **Fig. 1**. Since no crystal data were available for the compound itself, the data for the rubidium salt are used here; orthorhombic, P_{mn} , $a_0=7.83$, $b_0=39.06$, $c_0=6.57$ Å, $z=4$.³⁾ The structure should be the same with the potassium salt, since the ionic radii of Rb^+ and K^+ are nearly equal. The thickness of a niobate sheet ($=1/4b_0$) is about 1 nm.

As shown in **Fig. 1**, the water molecules form $\text{K}-(\text{water})_2\text{-K}$ chain structure in the rugged interlayer I.³⁾ The water molecules also connect the niobate sheets through hydrogen bonds with niobate oxygens. On the other hand, the sheets are connected solely by K-O ionic bonds at the smooth interlayer II.

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Fig. 1 Crystal structure of $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$.³⁾ Only the rugged interlayer I is hydrated, 'W' denotes the oxygen atoms of the water molecules. The water molecules combine niobate layers by hydrogen-bonding with O atoms in the niobate layers and by coordinating with K ions. Only K-O ionic bonds combine the niobate layers in the interlayer II.

The cleavage at the two interlayers are easily distinguished by comparing observed atomic arrangement with computer models of the cleaved surfaces.¹⁾ When a weak tensile force was applied by peeling off the Scotch tape as slowly as possible, cleavage always occurred at the interlayer I. When steps are observed, the heights are always the bilayer thickness of 2 nm, or its multiples.²⁾ It is concluded that the hydrogen bonds between water molecules and niobate oxygen in the interlayer I are weaker than the K-O ionic bonds in the interlayer II.

However, different results were obtained when the crystal was cleaved by peeling off the sticking tape very quickly and giving a large tensile strength. A $2\text{ }\mu\text{m}$ square AFM image of the surface thus obtained is shown in **Fig. 2**. The step height at the edges of the triangular region is 0.9~1.0 nm, which corresponds to one niobate sheet. It indicates that cleavage at the interlayer II occurred either inside or outside of the triangle.

Atom-resolved AFM height images observed at inside and outside of the triangle are shown in **Figs. 3**

Fig. 2 AFM height image ($2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$) after 'rapid' cleavage. The step height at the edges of the triangle corresponds to one niobate sheet, or $1/4 b_0$. The cleavage both at the interlayer I and II occurred simultaneously inside and outside the triangle, respectively. The atom-resolved images are shown in Fig. 3.

Fig. 3 Atom-resolved AFM height images (6nm $\times$ 6nm) observed at (a) inside and (b) outside of the triangle shown in Fig. 2, respectively. The zigzag spot pattern in (a) corresponds to the cleavage at the interlayer I followed by evaporation of the water molecules.¹⁾ The spots on straight lines in (b) correspond to the arrangement of K ions after cleavage at the interlayer II.

(a) and 3(b), respectively. The image in Fig. 3(a) corresponds to the cleavage at the interlayer I.¹⁾ The arrangement of the K ions and the uppermost O atoms of the niobate sheet are observed. When the water molecules are lost upon the cleavage, the K ions forming the K-(water)₂-K chains fall down to a lower level, giving the structure similar to the cleaved surface of the anhydrate. That is why the larger K ions are detected as less bright spots compared to the uppermost O atoms.

On the other hand, the spot pattern in Fig. 3(b) corresponds to the arrangement of K ions after cleavage at the interlayer II.¹⁾ As seen in Fig. 1, the O and K atoms are located at the same level along the *b*-axis. However, only K ions were detected in Fig. 3(b) since the ionic radius of oxygen is smaller.

When a much wider area was surveyed, many triangles as shown in Fig. 2 were observed. As a whole, however, the cleavage at the interlayer II prevailed.

3. Discussion

Cleavage investigations in relation to atomic structures of crystals originated from the work by Bravais⁴⁾ in 1851. Many works followed since then.⁵⁾ Cleavability of ionic crystals has been estimated from structure data in several ways. Shappell defined the cleavability in a way closely related to the mechanical properties, such as the tensile strength, rather than energy terms.⁵⁾ He estimated bond strengths of ionic pairs crossing a cleavage plane, calculated their normal components, and took summation within unit area. The reciprocal of the sum was defined as the cleavability along the crystal plane.

As discussed by Wells, this approach is not universally applicable, since there were lots of exceptions.⁶⁾ However, the definition by Shappell seems appropriate in the cases of cleaving layered compounds with a sticking tape. Actually, his theory successfully predicted highest cleavability of layered muscovite (a kind of mica) in (001) direction, due to the comparatively weak K-O bonds holding strong layers together.

Similarly, it is predictable that cleavage in (010) direction is easiest for the niobate. However, there are two possibilities. The 'slow' cleavage of the niobate at the interlayer I indicates that the breaking strength takes the minimum there, not at the interlayer II. It is quite reasonable since hydrogen bonds are generally weak. As stated by Huggins⁷⁾, weak bonds would be ruptured in preference to strong bonds.

On the other hand, dynamic factors must be taken into account in explaining the 'rapid' cleavage at the interlayer II. When excessive force is applied to a crystal, the cleavage does not necessarily occur at the plane having the minimum breaking strength.

Although microscopic mechanism of advancement of the cleavage front is not known yet, we speculate that a more flexible structure of the interlayer I prevent it from breaking first. On stressing the crystal, the network structure of the interlayer I will be distorted considerably. However, the breaking strength will not drop quickly during the straining process, since changes in the shape and positions of the water molecules will try to sustain the bond strengths. It will take some time to strain the interlayer I to the point where it becomes irreversible.

On the other hand, the interlayer II has a rigid structure. When the crystal gets a stress, the interlayer will be strained, too. However, the bonds connecting the sheets there is mostly ionic. The breaking strength of interlayer II will fall rather quickly in the straining process since there is no damper mechanism. The net result is, cleavage occurs at the interlayer II before the strain at the interlayer I becomes irreversible. Theories on cleavage should be modified to include dynamic factors.

Detailed calculations will be necessary to support the above discussion. However, it is rather difficult to estimate the strength of the hydrogen bonds. At present, we just state that several well-defined substrates can be selectively obtained from a layered compound simply by changing the way of cleavage.

Presence of defects in the crystal might give an alternative explanation for the different patterns of cleavage. As reported by de Wainer and Bassett⁸⁾ on the cleavage of rock salt crystal, different step structures are obtained depending on the speeds of crack propagation and dislocation movements.

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