

# Theoretical and experimental evidence for “true” atomic resolution under non-vacuum conditions

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Imaging of atomic scale features (Angstrom resolution) such as individual atoms using an atomic force microscope (AFM) remains highly controversial. Arguments that such resolution is not achievable revolve around two points: (1) that atomic scale defects are not observed and (2) often the experimental images are not reproduced theoretically. Here we show that the AFM is capable of imaging atomic features by presenting images of atomic scale defects at  $\sim 1$  Å resolution. Dislocation defects and monatomic growth steps on the {001} surface of the mineral anhydrite ( $\text{CaSO}_4$ ) are observed in unfiltered AFM images. Furthermore, the atomic features observed in the experimental AFM images are reproduced by numerical simulation; conclusively addressing the two points above. The combination of experimental images and theoretical simulations enables the comprehensive interpretation of the images. The images of the {001} surface indicate that the AFM observes both the calcium and oxygen atoms at the cleavage plane. In addition, two configurations of the oxygen atoms are observed; a dumbbell shaped feature due to two oxygens (from two different  $\text{SO}_4$  tetrahedra) sitting just below the cleavage plane and a doughnut shaped feature composed of oxygens from four different  $\text{SO}_4$  tetrahedra (the two above and two standing above the cleavage plane). The latter are partly due to tip deformation of the surface and are the most common features in experimental images. © 1999 American Institute of Physics. [S0021-8979(99)04822-7]

## INTRODUCTION

Invented 10 yrs ago, the atomic force microscope (AFM) has been a powerful tool for the study of surfaces. The great advantage of AFM in comparison with its twin, the scanning tunneling microscope (STM) is its ability to image virtually any surface of sufficient rigidity. The AFM works by bringing a very sharp needle (AFM tip) attached to a flexible cantilever toward the sample until it gently touches the surface. This leads to a bending or deflection of the cantilever. This deflection can be measured and a three-dimensional image of the surface built up by scanning the tip across the sample and recording the deflection during the scan. The topography of the sample surface is displayed as variations in cantilever deflection; the higher a surface feature the larger the recorded deflection. If one has the sharpest possible AFM tip (one atom at the apex) each surface atom is convoluted by the apex tip atom giving a unique spot in the image. Consequently, the AFM is capable of image resolution in which individual atoms can be seen.<sup>1</sup>

In 1993 Ohnesorge and Binnig<sup>2</sup> first reported achievement of “true”<sup>3</sup> atomic resolution on a state-of-the-art homemade AFM. They imaged mono/diatomic steps and kinks on the surface of calcite ( $\text{CaCO}_3$ ) in water. Since that

time all successful studies that obtained “true” atomic resolution by AFM were performed in ultrahigh vacuum (UHV) and were dealing with relatively simple structures such as InP(110) and silicon (111) $7\times 7$  surfaces.<sup>4,5</sup> Despite the results reported by Ohnesorge and Binnig, the ability of the AFM to achieve atomic resolution under non-UHV conditions remains controversial, with many people remaining unconvinced. This skepticism can be attributed to two factors: (1) atomic scale defects are not observed in raw AFM images and (2) theoretical calculations often fail to reproduce the observed images.

The explanation for the lack of observed atomic defects stems from the shear force experienced by the AFM tip during scanning. If there is a vacancy on the surface (a missing atom) one should see a hole in the recorded image. In reality, during scanning, the tip experiences a large shear force that can “destroy” the defects<sup>5</sup> or remove the apex atom. The latter produces a tip that can have two or more atoms located at the apex, each of which may convolute the surface atoms. This results in what has been termed “averaging” of the image and the AFM is not able to detect any atomic defects. Evidence for “averaging” has been reported by Hahn *et al.*<sup>6</sup> in which the surface of graphite was bombarded by  $\text{Ar}^+$  ions to create atomic scale defects. The sample was then imaged

