k-space Microscopy of Bi2Sr2CaCu2O8+ :Fermiology and Many-body Effects
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This chapter describes a detailed experimental description and analysis of the shadow Fermi Surface (SFS) seen in the ARPES data of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ and related systems. In introduction, the status of SFS is given, then followed by the way how one could devise an experiment to resolve the origin of the SFS band. Based on a symmetry argument we can distinguish between initial and final state effects in the photoemission signal from the main band (MB) and SFS bands. This evidence, along with low energy electron diffraction (LEED) data led to the explanation of the SFS’s structural origin, being due to orthorhombic distortions from the initial tetragonal symmetry. This has resolved an open question in high $T_C$ research since 1994.

3.1. Introduction to the fermiology of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

The Fermi surface (FS) is a surface of constant energy in reciprocal space ($k$-space). Since the electronic excitations at low energy across the FS determine the low energy properties of a material, this makes the FS one of the central concepts in condensed matter physics.
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Figure 3.1: (a) $k_{\parallel}$ intensity mapping of modulation-free Bi-based HTSC shows two primary features, i.e. the main band (MB, shown here using a red line) and shadow Fermi surface (SFS, shown here in blue). This intensity map was taken using photon energy of 21.2 eV on overdoped Pb-Bi2212. The green area shown the data recorded, which have been symmetrised to give the whole figure.

In the photoemission data of the Bi-based HTSC, two primary FS features are observed, namely the main band (MB) FS and the SFS. The MB FS is located and centered around X and Y in the 2D BZ, while the SFS is located around $\Gamma$ and equivalent points [58] (see Fig. 3.1). While the MB feature has been heavily studied and investigated, as have the superconducting gap [6, 34], pseudogap and many body interactions seen in the spectra, only few studies have been carried out on the SFS.

The SFS was observed for the first time by Aebi et al. in 1994 [58] and since then its origin has been a matter of controversy. At a first glance, the SFS looks like a $(\pi, \pi)$-shifted copy of the MB FS but with less intensity and therefore short-range antiferromagnetic (AFM) spin fluctuations which are present in all cuprates were initially suggested as its origin [58, 94], since these will give rise to a scattering vector that would connect the MB and SFS. Many theoretical and experimental studies have been published agreeing with this magnetic origin [95–101].

The second group of mechanisms for SFS formation is non-magnetic in origin. The SFS is suggested to come from backfolding of bands due to departure from
Figure 3.2: From Ref. [102] LEED pattern of Bi2212 recorded with very low energy electrons. (a) clear c(2 × 2) like spots are highlighted in red. (b) The beam energy dependence of the spots indicated. Above 25 eV the c(2 × 2)LEED spots is graduating vanish.

the ideal tetragonal structure of Bi-based HTSC [103] or due to a c(2 × 2) surface reconstruction [104]. Both modifications of the lattice induce a smaller Brillouin zone.

In the AFM scenario, significant renormalisation of the SFS dispersion with respect to that of MB should exist, and the SFS band intensity should be strongly dependent on both the doping level and temperature, *i.e.*: firstly it should be stronger in the underdoped (UD) region and weaker for overdoping (OD) since from the phase diagram in the preceding chapter it is known that a reduction in hole-doping (UD) means that the system approaches the AF region. Secondly, the AFM scenario leads to the prediction that the SFS band should be strongly temperature dependent *i.e.*: increasing as the temperature is lowered, in keeping with the temperature dependence of spin fluctuations measured at Q (π, π) in neutron scattering [105].

These characteristics of the AFM origin of the SFS allow for an experimental check of the validity of this mechanism for its formation. Following this strategy, a recent ARPES study [106] has argued convincingly against this AFM scenario. This study has shown a lack of additional dispersion renormalisation, and of doping, or temperature dependence of SFS band signal in ARPES. Additionally, a very low-energy electron diffraction (VLEED) study revealed what was interpreted as a hidden c(2 × 2) periodicity in pristine Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ [102] (see Fig. 3.2), which is more consistent with the structural origin. In this study, the c(2 × 2) periodicity which is similar to the periodicity of SFS band...
observed in ARPES, appears due to the multiple scattering process involving CuO planes, the outer SrO and BiO planes as well as their incommensurate modulation. Thus, it is clear that VLEED probes the final states of photoemission, but one could ask the question: is the SFS in these particular cuprates a phenomenon residing in the final states, or is it an initial state effect and thus relevant not only for photoemission but also for transport and other physical properties? This question was answered comprehensively by the authors of Ref. [51] and forms the anchor and framework of this chapter.

3.2. Experimental

The ARPES experiments were performed at the Surface and Interface Spectroscopy (SIS) beamline of the Swiss Light Source (SLS), using a Scienta 2002 spectrometer. Energy and angular resolution were better than 40 meV and 0.3° (which would correspond to 0.03 Å⁻¹ for a photon energy of 100 eV), respectively. High quality pristine Bi2212 and Pb-doped Bi2212 untwinned single crystals were grown using the travelling solvent floating zone method and were mounted on a 5-axis cryomanipulator that allows polar and azimuthal rotation of the sample in ultra-high vacuum (ca. 10⁻¹⁰ mbar) with a precision of 0.1°. Cleavage and measurement took place at T = 15 K.

