Photoemission studies of the near $E_F$ spectral weight shifts in FeSe$_{1-x}$Te$_x$ superconductor

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Abstract
Our valence band photoelectron spectroscopic studies show a temperature dependent spectral weight transfer near the Fermi level in the Fe-based superconductor FeSe$_{1-x}$Te$_x$. Using theoretical band structure calculations we have shown that the weight transfer is due to the temperature induced changes in the Fe(Se,Te)$_4$ tetrahedra. These structural changes lead to shifts in the electron occupancy from the $xz/yz$ and $x^2-y^2$ orbitals to the $3z^2-r^2$ orbitals indicating a temperature induced crossover from a metallic state to an Orbital Selective Mott (OSM) Phase. Our study presents an observation of a temperature induced crossover to a low temperature OSM phase in the family of Fe chalcogenides.

Keywords: UV photoemission spectroscopy, superconductor, electronic structure, pseudogap regime

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

1. Introduction

The unconventional superconductivity [1] in iron based compounds [2, 3] has attracted much attention due to its importance in elucidating a consolidated understanding of superconductivity in general. Unlike the cuprate High $T_c$ materials, superconductivity in these compounds involves some exotic interplay of structural and magnetic degrees of freedom. Among them, although Fe(Se,Te) is rather simple from a structural point of view, it shows a strong bearing of the spin fluctuations and structural and magnetic disorder on its superconducting properties. Despite a number of reports addressing many of these issues, the roles of electron–phonon coupling, spin density wave states, quasiparticles etc. are still under intense debate.

The structure of FeSe$_{1-x}$Te$_x$ compounds consists of a stacking of edge sharing Fe(Se,Te)$_4$ tetrahedra without any spacer layer in between [3]. The parent compound FeTe is a non superconductor and exhibits a monoclinic structure at low temperature. It also shows an antiferromagnetic spin density wave (SDW) transition at 70 K [4]. The other parent, FeSe is a superconductor with a $T_c$ of 8 K [5]. Substitution of Se at the Te site enhances the $T_c$ to a maximum of 15 K for $x = 0.5$ [3]. This enhancement is reported to be linked to the local structural symmetry breaking [6] and the degree of disorder caused by the smaller ionic radius of Se [3], which is counter intuitive as disorder is expected to reduce the superconducting transition temperature [7]. Furthermore, the electronic properties of these superconductors with their moderate electron correlations, are controlled mostly by the competing inter- and intra-orbital interactions near the $E_F$ region. It has been pointed out [8] that these interactions generate an Orbital Selective Mott Phase (OSMP) in which electrons in some orbitals are Mott localized, while others remain itinerant. Earlier, such an OSMP was identified in Ca$_{2-x}$Sr$_x$RuO$_4$ [9, 10]. Recently, a doping dependent OSMP was proposed to be present in Fe(Se,Te) by Craco et al and Aichhorn et al [11, 12] from a theoretical point of view.

Electron spectroscopic studies, particularly using ultra-violet photoelectron spectroscopy, have shown that the near $E_F$
Figure 1. (a) Structure of Fe(Se,Te)₄ tetrahedra showing the chalcogen height Z and angle α. (b) He I Valence band spectra measured at 300 K for FeSe₁₋ₓTeₓ (x = 1, 0.5, 0). The features are marked as A, B, C and D. (c) High resolution He I spectra measured at 300 K (black) and 77 K (red). Features A’ and A’’ are denoted by black bars. (d) Enlarged view of near E_F spectra showing the pseudogap. (e) High resolution He I spectra at 300 K. The inset shows the expanded view near the E_F.

