

# Observation of unreconstructed square atomic square lattice in $\text{Ca}(\text{Fe}_{0.965}\text{Co}_{0.035})_2\text{As}_2$ cleaved at very low temperatures

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**Abstract.** Scanning tunneling microscopy (STM) has been by now made in many pnictide layered superconductors. In  $A\text{Fe}_2\text{As}_2$  ( $A=\text{Ca}, \text{Sr}, \text{Ba}$ ), surface reconstructions dominate the STM topographic images and no surface termination with the bulk atomic lattice has been reported. Here, we present STM measurements on the surface of  $\text{Ca}(\text{Fe}_{0.965}\text{Co}_{0.035})_2\text{As}_2$  cleaved in-situ below liquid helium temperatures. We observe the ubiquitous surface reconstruction consisting of 1D stripes that can adopt two degenerate orientations with respect to the crystal lattice. By searching over many different scanning windows, we find that low temperature cleaving also exposes surfaces showing the As unreconstructed lattice of the bulk tetragonal crystal, over areas of some tens of nm lateral size.

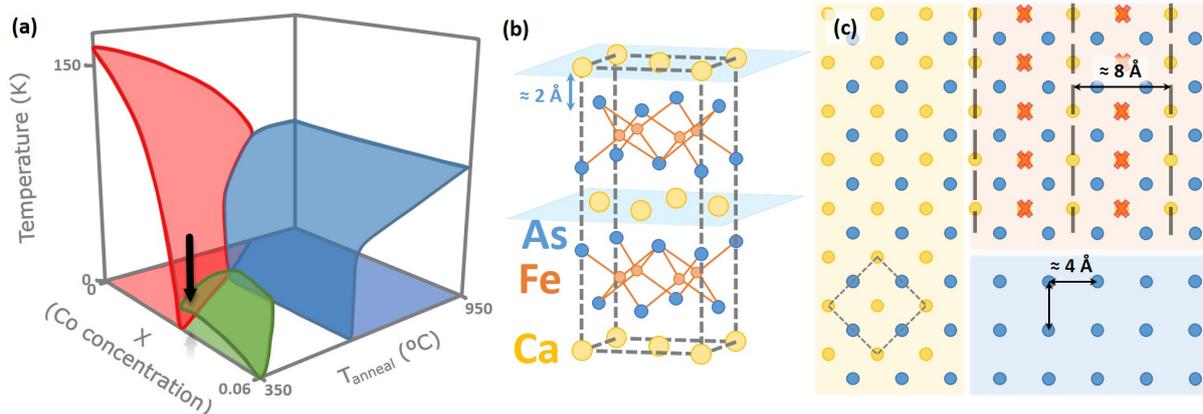
## 1. Introduction

Iron based compounds have phase diagrams showing magnetism, structural transitions and superconductivity. Different phases are obtained by small compositional changes, pressure or internal stress produced by annealing[1, 2, 3, 4, 5, 6]. Scanning tunneling microscopy and spectroscopy (STM) has been widely used to study normal and superconducting properties of pnictide and related superconductors[7, 8, 9, 10]. In the case of doped  $\text{CaFe}_2\text{As}_2$ , quasiparticle interference scattering has provided evidence for nematicity in the normal state and a detailed measurement of the bandstructure[7, 11, 12, 13]. STM topographies ubiquitously show reconstructed surfaces. However, it has been shown that quasiparticle interference is not influenced by the surface reconstruction and provides relevant bulk electronic features[7, 11, 12, 13, 14].

