Effective band structure of Ru-doped BaFe$_2$As$_2$

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Abstract. The use of lattice cells in real space that are arbitrarily larger than the primitive one, is nowadays more and more often required by ab initio calculations to study disorder, vacancy or doping effects in real materials. This leads, however, to complex band structures which are hard to interpret. Therefore an unfolding procedure is sought for in order to obtain useful data, directly comparable with experimental results, such as angle-resolved photoemission spectroscopy measurements.

Here, we present an extension of the unfolding procedure recently implemented in the VASP code, which includes a projection scheme that leads to a full reconstruction of the primitive space. As a test case, we apply this newly implemented scheme to the Ru-doped BaFe$_2$As$_2$ superconducting compound. The results provide a clear description of the effective electronic band structure in the conventional Brillouin zone, highlighting the crucial role played by doping in this compound.

1 Introduction

The ab initio computational studies of systems with a broken lattice periodicity can be made easier using unfolding techniques. In fact, the unfolding is a procedure that enables to manage, and to easily interpret, the states folded into the momentum space of any supercell.

As a matter of fact, simulations often use supercells, rather than primitive cells, in order to handle the loss of translation symmetry of the lattice occurring in real systems. The break of periodicity can in fact arise every time one is dealing with some sort of disorder, such as systems with impurities (vacancies, dislocations, substitutions) or different spin configurations, as well as in case of doped materials and alloys. In all these cases, the use of a supercell allows to model random and disordered configurations by considering a periodic system having a larger unit cell volume.

However, using a supercell in real space implies a contraction of the corresponding unit cell in reciprocal space (i.e. the Brillouin zone), and hence the appearance of folded states. Theories of unfolding methods appeared in recent times and have already been computationally implemented and used for realistic applications [1–4]. In this work, we complement the unfolding procedure implemented in the VASP code [3,5,6] with a projection scheme for any vector in the primitive and supercell reciprocal spaces and apply our implementation to the iron based superconductor BaFe$_2$(1–$x$)Ru$_2x$As$_2$.

As well known [7] the pure iron-based pnictide families are not superconductors; however, substitution of other transition metals on Fe sites is able to drive these compounds into a
superconducting state. In order to single out the mechanisms leading to superconductivity, it is therefore very important to study and understand the effects of the dopant on the electronic states of the pure compound. In these cases unfolding procedures are expected to be a convenient and powerful tool. In the following we describe the methodology (section 2) and then discuss its application to the BaFe$_2$(1−x)Ru$_{22}$As$_2$ test case (section 3). Finally we will draw our conclusions.

2 The unfolding method

Our goal is to describe the energy band $E(K)$ obtained in the $K$-vector reciprocal space related to the supercell in term of the $k$-vector reciprocal space linked to the primitive cell. The result is a so called effective band structure (EBS) $E(k)$.

The connection between the primitive and supercell spaces is contained in the transformation matrix $M$ (invertible and with integer elements $m_{ij} \in \mathbb{Z}$) defined by the following equation

$$A = M \mathbf{a}$$

or, more explicitly,

$$
\begin{pmatrix}
A_1 \\
A_2 \\
A_3
\end{pmatrix} =
\begin{pmatrix}
m_{11} & m_{12} & m_{13} \\
m_{21} & m_{22} & m_{23} \\
m_{31} & m_{32} & m_{33}
\end{pmatrix}
\begin{pmatrix}
a_1 \\
a_2 \\
a_3
\end{pmatrix}
$$

(1)

where $A$ and $a$ are the two sets of basis lattice vectors $A_i$ and $a_i$ (with $i = 1, 2, 3$) related to the super and primitive cell, respectively.

The unit cell vectors of the reciprocal space $B_i$ and $b_i$ are related by an analogous equation:

$$B = (M^{-1})^T b.$$  

(2)

It should be underlined that in the original formulation of the EBS method [2] the matrix $B$ is given instead by $B = M^{-1} b$. However, it can be easily proven, using the well known definition of reciprocal vector in terms of vectorial products of lattice vectors, that the latter equation is not valid for supercells associated with a non-symmetric transformation matrix $M$. In this case and in general, Eq. 2, that includes the transpose operation, holds instead.

A wave vector belonging to the $k$-space is said to be folded into a wave vector of the $K$-space, if there exists a reciprocal lattice vector $G_n$ such that $K = k - G_n$. Likewise, a $K$-vector unfolds to $N$ $k_i$-vectors defined by the following equation: $k_i = K + G_i$ with $i = 1, \ldots, N$, where $N$ is given by the determinant of the transformation matrix $M$, representing the ratio of the two cells volumes, and $G_i$ are the reciprocal lattice vectors obtained by linear combinations of the unit cell vector of the reciprocal space. Clearly, for a given $k$-vector, there exists only a unique $(K, G_n)$ pair fulfilling the previous relation, meaning that each $k$-vector is folded into a single $K$-vector. On the other hand, a $K$-vector unfolds into $N$ wave vector of the $k$-space.