In order to distinguish between the final and initial states, we devised an experimental geometry that exploited the polarisation of the incoming photons as shown in Fig. 3.3. In the geometry used, the incoming synchrotron radiation, the sample surface normal and the detected photoelectrons all lie in the same plane.
The Fermiology of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$: The Origin of the Shadow Fermi Surface

Figure 3.4: (a) Mirror planes for Zhang-Rice singlet (ZRS) states which are relevant for the Bi-based cuprates. M1 is a mirror plane which connects the (0,0) and ($\pi$,0) points in the 2D BZ. M2 is the mirror plane which connects the (0,0) and ($\pi$, $\pi$) points. (b) Schematic drawing of Bi2212 Fermi surface. Solid red and blue lines represent the MB FS and SFS, respectively. The dotted black box represents the tetragonal first BZ. M1 and M2 are the same mirror planes as described in (a). Note that the conventional notation for the high symmetry points in the 2D BZ is: (0,0) is the $\Gamma$ point, ($\pi$, $\pi$) is the Y point, ($\pi$, $-\pi$) is the X point, and ($\pi$, 0) is the M point. (c) This sketch shows the sample oriented such that the $\Gamma X(Y)$ direction lies horizontal.

horizontal plane (shown in green in Fig. 3.4(c)). Three different polarisations have been used in the experiment: linear horizontal [$p$], linear vertical [$s$] and circular left [$\sigma^+$]. Due to the undulator design, pure $s$ polarised radiation is only available for photon energies $\geq$ 100 eV.

The ARPES intensity is proportional to the matrix element $\langle \phi_f | p \cdot A | \phi_i \rangle$ as described in chapter 2 and is given by,

$$I \propto \sum_{f,i} |\langle \phi_f | p \cdot A | \phi_i \rangle|^2 A(k,E) f(E) \otimes R_E \otimes R_k + BG,$$

where $\phi_f$ and $\phi_i$ are final and initial states, $p$ and $A$ are the momentum vector of photoelectron and the electromagnetic vector potential, respectively, $A(k,E)$ is the spectral function and $f(E)$ is the Fermi-Dirac distribution function. $R_E, R_k,$ and BG denote the experimental energy resolution, momentum resolution, and background, respectively.

In the following we show that one can use the photon polarisation to probe the symmetry of the initial states. As shown in Fig. 3.4(a), the Zhang-Rice singlet (ZRS) states which are relevant to our Bi2212 sample [6, 107], have a defined reflection symmetry in two mirror planes, denoted M1 and M2. The mirror plane M1 in reciprocal space is equal to the line that joins the (0,0) and ($\pi$,0) points, while the mirror plane M2 is equal to the line that joins the (0,0) and ($\pi$, $\pi$) in the reciprocal space. If the sample is oriented such as shown in Fig. 3.4(c), then the mirror plane can be arranged to contain the Poynting vector of

\[\text{sample}\]
the synchrotron radiation, the surface normal and the photoelectrons. In this case, the initial state has odd symmetry with respect to the mirror plane [6].

As it was described previously in the matrix element subsection of Chapter 2 (see Table 2.1 on page 44), in order to get non-vanishing intensity at the detector, the final state symmetry has to be even. This constraint means that $p \cdot A|\phi_i\rangle$ should be even. In the case of an even initial state, this requires $p$-polarised light, while odd initial state, will require $s$-polarised light. This leads to the conclusion that with $p$-polarised light, only the even component of the initial state will be observed, while with $s$-polarised light, only the odd component will be observed. In this context, $\sigma^\pm$-polarised light can be considered as a superposition of $p$ and $s$ polarisation and consequently it is used in the following to catalogue all features concerned.

### 3.3. Results from pristine Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

A sketch of the pristine Bi2212 FS is shown in Fig. 3.5(a). The main FS, which consist of barrels centered around the corner points X and Y of the tetragonal BZ, is represented by a solid red line. The SFS is represented using a solid blue line and is centered around $\Gamma$ point and equivalent k-points. The diffraction replicas (DRs) of these primary features are represented by dotted lines of appropriate colour. The presence of DRs is due to an incommensurate modulation of the BiO planes along the b axis ($\Gamma Y$). The modulation vector is denoted by $q$. For reasons of simplicity, the FS barrels sketched in Fig. 3.5(a) are represented as circles, and the c-axis bilayer splitting due to the present of two adjacent Cu-O layers is neglected.

Fig. 3.5(c) shows an energy momentum map (EDM) recorded along cut I (i.e. in the $\Gamma Y$ direction), measured with $\sigma^+$-polarised light. As one can see from Fig. 3.5, the features from both the EDM and MDC (momentum distribution curves) can be identified as: (1) the MB, (2) 1st order SFS DR, (3) 1st order MB DR, (4) SFS band, (5) 2nd order MB DR. Fig. 3.5(d) and 3.5(e) show the same cut but now measured with $p$ and $s$-polarised light, respectively. The MB features should have purely odd symmetry with respect to M2 ($\Gamma Y$ plane) as expected from their Zhang-Rice singlet (ZRS) character [107]. In such a case, $p$-polarisation disallows the MB excitation and one can see from Fig. 3.5(d), that there is, indeed, a complete suppression of the MB features (labelled 1, 3 and 5 in Fig. 3.5(c)). On the contrary, the SFS band (and its DR’s) does not vanish with
In Fig. 3.5(e), however, the situation is reversed. When measuring with s-polarised light, the SFS band features are wholly suppressed while the MB features remain present. Fig. 3.5(b) illustrates not only that the “switching-off” of the MB (in fact a DR of the MB, labelled 3 in panel (c)) is effective only within a range ± 2° in azimuthal angle within the ΓY azimuth, but also that the SFS band intensity is maximal exactly along the nodal line. These data are the first evidence that the SFS band states have even symmetry with respect to the mirror plane M2 (ΓY), while the MB states are odd along ΓY.

