

Investigation of the (001) cleavage plane of potassium bromide with an atomic force microscope at 4.2 K in ultra-high vacuum

F.J. Giessibl and G. Binnig

Physics Group Munich, IBM Research Division, clo Universität München, Schellingstrasse 4, W-8000 München 40, Germany

Received 12 August 1991

We have imaged the (001) surface of KBr with a UHV atomic force microscope at 4.2 K and 300 K. The sample was prepared by cleaving it in UHV along the (001) plane. We achieved atomic resolution at 4.2 K and resolved both the potassium and the bromium ions. We show atomically resolved images of flat terraces as large as 25 nm by 25 nm. Force-versus-distance measurements were taken, and the influence of the loading force acting between sample and cantilever on the appearance of friction effects and sample damage was studied.

1. Introduction

The atomic force microscope (AFM) is a tool that allows the study of nonconducting surfaces on the atomic scale. It has been operated in air [1], water [2], ultra-high vacuum (UHV) [3], liquid helium [4] and UHV at liquid-helium temperature [5]. Recently the AFM has been used to study electrochemical deposition processes on the atomic scale [6].

The contribution of the AFM to the understanding of the physics and chemistry of surfaces is so far much less significant than that of the scanning tunneling microscope (STM). In the STM, the tunneling current is the parameter which is used to form an image and even delivers information about the chemical nature of the surface. The tunneling current decays extremely fast (for common work functions a change of 0.1 nm in the tip-sample distance causes a change in the tunneling current of a factor of 10). Therefore, it is relatively easy to make a tunneling tip in which the electrons tunnel mainly from one atom. The dependence of the tunneling current I on the distance z between tip and sample is $I = I_0 \exp(-2kz)$ to a very good approximation.

In AFM the situation is different. The deflection of the cantilever of an AFM is caused by a force acting between the sample and the tip of the cantilever. However, this interaction force can have a fairly complicated nature, particularly if the AFM is operated in air or water. In general, one cannot assume that the deflection of the cantilever is caused by the interaction of the topmost tip atom and the sample as in STM. In air, meniscus forces of contaminants cause a strong attraction between tip and sample. Furthermore, there are long-range (compared to interatomic distances) van der Waals forces. Therefore the net attractive force depends crucially on the usually unknown shape of the tip and it is quite difficult to estimate the actual spacing between tip and sample.

The resolution of a scanning probe microscope is of the same order as the decay length of the interaction used for probing. The repulsive forces, which arise when two solids are brought into contact, have a very strong distance dependence. Therefore, imaging in the repulsive mode allows atomic resolution.

We have cleaved our crystal in UHV in order to avoid a contamination of the sample. There-

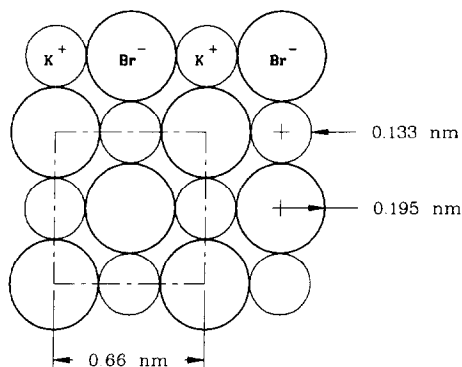


Fig. 1. Surface structure of KBr (001). KBr crystallizes into an fcc lattice with a lattice constant of 0.66 nm. The large circles represent the Br⁻ ions (bare ion radius is 0.195 nm), the small circles represent the K⁺ ions (bare ion radius is 0.133 nm). The crystal can be considered to be composed of positively and negatively charged hard spheres to an excellent approximation [7].

fore, the sample surface is much better defined than surfaces prepared in air.

Alkali halides can be seen as consisting of hard spheres which are charged by plus/minus one unit charge [7] to an excellent approximation. Most of them crystallize into an fcc lattice with two atoms in the basis (the anion at zero and the cation displaced by half a lattice constant in the [100] direction). The natural cleavage plane is (100) since this plane has zero net charge. Fig. 1 shows the KBr surface lattice. The corrugation is 0.062 nm assuming the hard-sphere model. KBr cleaves well, and the cleavage planes look mirror-like.

