Fast Track Communication

Origin of structural and magnetic transitions in BaFe$_{2-x}$Ru$_x$As$_2$ materials

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Abstract

Using the experimentally measured temperature- and doping-dependent structural parameters on Ru-doped BaFe$_2$As$_2$, orbital-dependent reconstruction of the electronic structure across the magnetostructural transition is found, through first principles simulations. Below structural transition there exist two distinct Fe–Fe bond distances which modify the Fe–d$_{xy}$ orbital largely due to its planar spatial extension leading to Lifshitz transition, while the otherwise degenerate Fe–d$_{xz}$ and d$_{yz}$ orbitals become non-degenerate, giving rise to orbital order. The orbital order follows the temperature dependence of orthorhombocity and is also the cause of two distinct Fe–Fe bond distances. Doping-dependent Fermi surfaces show nearly equal expansion of both the electron and the hole-like Fermi surfaces, whereas the hole Fermi surface shrinks with increasing temperature and the electron Fermi surface expands comparatively slowly. The observed structural transition in this compound is electronic in origin, and occurs close to the Lifshitz transition, whereas the suppression of the concurrent magnetic transition is due to the loss of temperature dependent nesting of Fermi surface.

Keywords: electronic structure, Fermi surface: calculations and measurements, Fe-based superconducting materials

(Some figures may appear in colour only in the online journal)

Discovery of superconductivity in a plethora of Fe-based compounds has been significant to the history of superconductivity, as they bear a strong similarity to oxide superconductors, in terms of phase diagrams, but their properties are fundamentally different [1]. These differences include their superiorities in technological applicability, due to high critical current at high fields [2], over the other high-temperature superconductors; apart from various unconventional properties [3] like different fermiology, BCS characteristic ratio, jump in specific heat proportional to T$_c^2$, no oxygen isotope shift (but Fe), linear temperature dependence of spin susceptibility, scaling of spin resonance with T$_c$, structural and magnetic transition etc. While the mechanism of superconductivity in Fe-based materials is still unknown, several of the properties mentioned above are consistently observed. The whole family of Fe-based materials may be broadly classified into six categories e.g., 1111 (like LaOFeAs), 122 (like BaFe$_2$As$_2$), 111 (like LiFeAs), 11 (like FeSe), 122’ (A$_{Fe_{2-x}Se_2}$, A = K, Rb, Cs), and 21311 (Sr$_2$ScO$_3$FeP); among them in 122,11 materials structural and magnetic transitions occurring at the same temperature, whereas in 1111 and 122’ they occur at different temperatures [4–8]. Proximity of the superconducting phase to magnetic and structural transitions indicates a possible influence on the former by the latter [9–14]. The magnetic spin density wave (SDW) state appear due to an antiferromagnetic (AFM)-like arrangement of Fe spins and nesting of the Fermi surface; there is growing evidence that the structural transition also has an electronic origin [15].
Structurally, the building block of all families of Fe-based materials is Fe-pnictogen/chalcogen layers in which the pnictogens/chalcogens are slightly above or below the Fe-plane. There exists a definite correlation among structural lattice parameters like \( z_{AB} ( \text{anion height}) \), bond lengths (Fe–Fe and Fe–As), As–Fe–As bond angles, and superconducting transition temperature \( T_c \) in all families of Fe-based superconductors [16–18]. In particular, superconducting transition temperature \( (T_c) \) is very closely related to anion height from the Fe layer (directly related to \( z_{xz} \)). For most of the Fe-based families like 1111, 122, 111, and 11 the anion height as a function of \( T_c \) follows a universal trend in ambient pressure as well as under high pressure [16]. The relation between Fe–Fe and Fe–As bond distances and \( T_c \) is also available in the literature [18]. The bond angle of As–Fe–As is also related to \( T_c \) as the distortion of FeAs\(_4\) tetrahedron reduces \( T_c \) and maximum \( T_c \) is obtained when the FeAs\(_4\) tetrahedron is perfectly regular [17, 19]. All these structural parameters described above are very sensitive functions of temperature, doping etc. Any microscopic understanding of the origin of various temperature-dependent experimental observations (e.g., temperature-dependent angle resolved photo emission (ARPES) studies etc. [20]) calls for temperature-dependent first principles studies. However, first principles studies which evolve from solution of many body Schrödinger equation cannot account for such temperature-dependencies. On the other hand, density functional theory has failed to produce optimized structures reproducing experimental values of \( z_{AB} \) (even if one uses temperature-dependent basic lattice parameters \( a(T), b(T), c(T) \)), parameters which have been found to be extremely crucial in reproducing other experimentally observed structural parameters and associated physical properties [21–24]. Therefore, hybridization of experimental inputs of temperature/doping/pressure-dependent basic lattice parameters along with \( z_{AB} \) in density functional theory would be a state-of-the-art first principles approach for understanding experimental observations on Fe-based materials. For example, the temperature-dependent ARPES data by Dhaka et al. [20] could not be analyzed satisfactorily by themselves because of the absence of temperature-dependent crystallographic structural parameters (like \( z_{AB} \)).