In the ΓX direction (cut II in Fig. 3.5(a)), the separation between the primary features (both MB and SFS band) and their replicas is only 0.07 Å−1, which makes the situation complicated. Fig. 3.6(a) shows a 100 eV ΓX EDM, measured with s-polarised light. The very low intensity of the SFS band is a further challenge. Direct inspection of Fig. 3.6(a), would suggest that the intense features on the left hand side (below 0.6 Å−1) are originating from the MB (and its
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Figure 3.6: (a-b): EDMs measured at cut II in Fig. 3.5(a) ($h\nu = 100$ eV) with $s$ and $p$-polarised light, respectively. (c-d): EDMs ($h\nu = 40$ eV) measured at the same cut as (a) and (b) using the polarisations indicated. The $E_F$ MDCs are shown as white lines. The inset in Fig. 3.6(c) shows the magnifications in the region of the shadow band, including a Lorentzian as a guide to the eye. (e) The comparison of MDCs at the $E_F$ ($h\nu = 100$ eV): $\sigma^+$ (black), $s$ (blue), and $p$-polarisation (red). The position of the MB, MB DR, and SFS band are indicated by vertical dotted lines.

replicas), while the weaker features on the right hand side (above 0.6 Å$^{-1}$) are coming from the SFS band (and its replicas). Note that since the intensity of the SFS band is very low, it has been adjusted in the figure, so as to make it more clear. From analysis of the MDC at $E_F$ (see Figs. 3.6(a) and 3.6(b)) one can see that the MB feature has two branches. The left branch belongs to the MB and the right branch belongs to MB DR. Since the intensity of SFS features are very low, the branching of SFS states cannot easily be observed.

What happens if one now switches the polarisation from $s$ to $p$? Fig. 3.5(b) shows the situation when the polarisation is switched. The intensity of the SFS branch (above 0.6 Å$^{-1}$) is absent, while the intensity in the MB region (below 0.6 Å$^{-1}$) now consists of only a single branch. A detailed analysis of the $E_F$ MDCs of all three polarisations would be helpful in order to attribute which branch belongs to which band. Fig. 3.6(e) shows such a compilation of MDCs, illustrating the splitting of the MB states into MB and MB DRs and the presence
of SFS band features for both the $\sigma^+$ and $s$ polarisation. In the $p$-polarisation MDC, however, the MB (0.41 Å$^{-1}$) is absent as is the SFS band feature. Only the MB DRs (0.48 Å$^{-1}$) are present. The peak at 0.23 Å$^{-1}$ can be attributed to 2$^{nd}$ order DRs. Therefore, it is clear that from an MDC analysis for data recorded along the $\Gamma X$ direction, both the MB and SFS bands show identical polarisation dependence, having odd symmetry with respect to the $\Gamma X$ M2 plane.

The separation in angle between the primary features (both the MB and SFS band) and their replicas can be made bigger by using a lower photon energy such as 40 eV. Although the lower photon energy means that pure $s$-polarised light is not available, the situation is nevertheless more simple compared to that when using 100 eV, as one can see in Fig. 3.6(c) and 3.6(d). Applying the same analysis as we did for a photon energy of 100 eV, again the same result is arrived at, namely that both the MB and SFS band show identical polarisation dependence by having odd symmetry in the M2 mirror plane.

Consequently, these data - recorded mainly with $h\nu = 100$ eV - make a very strong case for the fact that the main and shadow states have opposite mirror symmetry in the $\Gamma Y$ nodal mirror plane, but the same mirror symmetry in the $\Gamma X$ mirror plane. This is a surprising result, based in part on the absence of SFS intensity for $\Gamma Y$ and $s$-polarised light. From Eqn. (3.1), it is clear that the observed intensity in an ARPES experiment depends on both the energy and polarisation of the light. This means that failure to see the SFS for a particular photon energy and polarisation could be due to an ‘unlucky’ combination of photon energy and $k$-location and not due to initial state symmetry effects.

