A tunneler’s view on correlated oxides and iron based superconductors
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The cleavage surface of ‘122’ pnictide superconductors

The termination surface of single crystals of the BaCo$_x$Fe$_{2-x}$As$_2$ and Fe$_{1+y}$Se$_x$Te$_{1-x}$ families of the high temperature iron based superconductors is elucidated. By combining scanning tunneling microscopic data with low energy electron diffraction we prove that the termination layer of the BaCo$_x$Fe$_{2-x}$As$_2$, or Ba122, systems is a remnant of the Ba layer, which exhibits a complex diversity of ordered and disordered structures. The observed surface topographies and their accompanying superstructure reflections in electron diffraction depend on the cleavage temperature. In stark contrast, Fe$_{1+y}$Se$_x$Te$_{1-x}$ possesses only a single termination structure - that of the tetragonally ordered (Se,Te) layer. Measurements on a differently doped system, BaFe$_2$P$_x$As$_{2-x}$, where a third of the As atoms is replaced by P atoms strongly support our findings. First principles calculations of the surface structure energies and STM measurements on a related compound, CaCo$_x$Fe$_{2-x}$As$_2$, suggest that our findings hold in general for all members of the M122 family, where $M = \text{Ba, Ca, Sr or Eu}$.

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4.1 Introduction

Scanning tunneling microscopy and spectroscopy (STM/S) and angle resolved photoemission (ARPES) are powerful and direct probes of the electronic states of solids and are making important contributions to our understanding of the new iron pnictide superconductors [1, 106, 107]. Determination of the termination surface of the cleaved single crystals is a pre-requisite for meaningful application of STM/S and ARPES, as is clarification whether possible departures from the bulk structure and co-ordination at the surface have a significant effect on the near-surface electronic states. A recent hard x-ray photoemission study [83] of room temperature cleaved BaFe$_2$As$_2$ (or Ba122) showed that the surface supports electronic states similar to those in the bulk, underpinning the relevance and reliability of surface sensitive techniques in the investigation of the pnictide superconductors. As will be shown in the next chapter, low temperature STS of room temperature cleaved BaCo$_x$Fe$_{2-x}$As$_2$ also showed no correlation between the spatial superconducting gap variation and the surface topography [108]. However, studies on low temperature (<80K) cleaved samples report a correlation between features in the electronic spectra and the structure of the termination of the crystal, [109, 110] highlighting the role of the cleavage temperature. In the cuprate superconductors, it is known that macroscopic departures from the simple lattice structure such as the incommensurate modulation in Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$, can have a pronounced effect on the spectroscopic data, leading to diffraction replicas in ARPES which can complicate matters considerably [111]. In the pnictide superconductors, the existence of diffraction replicas in ARPES data has already been pointed out [110].

The first STM/S studies of cleaved single crystals of the 122-based family of superconductors [108–110, 112] either suggested or assumed that on average half of the alkaline earth ions (depending on the system involved) remain on each side of the cleave (see Fig. 3.2a for a figure of the crystal structure). Recent STM and low energy electron diffraction (LEED) studies, however, have concluded that the atomic contrast seen in STM of both Ba122 and Sr122 is from inequivalent As sites due to the spin density wave in the underlying Fe plane and that there is no cleavage temperature dependence [113, 114]. Obviously, the fundamental importance of the surface termination question and the contrasting reports make it imperative to resolve these issues. In this chapter, temperature dependent LEED analyses of cleaved BaCo$_x$Fe$_{2-x}$As$_2$ ($x=0.08$, 0.14 and 0.21) single crystals is presented, together with an extensive STM topographic database on this system obtained from cleavage both at low and high temperature. Comparison to the Fe$_{1+y}$Se$_x$Te$_{1-x}$ system which has the same Fe$Pn$ building block (where $Pn = As$, Se or Te) as Ba122 but lacks the interstitial Ba layer, consequently enables us to isolate the Ba contribution to the cleavage surface in the 122 systems.

This picture, published in Ref. [115], was later confirmed by additional measurements on two closely related systems, namely CaCo$_x$Fe$_{2-x}$As$_2$ and BaFe$_2$P$_x$As$_{2-x}$. In CaCo$_x$Fe$_{2-x}$As$_2$, the Ba cation layer is replaced by a Ca layer, while the structure is
otherwise unchanged. In line with first principles calculations, which predict a difference in the energetics of certain structures for different alkaline earth layers, the modal surface appearance on this compound is different from that of Ba122. The latter compound, BaFe$_2$P$_x$As$_{2-x}$ is a system where a considerable amount of As atoms is replaced by P atoms. If the As layer would be imaged instead of the Ba layer as is proposed here, replacement of As atoms should be reflected in the constant current images, which is not the case. Lastly, the apparent barrier height, or local work function, on various systems and on the variety of apparent surface topographies for measurements on the same system is investigated. This analysis further supports our findings and strongly suggests that the various surface structures seen on 122 pnictides are of identical origin.