In this paper, using temperature and doping-dependent lattice parameters \( a(x,T), b(x,T), c(x,T) \), and \( z_{AB}(x,T) \) obtained from Synchrotron radiation X-ray diffraction studies on Ru-doped BaFe\(_2\)As\(_2\) as inputs, we show that the results of first principles simulations reproduce experimentally observed ARPES data which have so far remained unexplained. In particular, we demonstrate through first principles simulations, that the temperature-dependent pnictide height \( (z_{AB}(T)) \) plays a very crucial role in structural and magnetic transition. Temperature dependencies of the electronic structure closely follow those of the \( z_{AB}(T) \) for \( x = 0.1 \) and are essential in explaining the temperature-dependent band shifts observed in ARPES studies. We further show, both experimentally and theoretically, that below the structural transition there exist two distinct Fe–Fe bond distances which modify the Fe-d\(_{xy}\) orbital largely due to its planar spatial extension leading to Lifshitz transition [25], whereas the Fe-d\(_{xz}\) and d\(_{yz}\) orbitals become non-degenerate, which were degenerate above the structural transition giving rise to orbital order. We establish that the orbital order follows the temperature dependence of the experimentally determined orthorhombicity, indicating electronic nature of the structural transition (see figure 1). On the other hand, the two distinct Fe–Fe bond distances (which would correspond to two different exchange couplings [26, 27]), are a consequence of complex orbital order and also mark the appearance of the magnetic ground state as evidenced by the temperature dependence of the net difference in the up and down spin electronic density of states at the Fermi level—resulting in a simultaneous electronic magneto-structural transition. Doping-dependent Fermi surfaces show nearly equal expansion of both the electron and hole-like Fermi surfaces up to 40% doping, whereas the hole Fermi surface shrinks with increasing temperature; the electron Fermi surface expands comparatively slowly. Therefore, the observed structural transition in this compound is electronic in origin, and occurs close to the Lifshitz transition, whereas the suppression of the concurrent magnetic transition is due to loss of temperature-dependent nesting of the Fermi surface. Furthermore, we show that by employing temperature- and doping-dependent basic lattice parameters \( a(T,x), b(T,x), c(T,x), \) and \( z_{AB}(T,x) \), a satisfactory explanation to the observed data by Dhaka et al. can be obtained. Claims made in the previous paragraph above are demonstrated in figures 1 to 4.