E. Meyer et al. have achieved atomic resolution of LiF (001) [8], while G. Meyer and Amer [9] have imaged NaCl (001) on the atomic scale. E. Meyer et al. have studied epitaxially grown films of AgBr(100) in air and achieved atomic resolution [10]. We also achieved atomic resolution on KBr. E. Meyer et al. and G. Meyer et al. have resolved the sublattice of one type of ions, and believe that they see the sublattice of the halide ions, as their bare ion radii are bigger. Now, for the first time, both types of ions of an alkali halide have been resolved in our experiment. Large terraces could be imaged with atomic resolution. We were able to operate our AFM

with a very small load and could clearly demonstrate that the imaging process is nondestructive. Furthermore, we were able to establish the crossover to destructive imaging by increasing the load.

2. Experimental set-up

Our AFM uses electron tunneling to determine the deflection of the cantilever. The cantilevers we used are made of Si₃N₄ with and without integrated tips [11–13]. The construction of our AFM is described in detail in ref. [5]. A few changes, however, have been made since then:

- A thermocouple was added to the sample holder. The temperature of the sample is 4.2 (+ max. 0.5) K when the AFM is immersed in liquid helium.
- The UHV chamber which houses the AFM (70 mm in diameter, 150 mm long) was mechanically decoupled from the vacuum system by a welded metal bellow and springs.
- The tungsten tunneling tips were sputtered with a 40 nm layer of platinum. This results in a much better defined tunneling junction. The DC resistance for direct contact between tunneling tip and gold-plated cantilever was 600 Ω with regular tungsten tips and as low as 20 Ω with platinum-coated tungsten tips. This suggests that the native oxide of tungsten causes a degradation of the tunneling contact.
- We have added a mechanism to the AFM which allows in situ cleaving of the sample.

We operated our AFM at 4 K when we took the images with a very low loading force. Working at 4 K offers several advantages. Thermal drift of the instrument is not noticeable anymore at this temperature. The thermal excitation amplitude of the cantilever (in our case the spring constant $k = 0.37$ N/m) is reduced from 0.14 nm at 300 K to 0.016 nm at 4 K (calculated by applying the equipartition theorem). The noise of the tunneling current is reduced dramatically.

When trying to image a sample with atomic resolution, it is clear that one keeps the loading

force as small as possible. For graphite, loads up to 1000 nN have been reported and the images still showed atomic resolution [14]. At such high loads, elastic deformation of the sample and tip will occur and the load is redistributed over a larger area [15]. A more recent theoretical paper [16] claims 5 nN as the threshold for a single atom AFM tip to puncture the surface of graphite. The interaction between a cantilever and a cleaved mica surface has been studied in air and water by Weisenhorn et al. [17]. For a SiO tip on a MgO surface, calculations of the expected images were made [18] and the best results are expected at loads of the order of 10 nN.

Imaging the van der Waals forces between tip and an alkali halide should also allow atomic resolution [19,20]. Presumably the largest part of the attractive force between a lever and the sample is the continuum van der Waals force [21]. The repulsive interaction can be described by applying the Gordon–Kim model [22], since the ions in an alkali halide have closed shells. However, there should also be another contribution to the attractive force that to our knowledge has not been discussed in the literature as far as we know. If one considers a clean, unrelaxed (001) surface of an ionic crystal, a first attempt to determine the interaction between the AFM tip and the surface is to look at the electrostatic field of the ionic crystal. Since the net charge of a (001) surface is zero, the electrostatic field at a fixed z distance averaged across a surface unit cell is zero. The electrostatic field at a plane parallel to the surface reflects the periodicity of the surface lattice. The magnitude of the field decays perpendicularly to the surface at a rate proportional to $\exp(-qz)$, where $q = 2\pi/\text{lattice constant}$ [23]. If one approaches an uncharged, but polarizable tip of a cantilever to the surface of an alkali halide, it should be attracted by the electrostatic field. Therefore, it should in principle be possible to obtain atomically resolved images of an alkali halide, even when even the topmost atom of the AFM tip is not in contact with the surface of the sample.