Thus, we would very much like an independent check of the vanishing SFS band intensity seen in Fig. 3.5(a) in the $\Gamma Y$ direction. Therefore, in order to prove that the SFS band state has even symmetry, further different checks have been performed, namely an investigation of the photon energy dependence, the dependence (if any) on the angle of incidence of the synchrotron radiation and, finally, whether the conclusion that the MB and SB have different symmetry depends on the incommensurate modulation inherent to the pristine Bi-based high-$T_c$ superconductor. The last check is carried on with the help of Pb-doped Bi2212 crystals, since by Pb-doping one can vary the wave length of the incommensurate modulation in Bi2212.
Figure 3.7: EDMs measured in the ΓY direction (cut I in Fig. 3.5(a)) in pristine Bi2212 for: \( h\nu = 40\,\text{eV} \) with (a) \( \sigma^+ \), (b) \( p \)-polarisation, \( h\nu = 52\,\text{eV} \) with (c) \( \sigma^+ \), (d) \( p \)-polarisation, \( h\nu = 91\,\text{eV} \) with (e) \( \sigma^+ \), (f) \( p \)-polarisation. (g) The intensity ratio of the shadow and main bands which was measured using \( \sigma^+ \)-polarised light as a function of photon energy for two different pristine Bi2212 crystals (open and closed symbols). (h) The fitting result for the 40 eV \( \sigma^+ \) \( E_F \) MDC with four Lorentzians yielding an identical momentum width of both MB and SB.
3.3.1. Photon energy dependence check

For the purpose of checking the photon energy dependence, we have performed the measurements in the \( \Gamma Y \) direction (cut I in Fig. 3.5(a)) using \( \sigma^+ \) and \( p \)-polarised light for \( h\nu < 100 \) eV. The left hand panels of Fig. 3.7 show data that are recorded using \( \sigma^+ \)-polarised light, and the right hand panels show the data recorded using \( p \)-polarised light. From the top to bottom of Fig. 3.7 the photon energies used are 40 eV (a) and (b), 52 eV (c) and (d), and 91 eV (e) and (f). For all photon energies, the \( \sigma^+ \) data show both MB and SB features, while using \( p \)-polarisation the MB features are clearly absent. These results are expected as the ZRS state has odd symmetry in M2 along the \( \Gamma Y \) direction. The SB features, on the other hand, are all visible for \( p \)-polarisation, proving that for \( k \) along \( \Gamma Y \) these initial states cannot be purely odd in character.

In order to unambiguously uncover the SB band symmetry, \( s \) polarisation is needed, which in our case can be achieved only with photon energy > 100 eV. The data shown in Fig. 3.5(e) give the clear message that the SB initial states have even symmetry, since the emission from these states are completely suppressed upon excitation with \( s \)-polarised radiation.

Fig. 3.7(g) shows the intensity ratio between the SB and the MB signal along the \( \Gamma Y \) direction of the first BZ as a function of photon energy, measured with \( \sigma^+ \)-polarised light for two different pristine Bi2212 samples. The MB and SB band intensities are obtained by fitting an MDC integrated within \( \pm 20 \) meV of \( E_F \) using four Lorentzian lineshapes. All of the Lorentzians have identical width (as we know from ref [106] and our own analysis such as that shown in Fig. 3.7(h) that the MB and the SB have the same MDC width).

In summary, it is clear that in the \( \Gamma Y \) direction the MB states are completely suppressed using \( p \) polarisation for all photon energies studied. The SB states are proven to be of other than purely odd character, for data taken with different photon energies, and their complete suppression for \( s \)-polarised 100 eV photon signals, strongly suggesting that their initial states have even character with respect to the M2 mirror plane.

3.3.2. Incident angle dependence check

The polarisation vector \( \mathbf{A} \) in Eqn. (3.1) consists of a component parallel to the sample surface, \( \mathbf{A}_\parallel \), and a component perpendicular to the sample surface, \( \mathbf{A}_\perp \) (see Fig. 3.3). All components of the polarisation vector must be taken into
account as possible origins for the vanishing SFS band intensity in the \(\Gamma Y\) direction. In the special case of normal incidence, \(A\) is completely parallel to the sample surface plane (\(A \perp = 0\)).

Fig. 3.3 shows the actual measurement geometry. The incoming light, sample normal and detected electrons are all lie in the mirror plane (shown in green), but the incoming light is not necessarily at normal incidence. In the case of \(s\)-polarised light, \(A \perp = 0\). In the case of \(p\)-polarised light, however, \(A \parallel\) is still in the same plane as the incoming light, sample normal and detected electrons, but now \(A \perp \neq 0\).

\(A \perp\) does not affect the parity of the \(A \cdot p\) term since it is not directly involved in the selection rule. However, its value affects the absolute value of the matrix element. Therefore we would like to check whether the suppression of the SB states in the \(\Gamma Y\) direction when using \(p\)-polarised light is an artifact due to there being a special value of \(A \perp\) which conspires to make the total matrix element indistinguishable from zero.

One method to test this is to vary the \(A \perp\) component by varying the incidence angle of the synchrotron radiation. In this manner, one can alter the angle between the Poynting vector of the incoming radiation and the surface normal \(\hat{n}\) and provided the detector is still situated at an equivalent point in the repeated zone scheme, one is still able to probe equivalent electronic states, but with a different \(A \perp\) contribution.