Temperature-dependent Rietveld quality data, particularly on \( z_{AB} \) of any of the Ba122 systems is rare. Recently, high-quality Rietveld data established a relationship among various structural lattice parameters like \( z_{AB} \), bond lengths (Fe–Fe and Fe–As), to the structural transition temperature in 5% Ru-doped BaFe\(_2\)As\(_2\) [22] material. Using temperature-dependent and doping-dependent experimental lattice parameters \( a(T,x), b(T,x), c(T,x), \) and \( z_{AB}(T,x) \) [22] as inputs in our first principles simulations, we obtained electronic band structure, density of states, Fermi surfaces as a function of temperature, as well as doping to explain the observed anomalies microscopically. Our first principles ab initio simulations of electronic structure calculations were performed employing the Material Studio 7.0 CASTEP package [28], which exploits the plane-wave pseudopotential method based on density functional theory (DFT). In all of our calculations the electronic exchange correlation was treated within the generalized gradient approximation (GGA) using Perdew-Burke-Enzerhof (PBE) functions [29]. Handling a small fraction of Ru substitution in place of Fe was accomplished by considering a virtual crystal approximation (VCA) based on the Mixture Atom Editor of the CASTEP program in Material Studio 7.0, as well as the super-cell approach. Spin polarized constrained optimization and single point energy calculations were performed using anti-ferromagnetic spin-stripe configuration [30] for the low temperature orthorhombic phase with space group symmetry Fm\( \bar{3} \)m (No.69) using ultrasoft pseudopotentials and plane wave basis set with energy cut off 400 eV and self consistent field (SCF) tolerance \( 10^{-6} \) eV/atom. The Brillouin zone was sampled in the \( \mathbf{k} \) space using Monkhorst-Pack scheme and grid size for the SCF calculation was \( 16 \times 16 \times 7 \). Non–spin-polarized and
Figure 1. Experimental temperature variation of (a) $z_{\text{As}}$, (b) Fe–As bond distance, (c) orthorhombicity $\delta$ of BaFe$_{1.9}$Ru$_{0.1}$As$_2$ from [22]. The orthorhombic distortion occurs rapidly after the high-temperature tetragonal phase transforms into the low-temperature orthorhombic phase around 125 K. Theoretically simulated thermal variations of (d) total density of state at the Fermi level, (e) difference of up and down electron density of states at the Fermi level, and (f) two distinct Fe–Fe bond distances in the second column. Thermal variations of density of states of Fe (g) up and (h) down electrons. (i) The total converged energy as a function of temperature also follows that of $z_{\text{As}}$, and the Fe–As and justifies the behavior of DOS. (j) Sum of the energies of the $d_{xz}$ at the $\Gamma$ and X points and the same for $d_{yz}$ as a function of temperature is the cause of two Fe–Fe-bond distances. (m) The orbital order as a function of temperature (see text for details). (k) Energies of the $d_{xy}$ band as a function of temperature at X and (n) $\Gamma$ points. (l) Partial density of states of As as a function of temperature. (o) Energies of $d_{xz}$ and $d_{yz}$ of Fe as a function of temperature at the X point.
spin-polarized calculations were performed for the high-
temperature tetragonal phase with space group symmetry
I4/mmm (No.139) using ultrasoft pseudopotentials; the plane
wave basis set was with the same energy cutoff and SCF
tolerance as above. The Brillouin zone was sampled in the k
space using Monkhorst-Pack scheme and grid size for the
SCF calculation was $16 \times 16 \times 5$.