4.2 Cleavage temperature dependence of BaCo$_x$Fe$_{2-x}$As$_2$ and Fe$_{1+y}$Se$_x$Te$_{1-x}$

Single crystals of BaCo$_x$Fe$_{2-x}$As$_2$ ($x=0.08, 0.14$ and $0.21$), Fe$_{1+y}$Se$_x$Te$_{1-x}$ ($x=0.45, y=0.07$), CaCo$_x$Fe$_{2-x}$As$_2$ ($x=0.14$) and BaFe$_2$P$_x$As$_{2-x}$ ($x=0.64$) were grown in self flux. All samples were characterised prior to the STM and LEED measurements by resistivity and AC susceptibility. Cleavage took place both at low ($<80$K) and room temperature at a pressure better than $5 \times 10^{-10}$ mbar directly before insertion into the STM head, where the samples were cooled to 4.2 K. LEED was performed in situ after each STM survey to obtain the azimuthal orientation of the crystal. The temperature dependent LEED experiments took place in a different vacuum system at a pressure of $7 \times 10^{-11}$ mbar using identical crystals as those studied using STM, but cleaved at $<25$ K.

Figure 4.1 shows typical STM topographs obtained for low temperature cleaves of BaFe$_{1.86}$Co$_{0.14}$As$_2$. In Fig. 4.1a the topography combines regions with very little contrast with stripe-like structures, the latter being very clear in Fig. 4.1b. This type of ($2 \times 1$) or stripe feature has been observed previously both in the superconducting and parent 122 compound [109,112,114]. Furthermore, the data clearly show that the stripes possess phase shifts of half a unit (perpendicular to the stripes), which results in a ribcage-like topography, in which the phase shift lines correspond to the backbone (marked with an arrow in Fig. 4.1b). The inset shows a Fourier transform of the topographic image exhibiting dominant spots corresponding to the stripe/ribcage structures with a period of 8 Å (arrow) as well as weaker tetragonal unit cell spots (marked by circles). We note that the predominant stripe orientation is perfectly along the lattice and roughly perpendicular to the direction in which cleavage was performed. A third type of topographic situation is that shown in Fig. 4.1c: with larger (~20 Å wide), one dimensional rod-like features displaying a relatively large corrugation of approximately 1.5 Å. Completing our topographic survey of low-T cleaved crystals, Fig. 4.1d shows a large field of view in which two previously mentioned structures (seen in Fig. 4.1a and b) can be seen to smoothly cross over. Interestingly, Fig. 4.1a and d show that the backbone-features often terminate on pinning
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Figure 4.1: Constant current images for cleavage of Ba122 (x=0.14) at low temperature (<80K). (a) and (b) are taken on the same cleave using a junction resistance $R_J=2.4 \, \Omega$, (c) and (d) on a different cleave ($R_J=0.65 \, \Omega$). Inset of (b): FFT of (b) highlighting the unit cell spots (circles) and (2×1) reconstruction spot (arrow). All topographic types shown have been observed on numerous cleaves. Line scans along the paths indicated are shown below each panel. The insets of (c) and (d) show enlargements of size 189 Å. Axes indicate the crystallographic orientation as determined from LEED.

centers taking the form of a very bright or dark spot. Finally, we note that the line-
scan shown in Fig. 4.1d lacks steps corresponding to inter-plane distances (i.e. of
Cleavage temperature dependence of $\text{BaCo}_x\text{Fe}_{2-x}\text{As}_2$ and $\text{Fe}_{1+y}\text{Se}_x\text{Te}_{1-x}$

order 1.4 Å and larger), thus indicating that the majority of the observed structures form part of the same crystallographic plane.

Figure 4.2: Constant current images for various cleaves of $\text{BaFe}_{1.86}\text{Co}_{0.14}\text{As}_2$ at room temperature ($R_I \sim 0.75 \Omega$). Line scans along the paths indicated are shown below each panel. The insets to (c) and (d) show enlargements of size 189 Å. Axes indicate the crystallographic orientation as determined from LEED.