Any eigenvector $|Km\rangle$ of the supercell can then be written in term of eigenvectors $|kn\rangle$ of the primitive cell, since they form a complete basis set, where $m$ and $n$ stand for band indices. The probability $P_{Km}(k_i)$ relating the contribution of the $|kn\rangle$ states to a $|Km\rangle$ state is given by the following equation

$$P_{Km}(k_i) = \sum_n \langle Km|kn\rangle^2,$$

(3)

that defines also a spectral function $A(k_i, E)$:

$$A(k_i, E) = \sum_m P_{Km}(k_i) \delta(E_m - E) = \sum_m \sum_n \langle Km|kn\rangle^2 \delta(E_m - E).$$

(4)

The quantity $P_{Km}(k_i)$ represents the amount of Bloch character of $|kn\rangle$ preserved in $|Km\rangle$ and is fundamental to calculate the effective band structure, that is the band structure $E(k)$ of the primitive cell calculated starting from the dispersion relation $E(K)$ of the supercell. In
fact, the Bloch character of each $|Km⟩$ state allows to unfold these states into the $k$-space of the primitive cell, since the eigenvalue $E(K)$ related to a $|Km⟩$ eigenstate is also related to the $|kn⟩$ states with a probability $P_{Km}(k_i)$ different from zero. If the supercell is a mere spatial repetition of identical primitive cells (i.e. same lattice vectors and same atomic basis), then there is only one $|kn⟩$ state contributing to $P_{Km}(k_i)$ for each $|Km⟩$ state. All other contributions to $P_{Km}(k_i)$ will vanish. In this case, the effective band structure calculated starting from the eigenvalues of a supercell is an exact reconstruction of the band structure of the primitive cell. Due to this perfect equivalence, there is no need to use the unfolding procedure.

On the other hand, the unfolding method becomes useful when the supercell is constructed with unit cells having the same lattice parameters (in order to maintain the relation $m_{ij} \in \mathbb{Z}$ valid), but with different atomic basis. In this situation, many different $|kn⟩$ will contribute to $P_{Km}(k_i)$ for a single $|Km⟩$. This is due to the fact that the $k$-vectors are not good quantum quantities anymore, since translational symmetry has been broken. In fact, translational symmetry in this case survives only in the $K$-space related to the supercell. The application of the unfolding scheme in this case leads to an effective band structure with broadened bands.

In the plane waves basis set used by the VASP code the Bloch character $P_{Km}(k)$ can be conveniently calculated starting from eigenvectors belonging to the supercell only, thus avoiding the calculation of the eigenvectors of the primitive cell, as shown in the following equation [2]:

$$P_{Km}(k) = \sum_{\{g\}} |C_{m,g+k}|^2 ,$$

where $\{g\}$ is the set of reciprocal vectors of the primitive cell and $C_{m,g+k}$ is the coefficient for the $|Km⟩$ eigenstate in a plane wave basis set expansion. The Bloch character coefficients $P_{Km}(k)$ are provided for the full set of $N$ primitive $k$-points $k_i = K + G_i$. However, since the analysis of the band structure is usually restricted to a limited set of primitive $k$-points, it would be useful to restrict the EBS scheme to such a set. Starting from Eqs. 1 and 2, we have implemented an efficient projection scheme of the $K$-points of the supercell into a limited set of $k$-points in the primitive one, freely chosen by the user. The folded $K$-points in the supercell are calculated automatically and then used internally in the code to calculate eigenvalues and Bloch character coefficients to obtain band structure plots after self-consistency is achieved, as usually done in ordinary band structure calculations.

Therefore, it is possible to obtain an effective band structure starting from a given supercell, the lattice vectors of a primitive cell and a chosen set of $k$ points, simplifying the complexity of the unfolding procedure.

3 Test case: BaFe$_{2}(1-x)$Ru$_{2x}$As$_2$

We have tested our implementation on the BaFe$_{2}(1-x)$Ru$_{2x}$As$_2$ compound. As mentioned before, transition metal doping in these compounds is able to induce superconductivity at certain optimal, usually small, concentrations [8, 9]. As the dopant concentration is increased, the impurity scattering brought about the dopant atoms, usually destroys the superconducting state. Ru doped BaFe$_2$As$_2$ compounds are a rather peculiar case since they exhibit a persistent resilience of superconductivity up to quite large concentrations of disordered impurities (about 40% Ru-substitution [10–13]). Then, at larger concentrations, the critical temperature for the onset of the superconducting state is seen to progressively decrease.

3.1 Computational setup

The calculations have been performed using the VASP [5,6] package and projected augmented-wave (PAW) [14] pseudopotentials, within the generalized gradient approximation [15] (GGA)
to the density functional theory, since this approximation is seen to better reproduce the main structural features of the Fe-based pnictides [16]. For the iron atoms, inclusion of \( p \)-electrons in the valence shell has been found to be relevant for a more accurate description of the system.