Performing the measurement at cut III in Fig. 3.5(a), will meet our conditions \textit{i.e.}: both the MB and SB are present, the symmetry selection rules are the same.
as those for cut I, but the value of $A_\perp$ is changed as the incidence angle is different. Fig. 3.8 shows the EDMs measured with 100 eV photons at cut III in Fig. 3.5(a) with $\sigma^+$, $s$, and $p$-polarisation, respectively. From closer inspection of Fig. 3.8 one can attribute A and C to the SB and MB respectively, while B and D are the first order MB DRs. The result of this check is identical to the observation made from Fig. 3.5(c) - 3.5(e): on one hand a complete suppression of the SB states using $s$-polarised light and the other hand the complete suppression of MB states using $p$-polarised light. In summary, the complete suppression of the SB for $s$-polarised light in the $\Gamma Y$ direction cannot be ascribed to a matrix element effect connected with the out-of-plane component of $A$.

### 3.4. Results from Pb-doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$: the incommensurate modulation dependence check

Up until now, all the indications point strongly to a situation in which the initial state mirror symmetry of both the MB and SB are odd with respect to the $\Gamma X$ M2 mirror plane and yet the SB states have even symmetry in the mirror plane parallel to $\Gamma Y$. Before we are completely satisfied that we are dealing with an initial state effect - *i.e.* an effect of relevance also for the non-ARPES part of the HTSC community - we would like to perform a final check as to whether the details of the structure of the BiO planes play a role in the observed behavior. Seeing as the CuO$_2$ plane photoelectrons will always have to travel through at
Figure 3.10: EDM’s measured with $h\nu = 100$ eV at cut I in Fig. 3.5(a) with $\sigma^+$ (a), $s$ (b), and $p$-polarisation (c), respectively. The sample (Pb,Bi)2212 with an intermediate level of Pb-doping thus leading to an incommensurate modulation of the (Pb,Bi)O planes of wavelength $9b$. The labels (1) and (3) refer to MB DRs, (2) MB and (4) SFS band.

least the outermost BiO plane, it is wise to investigate the SB in crystals in which the BiO plane structure has been extensively modified by partial substitution of Pb for Bi.

Since the presence of the diffraction replicas (DRs) can interfere with the interpretation of the data, we checked the validity of the surprising result in the $\Gamma Y$ direction for lead-doped Bi2212 samples with two different levels of Pb doping. It is known that the level of Pb doping is related to different wavelengths of the incommensurate modulation.

Fig. 3.9(a) shows a schematic drawing of the modulation-free Bi2212 FS. It has become much more simple now since the diffraction replicas (DRs) have been removed by doping the pristine crystals with 20% Pb ($\text{Pb}_{0.4}\text{Bi}_{1.6}\text{Sr}_2\text{CaCu}_2\text{O}_8$). The main FS, consisting of barrels centered around the corner points $X$ and $Y$ of the tetragonal BZ, are shown as solid red lines. The shadow FS is shown as a blue line and are centered around the $\Gamma$ and equivalent points.

Figures 3.9(b)-3.9(d) show the results for the $\Gamma Y$ direction for a modulation-free sample. Using $\sigma^+$-polarised light, one observes both the MB and SB (see Fig. 3.9(b)). For $p$-polarised radiation, only the SB is visible, whereas for $s$-polarisation, only the main band is apparent. Again this would be fully consistent with odd(even) symmetry for the main(shadow) band along $\Gamma Y$, also in fully modulation-free (Pb,Bi)-2212.

As one can see in Fig. 3.10, if we reduce the level of Pb-doping from 20% to ca 10%, the incommensurate modulation returns, but this time with a real-space period of almost twice that of the pristine Bi2212 case. Nevertheless, even with
a modulation of $9.09\text{b}$ corresponding to $q \approx 0.11\text{b}^*$, the symmetry behaviour of main and shadow bands along $\Gamma Y$ remains identical. The results from this sample clearly show that the SB features are suppressed by using $s$-polarised light and that the MB feature is suppressed upon use of $p$-polarised light. As is always the case, both the SB and MB features are visible with the use of $\sigma^+$ polarised light.

This dataset shows that the wavelength of the incommensurate modulation does not affect the SFS band features and in particular has no effect on the parity of the MB and SFS states in the $\Gamma Y$ direction.

### 3.5. Discussion

Summarising the experimental situation, the surprising result regarding the symmetry properties of the electronic states of Bi-based cuprates in the $\Gamma Y$ direction is robust regardless of photon energy, incident angle and incommensurate modulation of the BiO planes. This shows that the SB is an initial state property of both pristine and lead-doped Bi$_{2212}$, that the character of the SB is even with respect to $\Gamma Y$ direction while it is odd with respect to $\Gamma X$ mirror plane.

The swap of the initial state symmetry of SB with respect to two mirror planes in the basal plane of the 2D BZ which are orthogonal to each other is indeed the key to the origin of the SFS in these cuprates. The mechanism involving multiple scattering in the photoemission final state [102] can now be ruled out, since it is clear that SFS is an initial state effect. Thus the mechanism involving a structural origin becomes a natural candidate. Within this scenario, reduced symmetry coupled to the presence of an orthorhombic structure leads to a back-folding of the MB states into a smaller, orthorhombic BZ. There is also experimental evidence for such a structural modification from LEED [102], as well as x-ray and neutron diffraction data from pristine and lead-doped Bi$_{2212}$ [108, 109].