We now go on to show that room temperature cleavage results in quite a different set of constant current images of which four frequently occurring types are shown in Fig. 4.2. The top left panel shows a highly disordered cleavage surface layer, [108] whereby the most frequent separation is $\sim 8$ Å. Fig. 4.2b shows a very clear $\sqrt{2} \times$
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√2) topography with a period of 5.5 Å, cut by meandering anti-phase domain walls (‘black rivers’ in the topograph). Figure 4.2c displays one of the more exotic cleavage surface structures encountered: a two dimensional network of stripes and dots, with a relatively large corrugation. Lastly, a diffuse maze-like landscape without atomic resolution, seen both on superconducting Ba122 and the parent compound, [108] is shown in Fig. 4.2d and has also been reported in other studies [110].

Figure 4.3: Constant current images of Fe_{1.07}Se_{0.45}Te_{0.55}, V_{sample} = -20 mV, I_{set} = 40 pA. (a) Large field of view with the inset showing the Fourier transform with spots corresponding to the atomic lattice vector (black arrow) and higher order spots (grey arrow). (b) Zoom of panel (a) showing clear atomic resolution. As the atoms are still visible in the occasional bright blob, which can be shown to be located at the center of four surface atoms, these are attributed to sub-surface excess iron in the lattice.

We now turn our attention to Fe_{1+y}Se_xTe_{1-x}. For this system, both low and high temperature cleavage yield - without exception - identical results, in sharp contrast with the great variety of topographies observed in the Ba122 case. Fig. 4.3 shows a typical constant current image, in this case for a room temperature cleave. Very clear atomic resolution is obtained over the entire field of view, with a total corrugation of less than 2 Å and a periodicity of 3.9 Å corresponding to the (Se,Te)-(Se,Te) distance. Clearly, no reconstruction is present on these surfaces, the simple tetragonal lattice being the only coherent structural pattern. The Fourier transform in the inset of Fig. 4.3a emphasises this: only tetragonal spots, also as higher harmonics, are observed. An interesting feature of the Fe_{1+y}Se_xTe_{1-x} topographs is the occurrence of bright blobs on the field of view on top of which the atomic lattice is imaged. Their spatial abundance matches perfectly the excess Fe content (7%) in the crystals, which seems a highly plausible explanation for these features.

To summarise the STM results so far, a large variety of cleavage surface termination structures is observed in the BaFe_{1.86}Co_{0.14}As_2 compound, which possess a strong cleavage temperature dependence. In contrast, the Fe_{1+y}Se_xTe_{1-x} system,
which lacks the interstitial Ba layer, has only a single type of topography, independent of cleavage temperature.

### 4.3 The surfaces of CaCo$_x$Fe$_{2-x}$As$_2$, BaFe$_2$P$_x$As$_{2-x}$ - STM and first principles calculations

First principles calculations to determine the most energetically favourable surface structure of the M122 system have been reported in literature [116]. The strong bonds between the Fe and As atoms makes cleavage between these two layers highly unlikely, leaving two options: (i) cleavage between the Ba and As layer or (ii) cleavage within the Ba layer. The energy of the two ordered structures possible with half a Ba layer: ($\sqrt{2} \times \sqrt{2}$) and (2×1), has been compared to the energy of an unreconstructed (1×1) As plus (1×1) M surface layer where M is Ba or Ca.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$2 \times (\sqrt{2} \times \sqrt{2})$</th>
<th>$2 \times (2 \times 1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaFe$_2$As$_2$</td>
<td>-411.6</td>
<td>-217.8</td>
</tr>
<tr>
<td>CaFe$_2$As$_2$</td>
<td>-34.0</td>
<td>-97.0</td>
</tr>
</tbody>
</table>

**Table 4.1:** First principle calculations of the relative energies of two ($\sqrt{2} \times \sqrt{2}$) and two (2×1) reconstructed M surfaces with respect to an unreconstructed (1×1) As plus (1×1) M surface for two M122 materials. Surface energies are given in meV/(1×1 cell) and have been calculated for the tetragonal phase with the atoms in the bulk positions. Table adapted from [116].

As can be seen from Table 4.1, all relative energies are negative, meaning that it is energetically favourable to have a reconstructed Ba layer on either side of the cleave, as opposed to an unreconstructed full As and full Ba layer. From the energetics of the reconstructions of the two M atoms, it can be expected that the ($\sqrt{2} \times \sqrt{2}$) structure is more dominant in the Ba system than in the Ca system. From our extensive STM investigation described above on dozens of Ba122 samples, where on each sample multiple locations have been probed across the entire mm-sized surface, we conclude that the modal surface is ($\sqrt{2} \times \sqrt{2}$) reconstructed in this material, with the (2×1) reconstruction and disordered structures present in lesser amounts.