When estimating the maximal allowable force acting between cantilever and sample during a nondestructive imaging process in atomic resolu-

tion, a good approach is to compare it to the interatomic forces in the sample. For KBr, the magnitude of the electrostatic force between a K^+ ion and a Br^- ion at the equilibrium distance is 2.1 nN. This attractive force is balanced by the repulsion of the core electrons of K^+ and Br^- . It seems reasonable that an interaction force between tip and sample of this order of magnitude could destroy the sample locally.

The force acting between an AFM tip and the sample is determined by setting the zero point when the sample is far away, and then measuring the deflection and multiplying it by the spring constant after the sample has been approached. However, it is very difficult to eliminate thermal drift at room temperature, hence the loading force also drifts in such a way that there is a high probability that the lever will either jump away from the sample or will press too hard against it during an imaging cycle. With our instrument at 4 K a once-set loading force stays constant to within a nanonewton for at least hours. For a nonlayered material such as KBr this is very important since the surface will be destroyed by a load of only a few nanonewtons, as will be shown in the next section.

3. Results

Fig. 2 shows a 580 nm by 580 nm scan at room temperature in the constant force mode. The image shows flat terraces and some scratches and indentations which were probably made by the first sample approach. The steps are parallel to the [100] direction.

When we performed the low-temperature experiments, we cooled the instrument down to 4 K immediately after we had cleaved the sample in order to have optimal vacuum conditions. Then we approached the sample while monitoring the deflection of the cantilever. Fig. 3 shows four different force-versus-distance curves at arbitrarily chosen spots of the surface. At a distance of approximately 70 nm, we began to notice a slight attraction of the cantilever by the sample. The attractive force increased until the tip of the lever and the sample touched (i.e. the deflection of the

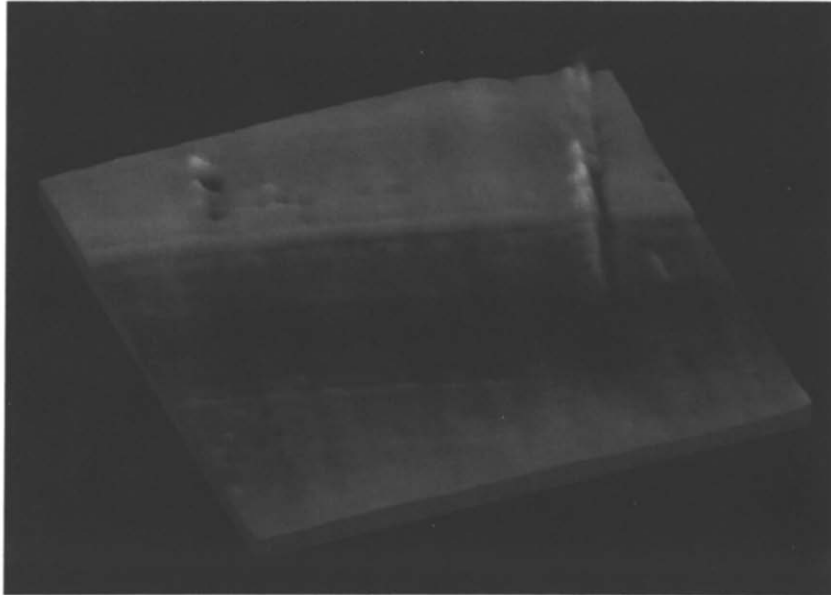


Fig. 2. AFM image of KBr (001) at 300 K. The sample was cleaved in UHV. Scan area 580 nm by 580 nm. The image shows large flat terraces plus some defects that were probably created by a rough lever-sample approach.

cantilever and the position of the sample changed at the same rate). The main difference between the curves in figs. 3a–3d is the maximum repulsive force applied. In (a) it was only approximately 1 nN; in (b) it was about 2 nN; in (c) it was increased to approximately 4 nN. Fig. 3d shows a maximum repulsive force of approximately 8 nN.