The tetragonal crystal structure of  $\text{CaFe}_2\text{As}_2$  can show different surface terminations. Calculations show that Fe-As bonds are too strong, so only Ca or As terminations are expected[15]. Surfaces studied until now are reconstructed and Ca terminated[14]. Here, we



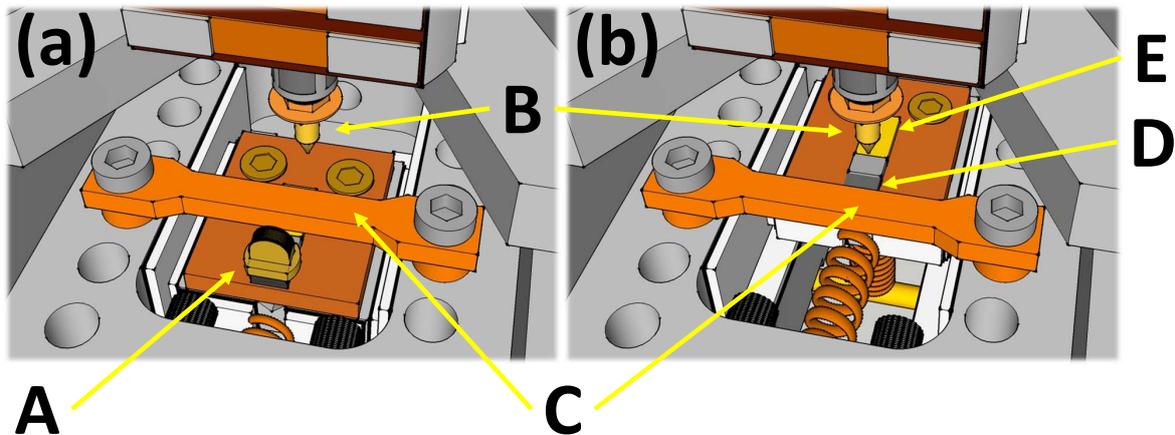
have made STM experiments at 100 mK in Co doped  $\text{CaFe}_2\text{As}_2$  and intensively searched for new surfaces using the in-situ positioning mechanism described in Ref.[9]. We have chosen  $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ , with  $x=0.035$ , where optimal  $T_c$  is obtained after annealing (Fig.1a and Ref.[5]). We indeed find unreconstructed areas, of lateral sizes up to 10 nm, showing square As surface with bulk interatomic distances.



**Figure 1.** In a we schematically show the phase diagram of  $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ . It highlights the different observed transition temperatures as a function of doping  $x$  and annealing temperature. The detailed phase diagram, including transition temperatures, is given in Ref. [5]. Red is the antiferromagnetic phase, blue is the collapsed tetragonal phase and green is the superconducting phase. Here we present results in the sample at the composition and annealing shown by the arrow, which is close to the optimal  $T_c$ . In b we show the crystal structure of  $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ , with the blue arrow representing the distance between As and Ca atoms. In c we show different surface terminations. Left panel shows the structure viewed from above, with only Ca and As atoms. Ca terminations are unstable and produce a surface reconstruction consisting of rows of Ca atoms, as shown in the upper right panel by the dashed black lines. Red crosses show missing Ca atomic rows. The unreconstructed As atomic lattice observed here in some areas at the surface is shown in the bottom right panel.

## 2. Experimental

Our sample,  $\text{Ca}(\text{Fe}_{0.965}\text{Co}_{0.035})_2\text{As}_2$ , is located at the phase diagram point represented by an arrow in Fig.1 and has been grown and annealed as described in [5, 16, 17]. We have used a microscope similar to the one described in Ref. [9], and present here data taken at constant current mode (a few nA) and at 100 mK, with a bias voltage of 10 mV. We cleave our sample by first gluing a brass piece on top of it and then hitting this piece in-situ at low temperatures. To do so, we move the sample holder with a mechanism described in Ref.[9]. First we fix a copper beam on the path of the sample holder at a few mm above the surface of the sample (Fig.2). We then glue a small piece of brass on top of the sample. Once the whole system is below 4.2 K, we move the sample holder. The copper beam hits the brass piece, breaking the sample. The brass piece flies away to the bottom of the internal vacuum chamber, and a fresh surface is exposed. We have used this system already five times, obtaining fresh and large surfaces with atomic resolution.