Although less extensively than the Ba122 system, we also investigated the Ca122 system using STM. Having scanned $\sim 0.5 \times 0.5$ µm on locations all over a 1x1 mm sample, only a tiny region of no more than 25×25nm$^2$ was found to have a ($\sqrt{2} \times \sqrt{2}$) reconstruction, see Fig. 4.4a. Everywhere else, (2×1) surface structures were encountered of which an example is shown in Fig. 4.4b, perfectly in line with the first principles calculations.

As a further test to see if an As terminated layer could be the surface layer, despite an overwhelming body of evidence pointing towards a Ba reconstructed surface, BaFe$_2$P$_x$As$_{2-x}$ samples were measured. With a doping concentration of x=0.64, a total of 32% of all As atoms are replaced by P atoms. Resistivity measurements on these samples showed sharp transitions into the superconducting state, $T_c = 31 \pm 1$ K, in-
4. THE CLEAVAGE SURFACE OF ‘122’ PNICTIDE SUPERCONDUCTORS

Figure 4.4: Constant current images on Ca122 and P doped Ba122, \( V_{\text{sample}}=50 \text{ mV}, I_{\text{set}}=40 \text{ pA.} \) 

(a) The only instance on CaCo\(_x\)Fe\(_{2-x}\)As\(_2\) a \((\sqrt{2} \times \sqrt{2})\) reconstructed surface was encountered on an otherwise completely \((2 \times 1)\) reconstructed surface of which an example is shown in (b). 

(c)-(d) \((2 \times 1)\) surface structures on BaFe\(_x\)P\(_x\)As\(_{2-x}\), which are identical in appearance to the \((2 \times 1)\) structures seen on compounds without substitution of the As atoms. All insets are 100×100\(\text{Å}^2\) enlargements of the areas indicated with boxes.

dicating that the samples are homogeneous, high quality crystals. With such a large fraction of As atoms replaced by the much smaller, but isovalent P atoms, one would expect to see a change in the constant current images if indeed the As surface would be imaged, similar to for instance N doping of As sites in GaAs [117]. However, as can be seen from Figs. 4.4c-d, the topographs obtained on BaFe\(_x\)P\(_x\)As\(_{2-x}\) are indistinguishable from those obtained on for instance BaCo\(_x\)Fe\(_{2-x}\)As\(_2\) or CaCo\(_x\)Fe\(_{2-x}\)As\(_2\).
4.4 Apparent barrier height on pnictides

An intriguing property of the 122 pnictides is the difficulty with which atomic resolution is obtained, for instance the individual atoms on the $(2 \times 1)$ reconstruction are only seen for rather high currents (i.e. small tip-to-sample distances). In case of the pnictides, this is a direct consequence of the unusual small value of the apparent barrier height, $\Phi$. From Equation (2.1) it follows that the work function can be extracted by measuring the tunneling current as a function of tip-to-sample distance, a so called I(z) measurement. As the barrier height is a measure of the steepness of the exponential drop in the current for increasing distance, the higher this value, the higher the z-resolution. This is the reason that one of the selection criteria for a good tunneling tip is a high work function when characterising the tip on Au(788). As mentioned in chapter 2, the barrier height or work function is a material dependent property and is usually a few eV. Several elemental work functions relevant in the context of the pnictides are listed in Table 4.2. For elemental Au, the work function is 5.1-5.47 eV, similar to the work functions of Pt and Ir (the tip material mainly used in the investigation of the 122 pnictides), values which are typically found for good tips on the Au(788) crystal.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Phi$ (eV)</th>
<th>Element</th>
<th>$\Phi$ (eV)</th>
<th>Element</th>
<th>$\Phi$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>5.9</td>
<td>Te</td>
<td>4.95</td>
<td>As</td>
<td>3.75</td>
</tr>
<tr>
<td>Pt</td>
<td>5.12-5.93</td>
<td>Fe</td>
<td>4.67-4.81</td>
<td>Ca</td>
<td>2.87</td>
</tr>
<tr>
<td>Au</td>
<td>5.1-5.47</td>
<td>Bi</td>
<td>4.34</td>
<td>Ba</td>
<td>2.52-2.7</td>
</tr>
<tr>
<td>Ir</td>
<td>5.00-5.67</td>
<td>Pb</td>
<td>4.25</td>
<td>K</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Table 4.2: List of work functions of several elemental materials, taken from Ref. [118]. For single crystalline materials different orientations can have a slightly different work function, indicated by the spread in the work function.