One can clearly see that hysteresis is not noticeable in fig. 3a but steadily increases from fig. 3b to fig. 3c and fig. 3d. We believe that increasing the force to a value higher than 1 nN already leads to severe sample damage and contamination of the cantilever with sample material. Fig. 3d strongly suggests that chemical bonds are cre-

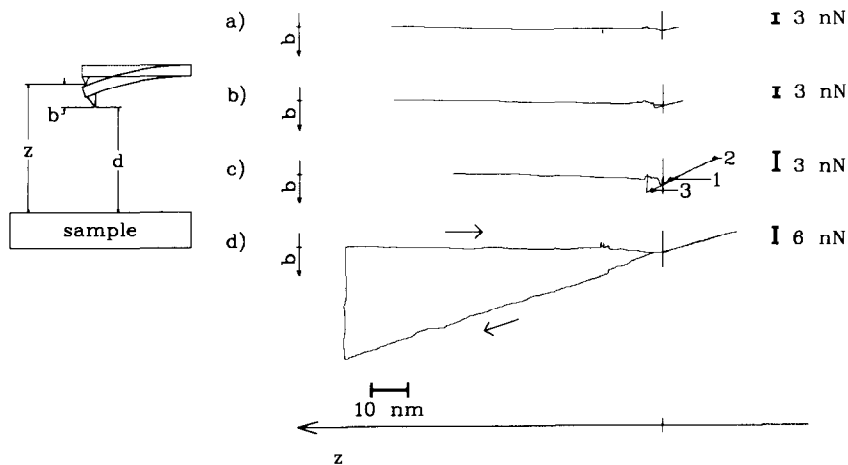


Fig. 3. Force-versus-distance curves. The force constant of the cantilever is 0.37 N/m. All curves show first an attractive section, then repulsion, attraction and finally repulsion again as the lever is in contact with the sample. In (d) the strong repulsive force destroyed the sample locally.

ated when pressing the cantilever onto the sample – we had to pull with a force of 32 nN to free the cantilever from the sample. This force corresponds to the binding strength of 16 pairs of an ionic binding of K^+ and Br^- at the equilibrium distance. The bond between silicon nitride and KBr is probably weaker than the bonds within KBr, suggesting that at least 16 bonds between cantilever and sample are created. In figs. 3a–3d a repulsive regime is embedded into two attractive ones. This we have only observed sometimes and we do not understand its origin. It might be caused by a tiny whisker on the AFM tip. However, the point we want to stress here is independent of this effect.

Taking a force-versus-distance curve first and then working at a very small force proved to be the key to obtaining our best images. If the first approach was too rough and the repulsive force exceeded several nanonewtons, it was no longer possible to obtain reproducible, atomically resolved images on this part of the surface.

The best images (in terms of signal-to-noise ratio) were achieved when the feedback was on the tunneling tip and the average z distance

between sample and lever was kept constant by applying a slope correction. The load was practically kept constant, with a small fluctuation due to the corrugation ($0.062 \text{ nm} \times 0.37 \text{ N/m}$ – which means the load was approximately 1 nN with a fluctuation of 0.01 nN).

We approached the sample until we observed a maximum attractive force and then stopped the approach. Scanning then yielded an image of the surface. Following this procedure, we achieved atomic resolution immediately and repeatedly. Our best results were obtained when the total force acting on the cantilever was approximately -1 nN (attractive). After scanning for an hour on the same area (at approximately 1 frame per 10 s), no damage to the surface was noticeable and no friction effects were visible (e.g. blurred or distorted images at the edges of the fast-scan direction).

Fig. 4 is a sequence of three images taken on the same section of the sample. The corresponding force–distance curve is shown in fig. 3c. Fig. 4a was taken at a loading force of approximately -1 nN . We then increased the force by moving the sample further towards the cantilever. At a