Electronic states in the Fe(Se,Te) compositions are dominated by the Fe 3d and chalcogen p states [13, 14]. Changes in the Fe 3d–Se 4p/Te 5p correlation strength with doping or temperature lead to noticeable spectral weight shifts in the near E_F states which could be intimately related to the superconducting properties of these materials. Although some of the earlier studies [15–17] have reported such spectral weight shifts and identified thereby the formation of a pseudogap, their origins and nature are still not clear. Furthermore, the correlation between the formation of the pseudogap and disorder has not been addressed. This study shows that the temperature dependent normal state pseudogap is intimately related to the insulating behaviour originating from the multi-orbital correlation and the Hund’s coupling. Based on our theoretical calculations we have shown that the formation of such a pseudogap could be a signature of the temperature induced Orbital Selective Mott Transition (OSMT).

2. Experimental

Polycrystalline samples of FeSe₁₋ₓTeₓ (x = 1, 0.5, 0) were synthesized via a solid state reaction route described elsewhere [18]. The stoichiometric compositions of the samples studied using x-ray diffraction and resistivity measurements have been published earlier [19]. It should be noted that the samples contain no excess Fe and are of a single phase nature. Angle integrated ultraviolet photoemission measurements were performed by using an ultra high vacuum system equipped with a high intensity vacuum-ultraviolet source and a hemispherical electron energy analyser (SCIENTA R3000). At the He I (hν = 21.2 eV) line, the photon flux was of the
order of $10^{16}$ photons/s/steradian with a beam spot of 2 mm diameter. Fermi energies for all measurements were calibrated by using a freshly evaporated Ag film on a sample holder. The total energy resolution, estimated from the width of the Fermi edge, was about 27 meV for He I excitation. All of the photoemission measurements were performed inside the analysis chamber under a base vacuum of $\sim 5$ mbar and the spectra were taken within 1 hour, so as to avoid any surface degradation. All measurements were repeated many times to ensure the reproducibility of the spectra. For the temperature dependent measurements, the samples were cooled by pumping liquid nitrogen through the sample manipulator fitted with a cryostat. Sample temperatures were measured using a silicon diode sensor touching the bottom of the stainless steel sample plate. The low temperature photoemission measurements at 77 K were performed immediately after cleaning the sample surface.

In order to understand the observed changes in the near $E_F$ electronic structure we used TBLMTO–ASA [20] calculations employing scalar relativistic corrections including combined correction term and Langreth–Meih–Hu gradient corrected von Barth Hedin parametrized energy and potential. The experimental lattice parameters at 300 K were used in the calculations [19]. The correlation effects of the Fe–d orbitals were taken into account by using the LDA + $U$ formalism with J as 0.9 eV [12] and $U$ as 3.5 eV for FeTe and 4.0 eV for FeSe [21]. For the FeSe$_{0.5}$Te$_{0.5}$ $U$ was taken as 3.8 eV, a value intermediate between those of FeTe and FeSe.

3. Results and discussion

Figure 1(b) shows the valence band spectra of FeSe$_{1-x}$Te$_x$ ($x = 1, 0.5, 0$) samples taken at He I photon energy. The spectral features marked A and B, positioned at 0.5 eV and 2 eV respectively, originate from the Fe 3d states. Peak C at 4 eV is due to the hybridized Fe 3d–Se 4p/Te 5p states while D at 6 eV corresponds to Se 4p/Te 5p states. Our calculations are based on the TBLMTO–ASA (figure 2(a)) and also other calculations [21, 22] conform to these assignments. The sharp feature of A seen in the case of FeSe transforms into a broadened one for FeTe. Feature C gets broadened and shifts to a lower binding energy with increasing $x$. Furthermore, feature D also shifts to a lower binding energy with doping.

In order to see the finer changes in the near $E_F$ electronic structure we have taken a set of high resolution spectra of this order.
point in the following paragraph. Yokoya et al [14] have earlier shown that the feature A consists of two features, A’ and A” (see figure 1(c)). As we go from FeTe to FeSe, the energy separation between these two features keeps decreasing and the intensity of A” increases. Thus, the doublet structure in the case of FeTe transforms into a prominent peak with a weak shoulder in the case of FeSe. This could be associated with the changes in the tetragonal crystal structure of FeSe(Se,Te). Substitution of Se for Te in FeTe leads to an increase in the Se/Te–Fe–Se/Te bond angle (α shown in figure 1(a)). The angle α which is 95° in the case of FeTe, approaches the ideal tetrahedron value of 109.5° with Se doping [23]. The bond angle is determinant to the overlap between the iron and chalcogen orbitals, resulting in a stronger hybridization between the Fe 3d and the chalcogen p orbitals.