How can we reconcile the parity swap of the SFS initial state with the structural data from LEED, and can this lead to the explanation of the origin of the SFS? It is known from X-ray diffraction that the Bi atom sub-lattice is, in fact, comprised of two sub-lattices, shifted slightly with respect to one another (0.1 Å in the crystallographic x direction). The shift is sketched in Fig. 3.11(b). In fact, this distortion, which gives the orthorhombic unit cell drawn in blue in Fig. 3.11(b) is present both the surface and in the bulk of the crystal. These displacement are the largest in the BiO planes but are felt by all layers, including
Figure 3.11: (a) Schematic drawing of an idealised orthorhombic Bi2212 unit cell. The tetragonal unit cell shown as the transparent red box. Only a quarter of the unit cell in the $c$ direction is shown. (b) Sketch of the shift of one Bi sub-lattice along the x-axis. $m \parallel xz$ and $g \parallel xz$ mark the mirror and glide-mirror plane, respectively. (c) LEED pattern of (Bi,Pb)2212, showing systematic extinctions (indicated with arrows), indexing has been carried out in the orthorhombic cell.

The CuO$_2$ layers i.e. the copper atoms are also slightly displaced. Our LEED data shown in Fig. 3.11(c) were the first to exhibit the systematic extinctions at $[hk]$ LEED spots where $h = \text{odd}$ and $k = 0$. Note that LEED measures mainly the topmost layer of Bi2212 compound, namely the BiO layer. The spots in Fig. 3.11(c) are indexed within the orthorhombic unit cells.

The systematic extinctions in LEED indicate that there is only a single nodal mirror plane running parallel to the $xz$ plane and that the $yz$ plane is rather a glide-mirror plane which transforms the object through the reflection operation following by a shift with the translational operation by half of the primitive lattice vector parallel to reflection plane [110, 111] (see Fig. 3.11(b)). For 10% Pb-doped Bi2212, the extinction line was seen in LEED to run parallel to the spot elongation direction as seen in LEED, and therefore also the glide-mirror plane is running parallel to the b direction. This structural information obtained from LEED is consistent with the result from bulk probes like XRD [108] or neutron diffraction [109], and confirms that the glide-mirror plane and the incommensurate modulation are not the same thing, but are independent, in-
3.5.1. Toy model: closing the loop

In order to make a clear connection between the presence of a glide-mirror plane such as indicated with the red dashed line in Fig. 3.11(b) and the even SFS band parity in the $\Gamma Y$ direction only, we introduce here a toy model. This describes the SFS state as if it were the difference between the distorted orthorhombic system and the non-displaced tetragonal system.

This toy model is illustrated in Fig. 3.12 using a pure $d_{x^2-y^2}$ wave function. Note that the replacement of the Zhang-Rice singlet (ZRS) states by a simple $d_{x^2-y^2}$ wave function in the toy model is justified since the $d_{x^2-y^2}$ possesses the correct symmetry, and mathematically it can be shown that the subtraction of any odd wave function from a shifted replica will give an even wave function.

In this context we define the tetragonal system as containing two identical (Bi or) Cu atoms per cell, yielding two identical bands and therefore one can regard it as a non-primitive unit cell. The nodal states of this undistorted system have odd parity with respect to reflection in the $xz$ and $yz$ planes in real space and therefore for the $\Gamma X$ and $\Gamma Y$ directions in $k$-space (see Fig. 3.12 for clarity). When the displacement is introduced, the adopted unit cell becomes the primitive unit cell. In $k$-space, this doubling of the unit cell with respect to the tetragonal system gives rise to a smaller Brillouin zone and back folding of the main band into the smaller (orthorhombic) zone. This would explain the
existence of the SFS as a back folded version of the MB FS, but would not yet offer an explanation for the anomalous symmetry properties of the SFS.

The orthorhombic displacement here means that the central Bi atom in Fig. 3.11(b) shifts from the red position to the blue position. In this situation a glide mirror plane is created parallel to the yz plane. The outcome of the toy model description is helpful at this stage. The left-most panel of Fig. 3.12 shows the “difference wave function”, and it can easily be seen that this SB wave function is odd with respect to the ΓX mirror plane, yet even with respect to the glide mirror plane, which captures the essence of the observed polarisation-dependent ARPES data.

If \( \phi(x, y) \) and \( D(x) \) denote the undistorted wave function and the distortion function in the \( x \) direction, respectively, then we can define the distorted wave function as \( \phi_D(x, y) = D(x) \phi(x, y) \). An undistorted wave function \( \phi(x, y) \) which is purely odd with respect to the \( xz \) mirror plane (since \( \phi(x, y) = -\phi(x, -y) \)), will stay odd when transformed into \( D(x) \phi(x, y) \), because \( D(x) \phi(x, y) = -D(x) \phi(x, -y) \). In the \( y \) direction on the other hand, the parity of the wave function is not necessarily conserved in the presence of displacements. The absence of a mirror plane parallel to the \( yz \) plane allows \( D(x) \) to be not purely even and odd. The same is implied for the \( D(x) \phi(x, y) \).