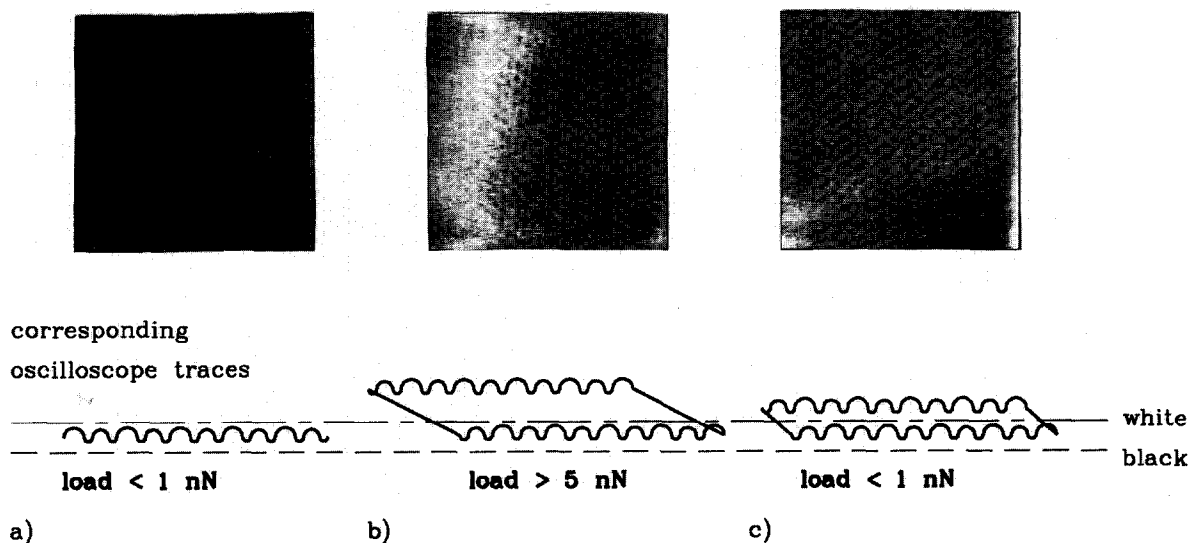


Fig. 4. AFM images of KBr (001) at 4 K. Scan size 10.6 nm by 10.6 nm in all images. The left-hand image was taken at approximately -1 nN (total force acting on the cantilever). Note that no friction is noticeable at this force. The middle image was taken at $+3 \text{ nN}$. At this force, the surface is damaged. For the right-hand image, the force was reduced to -1 nN again, but the debris of the former flat surface causes distortions at the edges of the scanned field.

repulsive force of 3 nN (point 2 in fig. 3c) we took image 4b. One can see the distortions at the edges and the oscilloscope traces showed a hysteresis between the forward and backward scan, a typical friction effect [24]. In fig. 4c we reduced the force again to approximately -1 nN, but the image still showed friction effects at the edges and particularly a hysteresis in the oscilloscope traces. We believe that debris formed by scanning at high loads in fig. 4b caused damage to the sample and gave rise to a high frictional force even though the loading force was very low.

On a very small scale we were even able to resolve both basis atoms of the lattice. The traces in fig. 5 show both the small (K^+) and the large ions (Br^-). Assuming the hard-sphere model for

tip and sample (and not allowing for a relaxation), the radius of the tip of the cantilever (for geometrical reasons) must be smaller than 0.9 nm to be able to image the K^+ ion.

The interaction between the stylus of an AFM and the sample is a very interesting problem, since it deals with the interaction of only a few atoms. Based on the fact that we observed a slight attraction in all our force-versus-distance curves when tip and sample were not yet in contact, we conclude that in our case (ionic crystal, Si_3N_4 lever) the dominant tip-sample interaction is not an electrostatic monopole interaction. Fig. 6 shows a model of the tip-sample interaction. The attractive force could be caused by a polarization of the tip of the lever due to the