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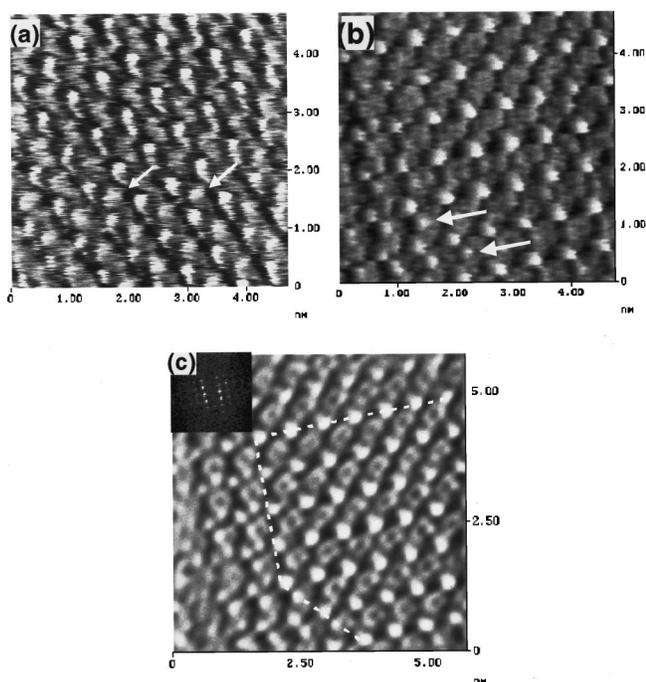


FIG. 1. Images of anhydrite surface. (a) and (b) are “raw” images while (c) is a Fourier filtered image with its associated FFT spectrum shown in the upper left corner. All the images display atomic scale defects. (a) and (b) exhibit dislocation defects (highlighted by arrows), while (c) contains a monatomic step (dashed line).

by STM and AFM. STM images showed defects while AFM images did not.

In the present study we demonstrate that the AFM technique is able to unambiguously attain “true” atomic resolution. We report here atomic resolution images of the surface of the mineral anhydrite ( $\text{CaSO}_4$ ) with unprecedented resolution of about 1 Å. Furthermore, we show that the experimentally obtained AFM images can be simulated theoretically. The simulated images reproduce the observed images remarkably well and provide an excellent means by which to analyze and evaluate the validity of the experimental data.

## EXPERIMENTAL RESULTS

Figure 1 shows three images of the anhydrite surface. Figures 1(a) and 1(b) are “raw”<sup>7</sup> images while 1(c) is a Fourier filtered<sup>8</sup> image with its associated fast Fourier transform (FFT) spectrum shown in the upper left corner. All the images display atomic scale defects. Figures 1(a) and 1(b) exhibit dislocation defects (highlighted by arrows), while 1(c) contains a monatomic step (dashed line). These images clearly indicate that we have satisfied the first argument used to disparage “atomic resolution” AFM images. We are able to observe atomic defects.

However, to be truly convincing we must also provide a theoretical explanation for how, and what, we are observing. First, we shall show that all the images shown here can only be obtained by means of an AFM tip that has a monatomic apex. This is important because if the images were collected with a “multiatom” tip, one would have averaging, as noted previously, which would result in disappearance of the