If the distortion is small then we can write, in the first approximation, that \( D(x) = (1 + xD'(0) + \ldots) \). The SB wavefunction which is generated from the difference between the undistorted and distorted wavefunction can be approximated as follows:

\[
\phi_{SB}(x, y) = \phi_D(x, y) - \phi(x, y) = [\phi(x, y) + xD'(0)\phi(x, y)] - \phi(x, y) = xD'(0)\phi(x, y),
\]

(3.2)

It is clear that the product between \( x \) and \( \phi(x, y) \) will be even since both functions have odd parity and hence this behavior resembles the polarisation dependence seen in the ARPES data. We note that a second order term (or other even numbered terms) in the perturbation would not lead to a parity swap: only the odd order terms can do this.
Figure 3.13: (a,b) *ab initio* photon energy dependent calculation along ΓX with s and p-polarisation, respectively. (c,d) Photoemission calculation for ΓY with s and p-polarisation, respectively. (e,f) ARPES Fermi surfaces maps calculated for 32.7 eV photons with the polarization vector (arrow) aligned along the x (e) and y-axes (f), respectively. The dotted boxes indicate the relevant polarisation and the black "1"s and "0"s mark the presence and suppression of the MB while the red "1"s and "0"s mark the presence and suppression of the SFS band. From ref. [51].
3.5.2. Support from DFT calculations

The parity swap of the shadow band initial state for $k$ along the tetragonal $\Gamma Y$ direction has also subsequently been confirmed by Density Functional Theory (DFT)-based calculations accompanied by a group theoretical analysis of the relevant symmetries [111]. In this calculation, which is based on a one-step photoemission code [111, 112], it is shown that the structural modification in Bi2212 from tetragonal to orthorhombic symmetry changes the selection rules in ARPES along the high symmetry lines in the $\Gamma Y$ direction. The glide-mirror plane produced by the orthorhombic displacements will leave $k_{\parallel}$ unchanged. The glide-mirror operation yields two different irreducible representations namely, $\Lambda$ and $\Lambda'$ [111].

Photoemission selection rules due to the presence of a glide-mirror plane have been considered by Pescia et al. [113]. In this context, the dipole matrix element $\langle \phi_f^{(\mu)} | (A \cdot p)^{\alpha} | \phi_i^{(\nu)} \rangle$ will vanish if the space group representation of the final state does not appear in the product of the space group representation of the initial state and the operator describing the interaction of the radiation with the solid. The superscripts $\mu$, $\alpha$, and $\nu$ denote the index of space group representation related to the final state, the dipole operator and the initial state, respectively. The space group representation of the final state belongs to $\Lambda$ in the 1st, 3rd, 5th,... repeated Brillouin zone (BZ) and belongs to $\Lambda'$ in the 2nd, 4th, 6th,... BZ. Since a non-vanishing dipole matrix element can only be obtained if the space group representation of the final state appears in the product between the space group of the initial state and the dipole operator, then, as a consequence, the initial state must belong to the same space group representation as the final state if the light polarisation is parallel ($p$-polarised or even) to the glide mirror plane and to the other representation if the light polarisation is perpendicular ($s$-polarised or odd) to the glide mirror plane [111].

The input of the calculation presented in Ref. [111] is modulation-free Bi2212 in the average structure from Ref. [109]. Fig. 3.13(e) and Fig. 3.13(f) show the result of this calculation for a Fermi surface map with polarisation vector along $x$ and $y$, respectively. It is clear that the calculation displays the expected behavior i.e.: the MB is suppressed along the $\Gamma Y$ direction for $p$-polarised light and is present for $s$-polarised light. On the contrary, the SFS features are suppressed along the $\Gamma Y$ direction for $s$-polarised light and are present for $p$-polarised light. In the $\Gamma X$ direction, the SFS and MB features exhibit the same behavior, both being visible only for $s$-polarised radiation.
Figure 3.14: (a) (color online): EDM ($h\nu = 100$ eV, recorded with $\sigma^+$ polarisation) from modulation-free (Bi,Pb)-2212 measured at location I in fig.3.9(a) (along $\Gamma Y$). (a) The full width at half maximum (FWHM) of the main band (MB) and shadow band (SB). (b) The dispersion of the MB and SB (c) The relative intensity ratio between SB and MB

Furthermore, the absence of the calculated SFS features for $s$-polarised light and the presence of the SFS features for $p$-polarised light along $\Gamma Y$ is independent of photon energy in the calculation as one can see in Figs. 3.13(a) - 3.13(d), and is also in full agreement with the photon energy dependent data presented in this chapter.

3.5.3. Is antiferromagnetism still involved?

Before we conclude that we have solved the SFS band question completely, it would be wise to see if the other candidate model, namely the antiferromagnetic (AFM) scenario, can indeed be excluded. This is, in essence, a check that the conclusions reached in Ref. [106] can be confirmed. In order to realise this, we performed two different checks. Firstly, we examined the ARPES data recorded with photon energy 100 eV and $\sigma^+$ polarised light, as seen in Fig. 3.14(a), in a similar way as carried out by Koitzsch et al. [106]. Secondly, the photoemission simulations were carried out by the Tampere group extended such that the consequences of an AFM-induced shadow band could be investigated.