The work function on the Ba122 pnictides, however, for the dozens of samples measured throughout this research is never seen to be higher than 1.8 eV, and is usually around 1.5 eV, see Fig. 4.5a for a typical example. Even though the work function is a property of the whole material, it will be most strongly affected by the surface layer. A monolayer of Ba on W(001) has for instance been reported to lower the work function with $\sim 2$ eV, to approximately the bulk Ba work function [119]. Looking at Table 4.2, the lowest work function of the pure elements of which Ba122 consists is that of Ba, followed by As and Fe, in steps of nearly 1 eV. This alone is already an indication that the surface layer is half a Ba layer, but is in itself inconclusive. Interesting to note at this point is that the work function is not seen to change as a function of surface topography on the 122 pnictides, i.e. the $(\sqrt{2} \times \sqrt{2})$ and $(2 \times 1)$ reconstructions have very similar work functions, suggesting that the two surface structures are both reconstructed Ba terminations.

From Table 4.2 it can be seen that elemental Ca has a slightly higher work function than Ba. As nothing is changed other than replacing the Ba layer for a Ca layer, it is
not an unreasonable assumption that the work function will track the difference in work function between Ba and Ca, but only if the Ba and Ca layers are at the cleavage surface. Indeed, the work function on (2×1) structures encountered on Ca122 is at 1.9 eV slightly higher (Fig. 4.5b). If As (or Fe) would be the surface layer, one would not have expected the work function to be influenced this much as the cation layer in that case would be buried deep underneath the top few layers. Although not a direct proof, this observation once again adds to the notion that indeed the M-layer is the topmost layer in the M122 pnictides.

Fe\textsubscript{1+y}Se\textsubscript{x}Te\textsubscript{1-x} on the other hand, where clear atomic contrast is readily obtained, and where the surface layer consists of Se (\(\Phi = 5.9\) eV) and Te (\(\Phi = 4.95\) eV) atoms, has a work function that is considerably higher than that seen on the M122 systems, see Fig. 4.5c. As a comparison to these iron based superconductors, three other materials are shown in Fig. 4.5d-f with a relatively large work functions where atoms are clearly resolved. As these materials are imaged using identical tips in the same setup as the pnictides were investigated in, the low work function seen in the pnictides is clearly shown to be a property of the material, that can only be explained by having a Ba (or equivalent) terminated surface layer.

One could still speculate that the work function seen with STM does not reflect the properties of the surface, but of the tip. Accidentally picking up a Ba atom during approach would change the work function of the tip and thereby the average work function of the sample and the tip that is actually measured. Since a large number of samples has been measured, most of which gave (2×1) or (\(\sqrt{2} \times \sqrt{2}\)) structures over a large field of view upon the first touchdown directly after characterisation on the Au(788) crystal, this scenario is highly unlikely. Moreover, many tips were confirmed to be unaltered after measuring a 122 pnictide by characterisation on the same Au(788) crystal afterwards.

### 4.5 Low energy electron diffraction on BaFe\textsubscript{1.86}Co\textsubscript{0.14}As\textsubscript{2} and Fe\textsubscript{1.07}Se\textsubscript{0.45}Te\textsubscript{0.55}

Figure 4.6 shows LEED data with \(E_0=110\) eV. In Fig. 4.6a, the low temperature cleavage surface (17 K) of the Ba122 superconductor gives rise to spots very clearly at positions other than those originating from the tetragonal unit cell of either Ba or As. Spots corresponding to both (\(\sqrt{2} \times \sqrt{2}\)) and (2×1) reconstructions in both a and b directions of the crystal are present. In the STM topographs of Fig. 1, we clearly image the (2×1) structures as the basic unit forming the ribcages. However, under our imaging conditions, the (\(\sqrt{2} \times \sqrt{2}\)) structures seen clearly in the high-T cleave do not generate sufficient contrast in the low-T cleaved data of Fig. 4.1a and b. For very low junction resistances, the (\(\sqrt{2} \times \sqrt{2}\)) topography has been imaged directly in the STM of low-T cleaved crystals of the parent compound Ba122 in Ref. [113].