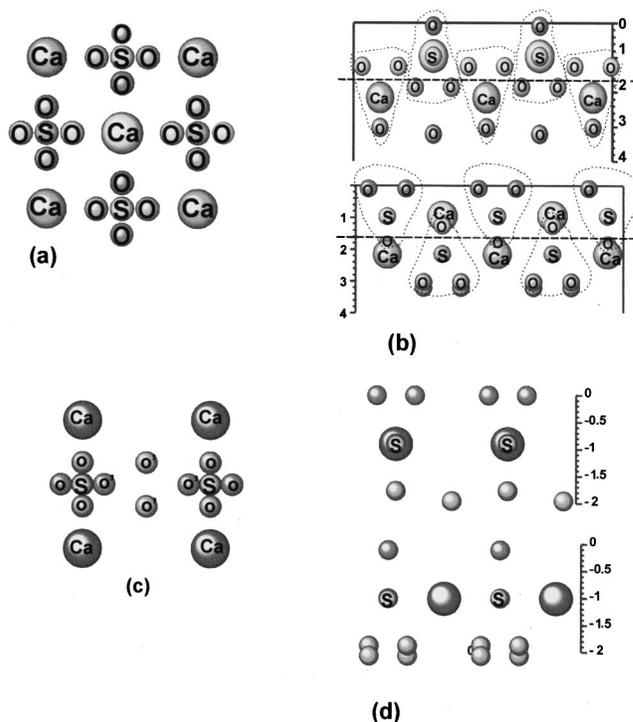


FIG. 2. a)  $\{001\}$  projection of the anhydrite structure viewed to a depth of 4 Å. It should be noted that some of the atoms in the projection are well below the surface and will not contribute to any height contrast in simulated AFM images which are representative of the structure at the surface, (b)  $\{010\}$  (top) and  $\{100\}$  (bottom) projections of (a); the dashed line is the suggested line of cleavage, (c)  $\{001\}$  projection of the anhydrite structure cleaved along the dashed line and viewed to a depth of 1.5 Å, (d)  $\{100\}$  (top) and  $\{010\}$  (bottom) projections of (c).

atomic resolution. Second, we shall show that the observed images are in excellent agreement with results of numerical simulations of the  $\{001\}$  anhydrite surface.

## MODEL SIMULATIONS

The high contrast features observed in Fig. 1 are 0.69 ( $\pm 0.01$ ) nm apart which is in very good agreement with the interatomic distance between surface Ca atoms (0.699 nm) determined from the model structure<sup>9</sup> shown in Fig. 2(a). This suggests that the high contrast features in the AFM images are the Ca atoms at the  $\{001\}$  surface of anhydrite (indicated by Ca), (Fig. 2). Analysis of the side views, [Fig. 2(b)], shows that the surface observed was cleaved along the horizontal dashed line shown in Fig. 2(b) and the calcium atoms and  $\text{SO}_4$  groups (surrounded by a dashed line) above the cleavage line were removed. A top view of the cleavage plane is shown in Fig. 2(c). Comparison with the AFM images indicates that we observe this cleavage with minor modifications discussed later. Confirmation of this is obtained from computer simulation of the force interactions between the AFM tip and the anhydrite structure shown in Fig. 2.

The numerical method used in our simulations has been described elsewhere.<sup>5</sup> The simulated scan conditions are similar to those described in Ref. 5 except that the scan force was chosen to be close to that used in our experiments (about 1 nN). The sample surface was the  $\{001\}$  plane shown in Fig.