The consequences of the AFM scenario are expected to show up clearly in the ARPES experiments and be manifest in the scattering rate of the quasiparticles within the MB and the shadow band (SB). The scattering from spin fluctuations
will give the SB a very different self energy $\Sigma$ than the MB. This will be observable in an ARPES experiment as a different dispersion and MDC width of the MB and SB, and a binding energy dependent intensity ratio of both bands. Fig. 3.14(a) displays an EDM obtained from cut I in Fig. 3.9(a) in modulation-free (Pb,Bi)$_2$2212 measured with $\sigma^+$ polarisation, with the MB on the left and the SB on the right. Panels (b) to (d) show the widths, dispersions and intensity ratio of the two bands, respectively, obtained by fitting Lorentzian line-shapes to the MDCs. To make a direct visual comparison possible, in Figs. 3.14(b) and 3.14(c) the SB dispersion has been mirrored around a horizontal line, and the SFB $k_F$ is adjusted to coincide with the MB $k_F$. The dispersions and widths of main and shadow bands are identical within the experimental error bars, and the intensity ratio is constant, all contrary to the predictions of the AFM scenario. These results confirm the findings of Koitzsch et al. [106], even though these data were recorded from crystals grown in a different manner and measured at different beamlines using different instrumentation.

In the following, the result of the employment of an artificial crystal structure for Bi2212 in order to simulate the AFM scenario are related. To avoid the presence of a shadow band with a pure structural origin (i.e. unrelated to AFM fluctuations), in the simulations all atoms reside at their ideal tetragonal positions. The true primitive unit cell is represented by the transparent red box in Fig. 3.11(a). However, a non-primitive unit cell is used that is twice the size with respect to the primitive one. The shadow band is then obtained in the calculations by introducing a difference in potential between two sub-lattices of copper atoms. The potential of one of the two subsets of Cu atoms has been raised by 0.8 eV, and the other lowered by the same amount, while the atoms themselves are not displaced. The inequivalence of the two Cu sites doubles the tetragonal unit cell, resulting in the presence of a SFS band. Since the Cu atoms remain at their original sites, the yz plane remains a regular structural mirror plane, and does not become a glide mirror plane. The artificial structure can be seen as representative for the AFM scenario: the different spins on the Cu sites are simulated in the calculation by the different potentials at the two subsets of Cu atoms.

Figs. 3.15(a) and 3.15(b) show the calculated $k_x$, $k_y$ maps of the $E_F$ spectral weight for the artificial structure representative for the AFM model. The polarisation vector is parallel to the x-axis in Fig. 3.15(a), and parallel to the y-axis in Fig. 3.15(b). In the highlighted regions, the polarization is indicated (linear
polarised, $s$ or $p$), together with a white ‘1’ or ‘0’, indicating the presence or absence of the main band, while the red ‘1’ or ‘0’, indicates the presence or absence of the shadow Fermi surface (SFS). A first comment is that, in order to generate significant shadow band intensity, a potential difference of $\pm 0.8$ eV has been introduced on each Cu sub-lattice. It is clear that this leads to significant alterations in the apparent FS shape, although the MB and SB features are still recognisable. The results show that the polarisation dependence of the SFS band follows the MB in both the $\Gamma X$ and $\Gamma Y$ directions, i.e., the SFS band is odd in both quadrants, just like the MB.

Thus, not only does the lack of difference in dispersion but also MDC width or an energy dependence of the SB/MB intensity ratio argue, as did the authors of Ref [106], against an AFM origin of the SFS, the DFT-based one-step photoemission results from the Tampere group presented here also provide compelling evidence that an AFM-like state would be unable to generate the parity flip seen for the SFS states along the $\Gamma Y$ direction in $k$-space.

Figure 3.15: Calculated Bi2212 ARPES Fermi surface maps for an artificial structure representative for the antiferromagnetic (AFM) scenario. (a) The linear polarisation is along the x axis. (b) The linear polarisation is along the y-axis. As the potential changes adopted in the calculation to mimic - at least in terms of symmetry - our AFM system lead to large distortions of the FS maps compared to those shown in Fig. 3.13(e) and 3.13(f), the regions of particular interest (around the nodal direction) have been emphasised. The white ‘1’s and ‘0’s represent the presence and absence of the main features while the red ‘1’ and ‘0’ denote the presence and absence of the shadow features. Figure provided courtesy of our theorist collaborators, Lindroos et al. (University of Tampere).
3.6. Conclusion

Based on the results described in Secs. 3.3, 3.4, and 3.5 we have argued that the SFS states have a structural origin, being due to orthorhombic displacements from tetragonal symmetry. The displacement yields a glide mirror plane in the $\Gamma Y$ direction which causes a parity swap of the initial states of the SFS band for this direction from odd to even. These orthorhombic displacements double the unit cell and the SFS band is a natural consequence of band back-folding of the MB.

Along with our LEED data and the results of DFT-based one step photoemission calculations, the orthorhombic displacements and therefore the SFS band are also found to have no relationship with the incommensurate modulation. The data presented here have solved a puzzle regarding the electronic states of the Bi-based family of HTSC that was existed for more than 12 years.

Finally we remark that as a consequence of our proof that the SFS is of bulk structural origin, we should - formally change our paradigm for 2D Brillouin zone from tetragonal to orthorhombic and thus depart from the simple picture of the $(\pi, \pi)$-centered "barrels" as the basal plane projection of the FS’s of the Bi-based HTSC. The new FS is indicated with light grey shading in Fig. 3.16.