**Figure 2.** View of the *in-situ* cleaving system. In a we show the sample, with a stick glued on the top (A). The tip (B) lies on top of an Au sample (shown in b). A copper bar (C) is used to push the stick when moving the sliding sample holder. The holder is moved using the device described in Ref. [9] In b we show the result after moving the sample holder. The stick has gone to the bottom of the vacuum chamber and the tip (B) now lies on top of the cleaved sample (D). The sample shows now a freshly exposed surface. The results shown here have been obtained with a sample broken at temperatures below liquid helium temperature.

### 3. Results

Low temperature cleaving of our sample exposes large and flat surfaces with atomic resolution. A typical image is shown in Fig.3a. The surface is completely covered by the  $2 \times 1$  reconstruction[7, 18, 13, 19, 20]. It consists of stripes made of one dimensional rows of atomic size, which extend over the whole surface (upper right panel of Fig.1c). We observe defects in the reconstruction due to missing rows or shifts in the wavelength of the striped modulation. The orientation of the reconstruction is degenerate with respect to the square in-plane cross section of the tetragonal lattice. Accordingly, we find reconstructions as shown in Fig.3a and along a perpendicular direction.

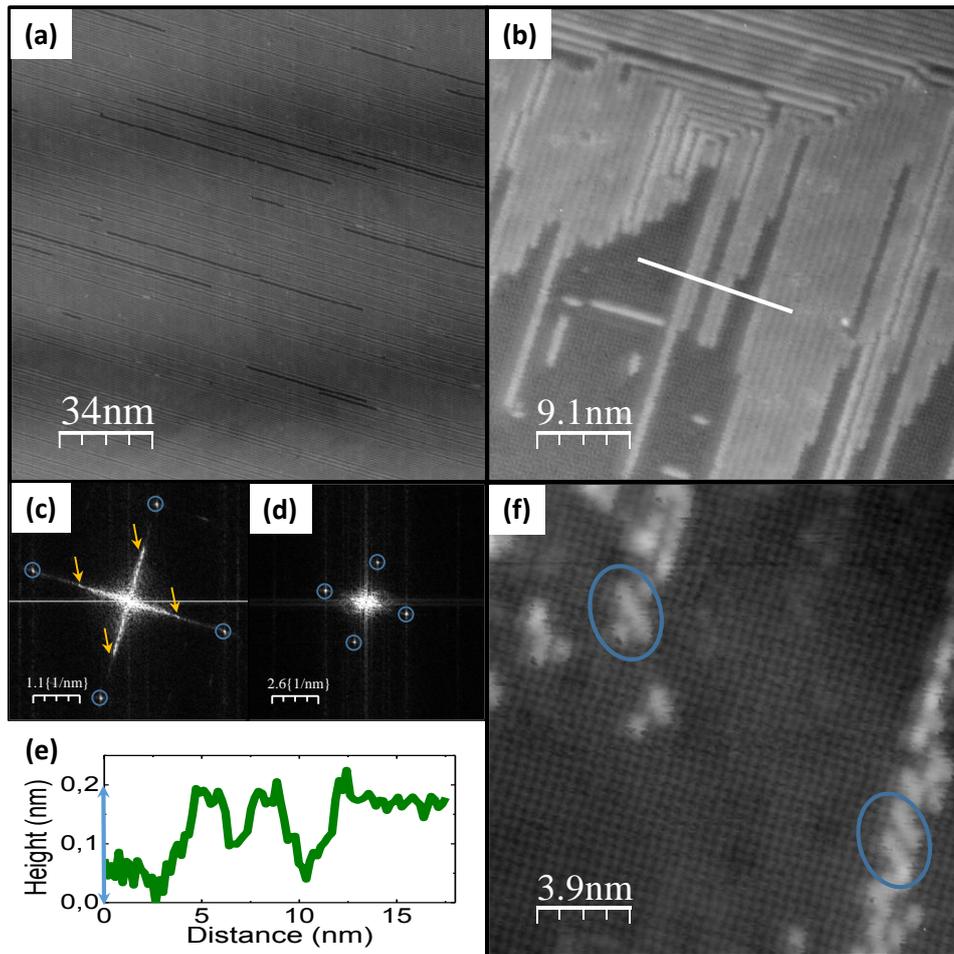
We have studied many different scanning windows using the positioning mechanism described in Ref.[9]. We have found mostly reconstructed surfaces along one of the two degenerate orientations of the  $2 \times 1$  reconstruction. But we have also found surfaces where we observe both directions at the same time. These are separated in different domains. Close to the domain boundaries, we can find areas as in figure 3b, where the two degenerate orientations for the stripes appear randomly. The reconstruction shows disorder, and there are places unveiling a square atomic lattice below.