Returning to the LEED data, upon increasing the temperature, all non-tetragonal LEED spots start to lose intensity above 100K, and by reaching 200K, only the tetragonal reflections remain (Fig. 4.6b). More importantly, on re-cooling the sample back
Figure 4.5: Typical constant current images (top) on various materials imaged on the same system using identical tips together with I(z) curves (bottom) taken on each surface. From the I(z) curves, the average work function of the sample and the tip, \( \Phi \), is extracted using Equation (2.1). The values for the work function are indicated in the I(z) curves, as well as the material in question. The unusually low work function seen on the M122 systems is a strong indication of a Ba as opposed to As terminated surface (panel (d) courtesy of J. Kaas).

to 17K, none of the non-tetragonal spots reappear. The main spots, however, be-
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Figure 4.6: Low energy electron diffraction, taken at 110eV, unless stated otherwise. (a) BaFe$_{1.86}$Co$_{0.14}$As$_2$ cleaved and measured at 17K. The spots marked with a circle are the tetragonal ($\frac{1}{2},0$) (white), ($\frac{1}{2},\frac{1}{2}$) (grey) and ($\frac{1}{2},1$) (black) reflections. (b) Same surface, but warmed up and measured at 200K. (c) Fe$_{1+y}$Se$_x$Te$_{1-x}$ cleaved and measured at 17K. (d) Low temperature cleaved CaCo$_x$Fe$_{2-x}$As$_2$, taken at 141 eV. The relative abundance of (2\times1) and (1\times2) structures with respect to the ($\sqrt{2} \times \sqrt{2}$) structure is reflected in the LEED pattern which only supports spots corresponding to striped reconstructions (marked by the black circles). (e) I(V) trace of the ($\frac{1}{2},\frac{1}{2}$) spot of Ba122. (f) LEED I(V) trace (top, red) and theoretical calculation (bottom) corresponding to the same spot as shown in (e) adapted from [113]. The mismatch rules out the As layer as the origin of the extra diffraction spots.

come more diffuse once the cleave is or has been at higher temperature, signalling increased surface disorder or the presence of structurally incoherent reconstructions. Having presented the LEED data for BaFe$_{1.86}$Co$_{0.14}$As$_2$, we now show in Fig. 4.6c a typical LEED pattern from the Fe$_{1+y}$Se$_x$Te$_{1-x}$ compound cleaved and measured at low temperature. Not surprisingly, since the STM images only show the tetragonal atomic lattice, none of the extra LEED spots appearing in the Ba122 case are present in the Fe$_{1+y}$Se$_x$Te$_{1-x}$ data. Similarly, the LEED data taken on the CaCo$_x$Fe$_{2-x}$As$_2$ system (see Fig. 4.6d), in which the surface structure seen with STM is dominated by (2\times1) and (1\times2) reconstructions, only supports spots corresponding to these two orientations of the striped structure, in line with the calculations.

Returning to the LEED data from the Ba122 system, tracking the intensity of the main (tetragonal) spots seen in Fig. 4.6a and b results in I(V) curves which follow the theoretical curves for diffraction from the As layer reported in Fig. 4a of Ref. [113].
Low energy electron diffraction on $\text{BaFe}_{1.86}\text{Co}_{0.14}\text{As}_2$ and $\text{Fe}_{1.07}\text{Se}_{0.45}\text{Te}_{0.55}$

This agreement between our data with LEED theory would appear to confirm that the outermost complete layer after cleavage consists of As atoms [113]. However, and importantly, the LEED data from the low temperature cleaves of $\text{BaFe}_{1.86}\text{Co}_{0.14}\text{As}_2$ and the parent compound $\text{BaFe}_2\text{As}_2$ (data not shown) clearly show $\left(\frac{1}{7},\frac{1}{7}\right)_{\text{tetragonal}}$ spots, in contrast to the data of Ref. [113]. The I(V) trace of our $\left(\frac{1}{7},\frac{1}{7}\right)_{\text{tetragonal}}$ spots (see Fig. 4.6e) is very different to both the experimental and theoretical I(V) curves in Ref. [113], possessing peaks and minima at totally different energy values, see Fig. 4.6f. The mismatch between our experiment and the theory in Ref. [113] rules out the As layer as the origin of our extra LEED spots, leaving the partially ordered Ba atom overlayer as the obvious candidate to explain the $\left(\frac{1}{7},\frac{1}{7}\right)_{\text{tetragonal}}$ spots in LEED and the topographic features seen in STM with periods greater than the tetragonal repeat unit of 3.9 Å. A surprising observation in the STM topograph of Fig. 4.2b is the clear $\left(\sqrt{2} \times \sqrt{2}\right)$ lattice on the surface of a high temperature cleaved sample, whereas the corresponding $\left(\frac{1}{7},\frac{1}{7}\right)_{\text{tetragonal}}$ spots in LEED have ceased to be observable above the background upon warming up the sample. At this point, we mention that theoretical calculations predict that the $\left(\sqrt{2} \times \sqrt{2}\right)$ (or checkerboard) reconstructed surface is the most energetically favourable ordered distribution of the remaining half of the Ba atoms on either side of the cleave [116]. One approach to understand why the $\left(\sqrt{2} \times \sqrt{2}\right)$ LEED spots disappear at higher temperature is offered by consideration of the dislocation networks seen in the STM topographic data in the high temperature cleaved surfaces (the ‘black rivers’ seen in Fig. 4.2b), which are absent in the low-T cleave topographs. Upon warm cleavage or increase of the sample temperature above ca. 200K, it is conceivable that fragmentation of the checkerboard order into nanoscopic domains causes the coherence length of the reconstruction to drop sufficiently such that the $\left(\sqrt{2} \times \sqrt{2}\right)$ spots fade into the background of the LEED pattern, which itself is the result of a measurement which spatially integrates on a mm length-scale.