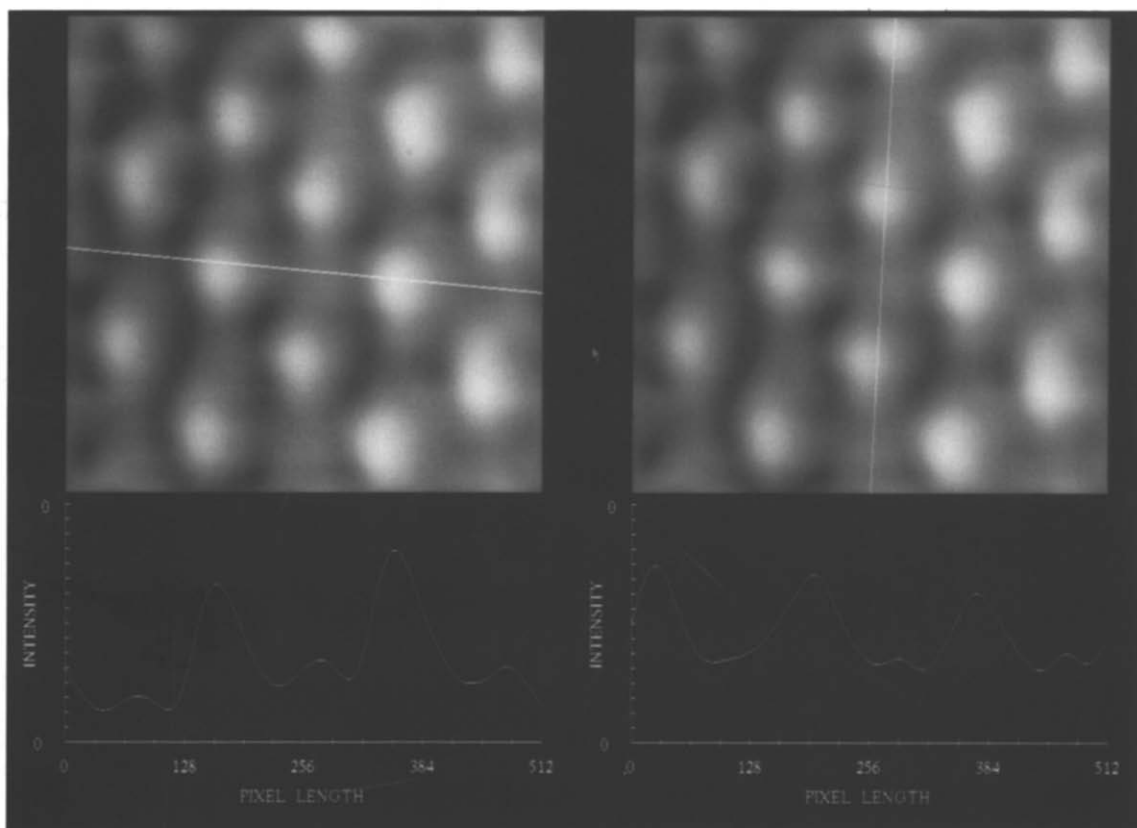


Fig. 5. AFM images of KBr (001) at 4 K. Scan size 1.3 nm by 1.3 nm. Both kinds of ions are resolved in this image. We assume the brighter spots represent the bromide atoms and the darker spots refer to the potassium atoms. The theoretical radius of the potassium ion is 0.133 nm, that of the bromide ion 0.195 nm. Both cuts along [100] and [010] show small protrusions where the smaller potassium ions are expected. In principle, such an image could be caused by a double tip, but it is very unlikely that both distance and angle of the two tips would have the correct value to mimic the basis of the lattice.

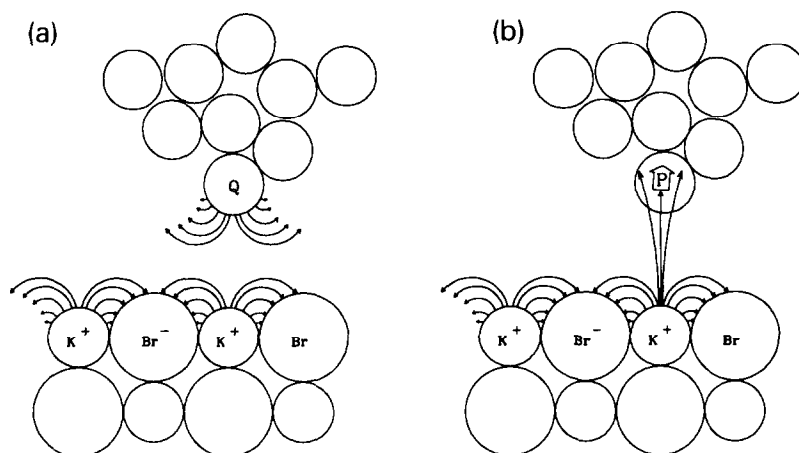


Fig. 6. Proposal for the imaging mechanism. The surface of an ionic crystal has a strong electrostatic field which decays exponentially (at a rate of $\exp(-2\pi z/\text{lattice constant})$) into the vacuum. If the AFM tip were charged (a), the interaction between tip and sample would be attractive for one kind of ion and repulsive for the other. Since all force-versus-distance curves in fig. 3 have an attractive part at the beginning, we conclude that the tip is polarized by the electrostatic field and thus attracted by either type of ion. However, it is not clear whether the outermost atom of the tip is already repelled by the surface during imaging.

electrostatic field of the surface. Since the electrostatic field decays much faster than the attractive forces between tip and sample, we believe that the main contribution to the attractive interaction is the continuum van der Waals interaction.