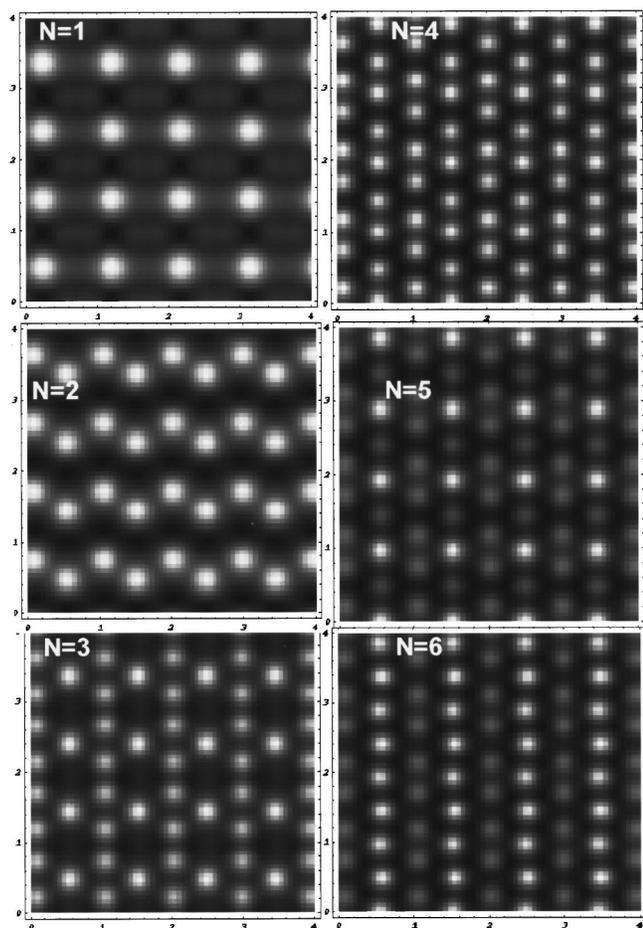


FIG. 3. Simulated images of the {001} surface of anhydrite for an AFM tip with one to six atoms at its apex ( $N=1-6$ ).

2(c) extended to  $3 \times 3$  unit cells. In addition, the top oxygen layer was removed since it is only weakly bound and has not been observed in any of our experimental images.

## DISCUSSION

The results of the simulations are shown in Fig. 3 for six scans with from one to six atoms at the tip apex. We have chosen to show the results of a single scan orientation although our conclusions are qualitatively valid for any angle. The simulation results show that we can reproduce our real images of the anhydrite surface if we have a single atom<sup>10</sup> at the tip apex. ( $N=1$  of Fig. 3). Since the calcium atoms at the {001} surface are distinctly visible in the experimental images, and this could only be observed if we had a monatomic AFM tip, we must conclude that we are observing “true” atomic resolution.

If our conclusions concerning attainment of “true” atomic resolution are valid, then we must also be able to reproduce theoretically, *all* surface features observed in the experimental images. Figure 4 shows two distinct sets of features that we commonly observe in the experimental images of the anhydrite surface. Numerical simulations are indeed able to reproduce both sets of features [Figs. 4(c) and 4(d)]. Figure 4(c) is the result of an AFM scan simulation in which the anhydrite surface structure [Fig. 2(c)] is used with-

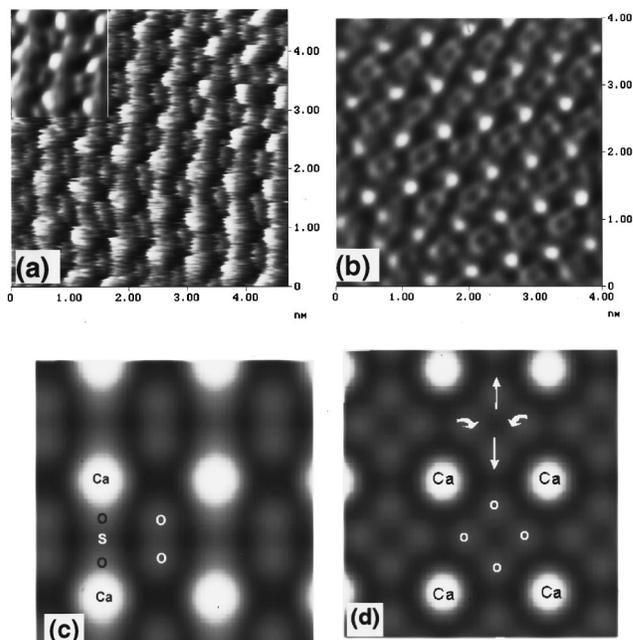


FIG. 4. Images of the two most common features observed by the AFM on the {001} surface. (a) Shows a series of high contrast features (Ca atoms) as well as “dumbbell” shaped features at the center of the four surface Ca atoms (in the top left corner is a FFT filtered portion of the raw image). (b) Shows a similar image but with “doughnut” shaped features centered between the Ca atoms (FFT filtering has been applied to emphasize the doughnut shapes). (c) A simulation using the cleavage surface shown in Fig. 2(c). (d) A similar simulation but the cleavage surface has been “deformed” with two oxygen atoms being “pushed” into the structure (indicated by heavy arrows). This deformation represents the AFM tip pushing down on the 2 oxygens that stand above the cleavage surface. The distance between the calcium atoms in (c) and (d) are 0.69 nm, the same distance between calcium atoms in (a) and (b).