The measurements presented above formed the basis of a more detailed LEED investigation, where in collaboration with M. Lindroos and co-workers the LEED I(V) data were fitted to calculations as was done in Ref. [113]. As the number of fitting parameters is rather large, for a reliable result it is imperative to have as many diffraction spots as possible tracked over an as large as possible energy range. To this end, more datasets were taken which were subsequently fitted to calculations of both an As terminated surface and a Ba terminated surface. In the fit, the positions of the surface atoms were not fixed, but free to reorganise, mimicking a surface reconstruction, to give the best result. I(V) curves for a number of spots are shown in Fig. 4.7 along with the fits to the experimental data.

To quantify the level of agreement of the experimental data and the simulations, so called Pendry R factors ($R_p$) were used [120]. These factors are calculated using the position and width in energy of diffraction spots, but are little affected by the intensity of the spots as this is a function of various factors that are not well understood. The lower the Pendry R factor, the higher the agreement between simulation and data, where a satisfactory fit generally has $R_p < 0.3$. Using only the half integer
4. The Cleavage Surface of ‘122’ PNictide Superconductors

Figure 4.7: LEED I(V) curves for various half-integer spots. The left and right parts correspond to spots originating from the (2×1) and (√2×√2) reconstruction respectively. Pendry R factors are indicated for each fit to a Ba terminated simulation, showing the excellent agreement. Courtesy of E. van Heumen.

spots, which are resulting from a surface reconstruction and cannot be a higher order diffraction of the bulk lattice, the experimental data was fitted with either a Ba or a As terminated simulation for both the (√2×√2) and (2×1) reconstructions. As expected from the initial measurements shown in Fig. 4.6e, the As surface termination gives unacceptably high Pendry factors of 0.42 and 0.48 for the two reconstructions respectively. A Ba terminated surface on the other hand gives remarkably low factors of $R_p = 0.19$ and 0.29 respectively, indicating the excellent agreement between experiment and simulation, and unambiguously showing that the cleavage surface is a reconstructed Ba layer. It should be noted that a Ba terminated surface alone is not sufficient to get this agreement, but a structural distortion of the first unit cell is required as well. As this distortion is seen to have a considerable impact on the surface density of states [121], its effect on the tunneling signal picked up in STM/S experiments should not be overlooked.
4.6 Surface model for the ‘122’ systems

By now it is clear that the topographical diversity of the cleavage surface of the alkaline earth-122 material family is due to the partial alkaline earth atom overlayer that remains after cleavage. In fact, we can reconcile all our experimental STM data from the 122 systems within a very simple structural model, based only on differences in the distribution of the Ba atoms within the overlayer that remains on the surface after cleavage. A sketch of the model is shown in Fig. 4.8. When a sample is cleaved at low temperature, the Ba surface atoms are not mobile enough to re-arrange themselves into the energetically most favourable structure, with metastable situations such as the \((2 \times 1)\), or rib-cage reconstruction as the result. Increasing temperature enables the overlayer atoms to re-arrange, thus patches of checkerboard reconstruction are formed separated by domain walls (‘black rivers’). Alternatively, more disordered configurations such as those seen in Fig. 4.2a are also possible, depending on the local concentration of Ba atoms.

Figure 4.8: Sketch of various possible Ba surface overlayer configurations. Large (small) circles indicate the presence (absence) of a Ba atom. The dotted atom (left top) indicates a missing atom resulting in a black spot in topography. Extra atoms can similarly lead to bright spots. Anti-phase boundaries (APB) are shown running along two observed directions. Broader ‘backbones’ in the ribcage structure are created by adding atoms at the phase-shift boundary.