The lattice parameter observed in unreconstructed surfaces is of  $\approx 4\text{\AA}$  and line scans from the square atomic lattice into the reconstruction show height changes of  $\approx 2\text{\AA}$  (blue arrow in Fig.3e). This height corresponds to the distance between Ca and As atoms in the structure of  $\text{Ca}(\text{Fe}_{0.965}\text{Co}_{0.035})_2\text{As}_2$  (Fig.1b).

In the unreconstructed areas we observe sometimes small groups possibly made of arrangements of Ca atoms. For instance, in Fig. 3f there are small sized stripes oriented along  $45^\circ$  from the atomic lattice (marked by blue ellipses).

### 4. Discussion

The surfaces of the  $A\text{Fe}_2\text{As}_2$  ( $A=\text{Ca}, \text{Sr}, \text{Ba}$ ) compounds have been reviewed in Ref. [14]. Two relevant structures have been discussed, the  $\sqrt{2} \times \sqrt{2}$  and the  $2 \times 1$ [15, 12]. The  $2 \times 1$



**Figure 3.** a) Topography of  $\text{Ca}(\text{Fe}_{0.965}\text{Co}_{0.035})_2\text{As}_2$  taken with a bias voltage of 10 mV and a current of 10 nA, at a temperature of 100 mK. We use constant current mode and the gray scale corresponds to a height change of 0.3 nm. Stripes showing the surface reconstruction dominate the whole figure. b) STM topography image at a smaller sized region in another scanning window using the same tunneling conditions. We also observe stripes due to the surface reconstruction. Nevertheless, a large part of the image shows the unreconstructed square lattice expected within the tetragonal structure. The corresponding Fourier transform is shown c. Blue circles give the atomic lattice Bragg peaks. We also highlight the  $2 \times 1$  surface reconstruction by orange arrows. Note that the Fourier transform does not show Bragg peaks but a cross, due to disorder. We also find regions where the atomic lattice is observed practically over the whole image, with only a few reconstructed rows. We show corresponding Fourier transform in d and topography image in f. In d, blue circles mark the atomic Bragg peak positions, and in f blue ellipses mark positions with Ca arrangements at  $45^\circ$  to the lattice. e shows a line scan between atomic lattice and reconstruction. Height difference matches approximately the distance between Ca (upper atomic rows) and As (lower atomic lattice) in the tetragonal crystal structure (Fig.1b).

reconstruction is schematically shown in Fig.1c (upper right panel). For the particular case of  $\text{CaFe}_2\text{As}_2$ , experiments until now have shown only the  $2 \times 1$  reconstruction [7, 18].

Here we find unreconstructed areas with the square atomic lattice of the tetragonal structure (Fig. 3f). These are found close to reconstructed areas with strongly disordered stripe

arrangements (Fig. 3b). Calculations of Ref.[15] show that the As atomic lattice over large areas is a metastable situation, but may well appear in a real cleave, because the energy difference between configurations is small[15].

It is interesting to raise the question if there are features in the bulk sample favoring the appearance of unreconstructed surfaces. Internal strain or stacking faults may favor the formation of small Ca free surfaces during the cleave at some locations. The observed disorder in the stripe arrangement is possibly also favored by defects or strain in the crystal. Our results show that low temperature cleaving can produce unreconstructed surface terminations over relatively large areas in the  $\text{CaFe}_2\text{As}_2$  compound. Spectroscopic measurements will reveal further properties of surfaces showing the bulk crystalline structure.

## 5. Acknowledgments

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