The isovalent substitution of Ru-atoms on Fe-sites was investigated using a supercell containing 16 Fe/Ru atoms, 8\( \times \) larger than the 2-Fe primitive cell of Fig. 1(a), with a

![Figure 1](image1.png)

**Figure 1.** \( \text{BaFe}_2\text{As}_2 \) structure: fig. 1(a) and 1(b) represent the primitive cell and the supercell respectively used in the current work (Ba-atoms are represented in green color, Fe in brown, As in blue). Bands are unfolded on the Brillouin zone relative to the primitive cell shown in fig. 1(c).

![Figure 2](image2.png)

**Figure 2.** Effective band structure (gradient of yellow) compared with the primitive cell (blue). The intensity of the unfolded bands represents the Bloch character \( P_K(k) \) normalized with respect to the contributions belonging to all the \( k \)-points connected by a \( G \)-vector to the \( K \)-point of the supercell. In this case the supercell used is without any impurity (i.e. \( x = 0 \)). Since it contains no impurities, the Bloch character is either one or zero for every \( k \)-point.
transformation matrix \( M \) (see eq. 1) defined by the following relation:

\[
M = \begin{pmatrix}
0 & 2 & 2 \\
2 & 0 & 2 \\
1 & 1 & 0
\end{pmatrix}
\]

implying

\[
\begin{align*}
A_1 &= 2a_2 + 2a_3 \\
A_2 &= 2a_1 + 2a_3 \\
A_3 &= a_1 + a_2
\end{align*}
\]

(6)

We considered the primitive cell with experimental lattice parameters and let the internal atomic positions relax, following the \textit{ab initio} calculated forces, performing spin-polarized calculations. Self consistency and convergence of the relaxed internal structural parameters were reached within a variation for the total free energy of \(10^{-4}\) eV and \(10^{-3}\) eV respectively, using 500 eV as energy cutoff. Integration of the irreducible Brillouin zone was performed considering \(8 \times 8 \times 3\) grids within the Monkhorst and Pack scheme \[17\]. Band structure eigenvalues were calculated on a finer grid (40 points per line) in the Brillouin zone. Then, we obtained the EBS by unfolding the band structure into the 2-Fe primitive cell of Fig. 1 using the improved unfolding scheme described above.

3.2 Results

In order to perform the test, a small \((2 \times)\) supercell without any impurities \((x = 0)\) was built: the EBS of this pure supercell, being simply a spatial repetition of identical primitive cells, should give exactly the same eigenvalues as those obtained from an ordinary band structure calculation of the pure \(\text{BaFe}_2\text{As}_2\) primitive cell. Figure 2 shows the good agreement between the effective and ordinary band structure. Due to the perfect translational symmetry of the primitive cells

![Figure 2](image_url)

Figure 2. Energy with respect to the Fermi level (eV) for \(x = 0\).

![Figure 3](image_url)

Figure 3. Effective band structure of \(\text{BaFe}_{2(1-x)}\text{Ru}_x\text{As}_2\) compound with \(x = 0.5\). The intensity of the unfolded eigenvalues represents the Bloch character \(P_k(k_i)\).
building the supercell system the bands are sharply resolved, i.e. the Bloch character is equal to one or zero for each point in the band structure, with vanishing probability for intermediate values. In this case in fact, only a single eigenstate of the primitive cell will contribute to the eigenstate of the supercell reciprocal K-space.

The effect of Ru-dopant atoms on the BaFe$_{2(1-x)}$Ru$_{2x}$As$_2$ compound have been studied for several concentration levels. Here we provide a description of the difference between the undoped and the 50% doped compound, in order to highlight the effect of the Ru-substitution. The results shown in Fig. 3 for $x = 0.5$ Ru-concentration make evident that the Ru-Fe substitution, even if it is usually considered to be isovalent, deeply modifies the electronic structure at the Fermi level. In particular, the hole pockets around the Γ-point in the Brillouin zone, shrinks with respect to the pure case (shown in Fig. 2) as the Ru-concentration is increased. On the other hand, the electron pocket at the X corner of the zone remains unchanged. An other effect of the Ru substitution is a broadening of the band structure. However, the bands appear to be broadened only in a region far from the Fermi level. Only the already described lowering of some bands affects the states at the Fermi level.

4 Conclusions

We discussed an improved unfolding procedure to calculate the effective band structure of supercells. The unfolding method implemented within the VASP code and here improved, has been applied to the BaFe$_{2(1-x)}$Ru$_{2x}$As$_2$ compound. The unfolding technique allows us to study the changes of the band structure upon Ru-substitution by means of a direct comparison with the pure compound. We have shown that the isovalent Ru-substitution causes the shrinking of the hole pockets around the Γ-point of the primitive cell, in good agreement with previous calculations [4]. These changes lead to modifications of the Fermi surface topology that might affect the pair coupling mechanisms. This procedure is general and can be applied to any compounds. We plan to apply this methodology for a systematic study of the role of dopant atoms in the superconducting properties of iron based pnictides.

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