Fig. 7 shows a perfectly flat section of KBr (001) of 25 nm by 25 nm. The feedback was virtually turned off while scanning across this terrace.

Fig. 8 shows a section of a cleavage plane which has a very high step density. In this image,

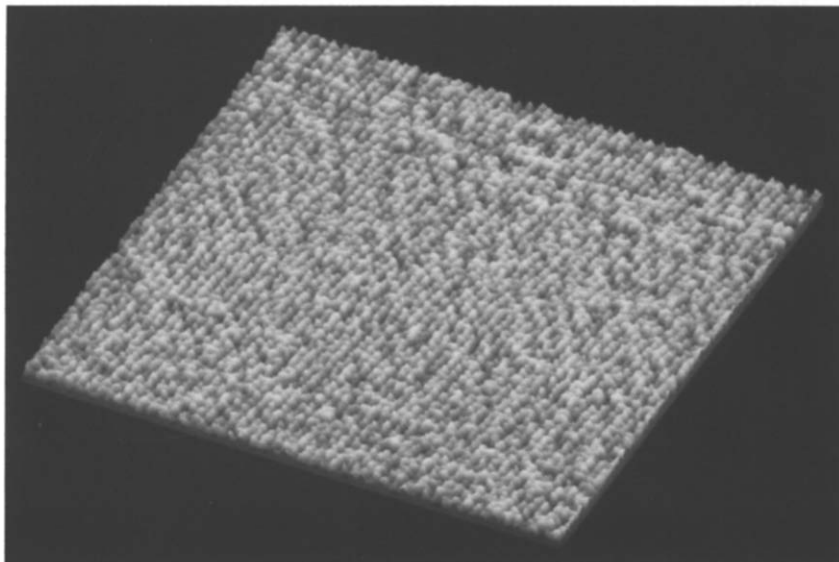


Fig. 7. KBr at 4.2 K in UHV, raw data – total force between sample and cantilever approximately -1 nN (attractive). Scan area is 25 nm by 25 nm. The rows are running in the [110] direction. No defects are visible on this terrace.

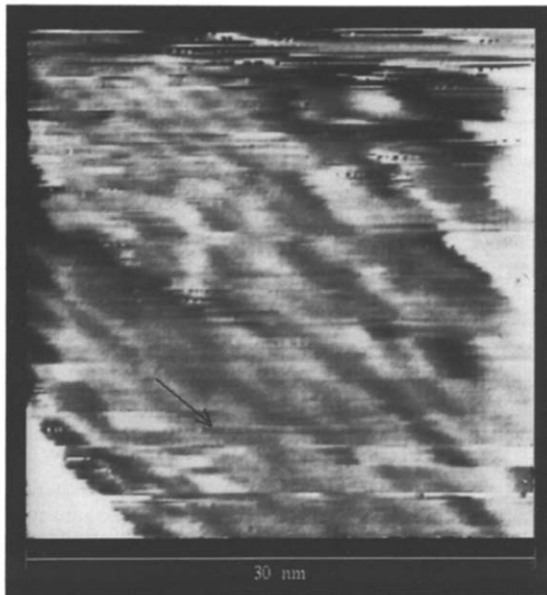


Fig. 8. KBr at 4.2 K in UHV. Scan area is 30 nm by 30 nm. This image shows a set of terraces bound by [110] edges. The surface forms an average (111) plane here since the separation of the steps is very small.

taken at 4 K, the crystal was cleaved in air and baked in UHV. The area where the image was taken had a density of about 1 step per 3 nm in [110] direction. The average direction of the surface plane vector is $[\bar{1}\bar{1}1]$, but because a (111) plane of an alkali halide is not stable (since all the surface atoms carry either plus or minus one unit charge, the surface energy would be very high), steps are formed [25]. This image was taken with a cantilever with an integrated tip [13].