Ordering of the Ba surface atoms in locally densely packed structures surrounded by a relatively Ba-free region could lead to an increased corrugation in STM, matching the rods seen in Fig. 4.1 and the bright regions in Fig. 4.2c. However, these kind of structures are still within the same Ba layer as the locally less densely packed ordered \((\sqrt{2} \times \sqrt{2})\) and \((2 \times 1)\) regions, and thus these different topographies can cross over into one another as indeed has been observed. Evidently, more random distribution of the Ba atoms in the overlayer could lead to topographs as in Fig. 4.2a and d.
4. THE CLEAVAGE SURFACE OF ‘122’ PNICIDE SUPERCONDUCTORS

Figure 4.9: (a) Regular (2×1) surface reconstruction imaged on a Ca122 sample (V_{sample} = 50 mV, I_{set} = 40 pA). After scanning the central part of the surface using a rather violent combination of bias voltage and setup current (a few mV and a tens of nA), this area is completely disordered as shown in (b), whereas the part of the surface where no such treatment has been performed remains identical.

A nice illustration of the ease with which the surface atoms are rearranged is shown in Fig. 4.9. In this example, initially a regular (2×1) surface structure on Ca122 is imaged (Fig. 4.9a). Subsequently, the tip is scanned over the central 10×10 nm² area using a rather violent combination of bias voltage and tunneling partial current, resulting in the tip stirring the surface¹. After a few minutes of playing with the surface atoms in this way, the original 40 nm square field of view is imaged again. The result shown in Fig. 4.9b shows an otherwise unaffected (2×1) structure, where the central 10 nm part is completely randomised, but where the average height is still identical to the rest of the image. No atoms have therefore been picked up or deposited on the surface, the surface atoms have only been rearranged. Once again, this could only be possible for loosely bound Ca surface atoms, and is unlikely in case strongly bound As atoms are the surface atoms being imaged in the STM measurements.

4.7 Summary

In summary, the Ba122 cleavage surface exhibits a large variety of topographies and has pronounced cleavage temperature dependence. In LEED, spots corresponding to large scale coherent structures of dimensions larger than the 3.9 Å tetragonal unit cell, i.e. (2×1) and (\sqrt{2} × \sqrt{2}), appear for low temperature cleaved samples. These spots vanish upon warming the sample to 200 K and do not reappear after cooling back to 17 K. Since superconducting BaFe_{1.86}Co_{0.14}As_2 possesses no spin density

¹similar to the rummaging around in a bowl of balls by contestants of the Dutch television show ‘Lingo’ after guessing a word right
wave at 4.5 K [122], the (2×1) and (√2 × √2) topographies in STM cannot be explained by a SDW-driven creation of two distinct As sites, but only by the ordering of the Ba atoms remaining on the surface after cleavage. It is proposed that the disappearance of the extra spots seen in LEED at higher temperatures is a signal of fragmentation of these structures due to a re-distribution of the Ba atoms at the surface into energetically more favourable configurations on a small length scale. These still appear as ordered patterns in STM, yet possess insufficient long range order to support LEED spots. The longer range order does not re-establish itself upon re-cooling, thus the non-tetragonal spots do not reappear and the tetragonal LEED spots themselves become more diffuse. The argument that the non-tetragonal LEED spots originate from the Ba termination layer is underpinned by the fact that our experimental LEED I(V) profiles of various fractional spots have an unusually high degree of resemblance to simulations using a Ba terminated surface, in contrast to calculations using As terminated surfaces. Furthermore, the observation of practically identical surface structures on both Ca122 and P doped Ba122 offer additional evidence that the observed surface topographies are dominated by the half-M layer on the cleavage surface of the crystal. These additional data also indicate that a generalisation to all M122 systems, where M=(Ba, Eu, Sr...) may be valid. Comparison of work functions on various pnictide superconductor cleavage surfaces all fall within the picture of a Ba terminated surface. Moreover, since the work function on various surface structures, i.e. (2×1), (√2 × √2), etc., on the same 122 sample with the same tip are identical, these different structures are all believed to reconstructed Ba terminations. In stark contrast to the richness and complexity of the surface topography of the 122 family of compounds, Fe1+ySe1−xTe displays only one type of cleavage surface and LEED pattern without any sign of reconstructions, independent of the cleavage temperature, explained by the undisputed cleavage between adjacent SeTe layers.