In figure 1 there are three columns. In the first column,
experimentally observed structural parameters are presented
(except the fourth and fifth rows). In the second and third
columns, theoretically computed results are presented. It is
clear from figures 1(a) and (b) that both the $\varepsilon_{\text{As}}(T)$ and Fe–
As (T) follow nearly the same temperature variation;
structural transition is marked by the evolution of the
orthorhombicity parameter $\delta$, which occurs at exactly the
same temperature at which both $\varepsilon_{\text{As}}(T)$ and Fe–As (T) show
an anomalously peaked value. Values of $\varepsilon_{\text{As}}$ or Fe–As bond
lengths are nearly the same at very low and high tempera-
tures but show very rapid temperature variations between
80 and 125 K, indicating the structural change. Similar
temperature dependencies are seen in figures 1(d), (g), (h),
and (i), which represent, respectively, the sum total of
electronic density of states of up and down spins at the
Fermi level, partial DOS of Fe up spins, partial DOS of Fe
down spins, and the total ground state energy of the 5% Ru-
doped BaFe$_2$As$_2$ system obtained through DFT simulations.
(The same temperature dependence is followed by the As–p
orbitals, shown in figure 1(l).) This is also the same tem-
perature at which $\varepsilon_{\text{As}}$ or Fe–As show anomalies and below
where there exist two distinct Fe–Fe distances [22] (see
figures 1(c), (f), and (j)). In figure 1(e), a difference in the
DOS of up and down spins (scaled as $10^3$) as a function of
temperature is presented. This observation corresponds to
AFM transition because just above the AFM transition
$N_{\uparrow}(E_F) - N_{\downarrow}(E_F) \neq 0$, whereas it is zero inside the AFM
phase, clearly indicating the onset of AF magnetic transi-
tion. The same behavior is also found in the temperature
dependence of the calculated net magnetic moment of the
unit cell (not shown here). In figure 1(f), we show that there
are two distinct Fe–Fe bond distances exactly below the
magnetic and structural transition—the two distinct Fe–Fe
distances are quite robust and are observable even in the
case of non-magnetic calculations. Two distinct Fe–Fe bond
distances would correspond to two distinct exchange coupling
constants, a scenario observed earlier by Yildirim
[26]. Furthermore, an important noticeable feature in all the
temperature-dependent structural parameters (see
figures 1(a), (b), (c), and (i)) is that below $T \sim 80$ K, all the
parameters increase with a decrease in temperature to reach
values closer to room temperature; exactly the same beha-
vior is seen in the thermal behaviors of the density of states.
Therefore, since the modifications in the temperature-
dependent electronic density of states correlate with all the
structural lattice parameters, the associated structural tran-
sition is electronic in origin. We discuss this further below.

The figures on the lowest two rows of figure 1 are
obtained from detailed temperature-dependent electronic
band structure calculations, glimpses of which are shown in
figure 2. In figure 2, electronic band structures around $\Gamma$
(1st/3rd row) and X (2nd/4th row) points are presented for
different temperatures. One of the most important obser-
vations from the band structures around the $\Gamma$ point is that
the Fe–d$_{xy}$ orbital width increases with increasing tempera-
ture so much (which will cause modifications in its occupa-
tion) that at 120 K it crosses the Fermi level. The observa-
tion of the Fe–d$_{xy}$ level going below the Fermi level at
$T=90$ K, 50 K gives rise to the Lifshitz transition [31].
Such temperature-dependent modifications in the electronic
bands crossing the Fermi level, as well as enhancements in
the widths, are the source of orbital fluctuations. The tip of
the d$_{xy}$ band around the $\Gamma$ and X points are shown in figure 1
(k), (n) respectively which actually follows the temperature
dependencies of As–Fe–As angles. The tips of the d$_{xz}$
and d$_{yz}$ bands at the $\Gamma$X point are degenerate at $T=125$ K
becomes non-degenerate in the orthorhombic phase$^4$,
calling an orbital ordering between the orbitals (d$_{xz}$, d$_{yz}$)
and two Fe-Fe distances (see figure 1(j) and follow below).
Such non-degenerate d$_{xz}$ and d$_{yz}$ bands have recently been
observed experimentally [32]. We define orbital order as
$<O> = \sum_{\sigma} E_{d_{\sigma}}(i) - E_{d_{\sigma}}(i)$, which is presented [33] as
a function of a temperature in the first two figures of the
down row of figure 1(m). Needless to say, the temperature
dependence of the orbital order $<O>$ reproduces that of
the experimentally determined orthorhombicity ($\delta$, compare
figures (c) and (m)), indicating that orbital ordering is the
principal origin of the structural transition. The temperature
dependence of the tips of the d$_{xz}$ and d$_{yz}$ (shown in figure 2)
bands at X point, given by $E_{d_{xz}}$ and $E_{d_{yz}}$ respectively,
follow the same temperature dependence as that of the $\varepsilon_{\text{As}}$
(cf 1 (o)). The sum of the energies at the X and $\Gamma$ points
of the d$_{xz}$ and d$_{yz}$ bands respectively are presented in
figure 1(j), showing a temperature dependence similar to that
of the two distinct Fe–Fe distances shown in figure 1(f).
These remarkable results clearly show that the structural
transition dictated by $\delta$, two Fe–Fe distances, and anion
height $\varepsilon_{\text{As}}$ is orbital-driven. Experimentally observed tem-
perature dependencies of $\varepsilon_{\text{As}}$, Fe–As bond distance,
and orthorhombicity parameter $\delta$ are consequences of the
temperature-dependent modifications in the electronic
structure and vice versa. This naturally supports a nematic
scenario in Fe-based superconductors [15].