4. Conclusion

We have studied the surface of KBr cleaved in situ in UHV by AFM. We observe well-defined steplines in the [100] direction. Large terraces were imaged with atomic resolution. The imaging is shown to be nondestructive, as consecutively taken images look identical and the z positions of sample, cantilever and tunneling tip remained stable for at least an hour while scanning across the same area of the sample. This means that both the tip of the cantilever and the sample are

not destroyed by the imaging process. For the first time both ionic species of an alkali halide could be resolved by AFM. AFM is now able to operate at 4 K, thus opening up the possibility to study low-temperature phenomena on insulators on the atomic scale.

Acknowledgements

We would like to thank Shinya Akamine and Prof. Calvin Quate for supplying us with micro-fabricated cantilevers.

References

- [1] G. Binnig, C.F. Quate and Ch. Gerber, *Phys. Rev. Lett.* 56 (1986) 939.
- [2] S. Gould, O. Marti, L. Hellemons, C.E. Brecker, P.K. Hansma, N.L. Keder, M.M. Eddy and G.D. Stucky, *Nature* 332 (1988) 332.
- [3] G. Meyer and N.M. Amer, *Appl. Phys. Lett.* 53 (1988) 1045.
- [4] M.D. Kirk, T.R. Albrecht and C.F. Quate, *Rev. Sci. Instr.* 59 (1988) 833.
- [5] F.J. Giessibl, Ch. Gerber and G. Binnig, *J. Vac. Sci. Technol. B* 9 (1991) 984.
- [6] S. Manne, P.K. Hansma, J. Massie, V.B. Elings and A.A. Gewirth, *Science* 251 (1991) 183.
- [7] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, PA, 1979) p. 379.
- [8] E. Meyer, H. Heinzelmann, H. Rudin and H.-J. Güntherodt, *Z. Phys. B* 79 (1990) 3.
- [9] G. Meyer and N.M. Amer, *Appl. Phys. Lett.* 56 (1990) 2100.
- [10] E. Meyer, H.J. Güntherodt, H. Haefke, G. Gerth and M. Krohn, *Europhys. Lett.* 15 (1991) 319.
- [11] T.R. Albrecht and C.F. Quate, *J. Vac. Sci. Technol. A* 6 (1988) 271.
- [12] Park Scientific Instruments, 1171 Borregas Avenue, Sunnyvale, CA, USA.
- [13] S. Akamine, R.C. Barrett and C.F. Quate, *Appl. Phys. Lett.* 57 (1990) 316.
- [14] T.R. Albrecht, *Advances in Atomic Force Microscopy and Scanning Tunneling Microscopy*, PhD Thesis, Stanford University (1989).
- [15] J.B. Pethica, *Phys. Rev. Lett.* 57 (1986) 3235.
- [16] W. Zhong, G. Overney and D. Tománek, *Europhys. Lett.* 15 (1991) 49.
- [17] A.L. Weisenhorn, P.K. Hansma, T.R. Albrecht and C.F. Quate, *Appl. Phys. Lett.* 54 (1989) 2651.
- [18] E. Kotomin, A. Shluger, M. Causa, R. Dovesi and F. Ricca, *Surf. Sci.* 323 (1990) 399.

- [19] C. Girard, D. Van Labeke and J.M. Vigoureux, *Phys. Rev. B* 40 (1989) 12133.
- [20] D. Van Labeke, B. Labani and C. Girard, *Chem. Phys. Lett.* 162 (1989) 399.
- [21] J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1985) section 10.3.
- [22] R.G. Gordon and Y.S. Kim, *J. Chem. Phys.* 56 (1972) 3122.
- [23] R.P. Feynman, R.B. Leighton and M. Sands, *The Feynman Lectures on Physics*, Vol. 2 (Addison-Wesley, Reading, MA, 1977) pp. 7–10.
- [24] C.M. Mate, G.M. McClelland, R. Erlandsson and S. Chiang, *Phys. Rev. Lett.* 59 (1989) 1942.
- [25] R. Lacman, *Colloques Internationaux du Centre National de la Recherche Scientifique N° 152, Adsorption et Croissance Cristalline*, Paris (1965).