out any changes (apart from removal of the two weakly bound oxygen atoms noted previously). Comparison of Figs. 4(a) and 4(c) clearly indicates that Fig. 4(a) represents the regular anhydrite surface structure shown in Fig. 2(c). The “dumbbell” features in the middle of each four-atom cell are the two single oxygen atoms in Fig. 2(c). The AFM tip is small enough that it can convolute both the Ca atoms and the oxygen atoms that lie in the cleavage plane but at a level slightly deeper than the Ca atoms.

The “doughnut” shaped features seen in Fig. 4(b) are somewhat more problematic but can also be theoretically reproduced. Comparison of the real image with the model structure suggests that the “doughnut” features are the oxygens of the sulfate groups. In particular, the “doughnut” appears to be the four oxygen atoms labeled O' in Fig. 2(c). Two of these oxygens are the same as in Fig. 4(a) but the other two come from two different sulfur groups and are the oxygens that we assumed were removed during cleavage [red atoms in Fig. 2(c)]. All four oxygen atoms are observed at about the same height level in the experimental images [Fig. 4(d)] which is inconsistent with the calculated structure of the cleavage plane shown in Fig. 2(c). In order for the four oxygens to be at equivalent heights across the cleavage plane, some deformation or relaxation of the surface must have occurred. The simplest explanation would be that pressure from the AFM tip “pushes” the two oxygens that stand

above the surface downwards during the scan. Concomitant with this is some small deformation of the surface, which manifests itself as a slight upward rotation of the other two oxygens. Results of the numerical simulations incorporating such a surface deformation are shown in Fig. 4(d). The assumed adjustments of the oxygen atoms are shown in the figure by white arrows. The numerical simulation is able to reproduce the observed images remarkably well.

## CONCLUSION

In conclusion, both our experimental images and theoretical simulations of the {001} surface of anhydrite satisfy the requirements for “true” atomic resolution. We observe atomic scale defects within the raw experimental images and, we can fully reproduce the observed surface features in our numerical simulations. Furthermore, the numerical simulations are shown to be essential for the correct interpretation of the images. Our results provide the strongest evidence to date for the attainment of atomic resolution with a commercial AFM under nonvacuum conditions.

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<sup>3</sup>By “true” atomic resolution we mean images of atoms that are not averaged due to multitip effects.

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<sup>6</sup>J. R. Hahn, H. Kang, S. Song, and I. C. Jeon, *Phys. Rev.*, **53**, R1725 (1996).

<sup>7</sup>By “raw” image we mean that no fast Fourier transform filtering (FFT) has been applied. The images have been processed with a single low pass filter, which does not affect any periodicity in the image.

<sup>8</sup>The FFT power spectrum is equivalent to the reciprocal lattice image of the surface and should correspond to a LEED image of the {001} plane of anhydrite. FFT filtered images were obtained by passing all observed periodicities in the power spectrum to the inverse FFT image.

<sup>9</sup>The anhydrite (CaSO<sub>4</sub>) model structure is orthorhombic, space group *A<sub>mma</sub>*, with unit-cell dimensions of  $a_0=6.991$ ,  $b_0=6.996$ ,  $c_0=6.238$  and is taken from the Cerius2™ software database (Molecular Simulation Incorporated).

<sup>10</sup>The simulation with five atoms at the apex ( $N=5$ ) could give the impression that it too has reproduced the {001} surface structure. However, the height contrast in this simulation is 0.01 nm and this is at the level of sensitivity of our AFM, and is not likely to be observed above the noise.