On the other hand, the feature that the tips of the d$_{xz}$
and d$_{yz}$ bands approach the Fermi level and that there is an
approximately 25 meV shift between the d$_{xz}(\Gamma)$ and d$_{yz}(\Gamma)$
downwards to the Fermi energy from 20 K to 125 K are
consistent with the ARPES studies of Dhaka et al. It should
further be noted that such temperature dependence was not
achieved when only thermal expansion of lattice parameters
was considered in their DFT simulations. Furthermore, the
widths of the d$_{xz}$ and d$_{yz}$ bands around the $\Gamma$ point (evaluated
along the $X$–$\Gamma$–$X$ path) decrease with increasing temperature,
wheras the same around the X point (evaluated along the $\Gamma$–
$X-\Gamma$ path) increases (comparatively) slowly. This causes the $d_{xz}$ and $d_{yz}$ bands to cross the Fermi level at a shorter $\Delta k$ around the $\Gamma$ point but at a somewhat larger $\Delta k$ around the $X$ point. This makes the hole Fermi surface around the $\Gamma$ point shrink, whereas that around the $X$ point expand a bit with temperature (see figure 3), causing a temperature dependent loss of Fermi surface nesting. This is the reason for the decrease in hole Fermi surface radius around the $Z$ point (also $\Gamma$ point) with increasing temperature. This naturally explains the momentum distribution curves obtained in ARPES studies [20]. Therefore, the orbital order that causes structural transition also causes damage to the FS nesting, suppressing SDW, and thus both are inter-coupled [34]. In figure 4, the fermiology of Ru-doped Ba122 systems is presented. Up to 40% (which is already in the tetragonal phase) Ru substitution, nesting of the Fermi surface remains intact—both the electron and hole Fermi surfaces expand equally. This feature is very much in agreement with the findings in the work done by Dhaka et al. [35].

We provide a microscopic origin of structural transition in BaFe$_{2-x}$Ru$_x$As$_2$. Using temperature-and doping-dependent lattice parameters on Ru-doped BaFe$_2$As$_2$, we show
through detailed first principles simulations that the electronic structure carries the ‘fingerprints’ of structural parameters like $z_{\text{As}}$, Fe–As bond distance and reproduces the experimentally observed angle resolved photo emission spectroscopy data that have so far remained unexplained. Below the structural transition an orbital order develops between the $d_{xz}$ and $d_{yz}$ orbitals of Fe. On the other hand, temperature-dependent modifications of the $d_{xz}$ and $d_{yz}$ bands cause loss of nesting, in turn causing suppression of spin density wave transition. Total band energies at high symmetric $\Gamma$ and $X$ points of the said bands give rise to an orbital order that follows the temperature dependence of the orthorhombicity parameter. Therefore, orbital fluctuations play a dominant role in the magneto-structural transition in Ru-doped BaFe$_2$As$_2$ systems. Ru substitutions (up to 40%) do not show the nature of charge carrier doping from Fermi surface evolution. The hole-like Fermi surface shrinks with increasing temperature but the electron Fermi surface expands comparatively slowly; this explains the momentum distribution curves observed in ARPES and the temperature-dependent loss of Fermi surface nesting. Finally, we demonstrated that the thermal variations of $z_{\text{As}}$ obtained from experiments, when used as inputs in first principles simulation studies, produce realistic theoretical results with respect to the electronic structure that is observed experimentally and perhaps should be used in all families of Fe-based materials in order to achieve better insight.

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