In figure 1(e) we plotted the valence band spectra from the three compositions taken at room temperature. As we can see, with an increase in the Se content from 0 to 1 the intensity of peak A increases. It can also be seen that, corresponding to this change in intensity, some of the electronic states at the $E_F$ become depleted and the spectral weight at the $E_F$ shifts to higher binding energy positions at A. Such a shift in spectral weight as a function of doping was observed earlier by Yokoya et al [14]. More importantly, the feature A shows an increase in its intensity as we go from 300 K to 77 K. This change is temperature induced. Although this increase is very small in the case of FeTe, substitution of half of the Te with Se results in a marked change. It should be noted that with a further increase in Se content this enhancement of the intensity of peak A becomes weaker, though still distinct. There is a depletion of states at the Fermi level associated with this increase in intensity. Furthermore, it can be seen that the area by which the A peak has increased does not match with the number of states depleted from the near $E_F$ position. This indicates that electrons from other orbitals also shift resulting in the increase in its intensity. It should be noted that depletion of these states from the near $E_F$ clearly indicates an opening up of a pseudogap as the temperature is lowered from 300 K to 77 K.

Figure 2(a) shows the calculated total density of states (DOS) over the valence band region. The calculated DOS matches with the earlier theoretical study [21,22] and also with the observed experimental data. Features A and B exhibit predominant Fe 3d character, C represents hybridized Fe 3d and Se/Te p states while D corresponds to Se 4p/Te 5p states. Se incorporation shifts feature C and D towards a higher binding energy owing to the greater electronegativity of Se (2.4) in comparison to Te (2.1). For FeTe, features B and C merge while in the case of FeSe, a clear gap is seen in the calculated DOS, which is in accordance with the experimental results. The features marked A’ (0.15 eV) and A” (1.0 eV) (shown in figure 2) correspond to the experimentally obtained features at 0.1 eV and 0.5 eV, respectively. The discrepancy in the energy positions could be due to the self-energy correction which is neglected in the calculations [24]. The partial density of states (PDOS) for Fe 3d orbitals for an energy range 0–2.5 eV is represented in figure 2(b). The PDOS (figure 2(b)) reveals that $xz/yz$ and $x^2 − y^2$ are the most populated ones at 0.15 eV (A’) while the feature at 1 eV (A”) corresponds to states mostly populated with $3z^2 − r^2$. Although, FeSe, FeTe and FeSe$_{0.5}$Te$_{0.5}$ have tetragonal symmetry, different Fe–Se and Fe–Te bond lengths in the case of FeSe$_{0.5}$Te$_{0.5}$ reduce the space group symmetry to 99 (P4mm) [25]. The lower symmetry in the case of FeSe$_{0.5}$Te$_{0.5}$ results in the lifting of the degeneracy of $xz/yz$ orbitals (as seen from figure 2(b)). The feature at ~0.15 eV shifts back to higher binding energy and becomes less prominent with doping of Se in place of Te. On the contrary, the feature at ~1.0 eV shifts towards $E_F$ and the plateau at ~0.8 eV reduces with Se incorporation. The above effect results in an enhanced DOS for FeSe in comparison to FeTe at 0.5 eV (experimentally). The change in the orbital contribution is related to the chalcogen height from the Fe plane. Replacement of Te by Se leads to a decrease in the chalcogen height, which affects the out of plane d orbitals, $3z^2 − r^2$ and $xz/yz$. The reduced chalcogen height leads to greater orbital overlap of $3z^2 − r^2$ and $xz/yz$ orbitals with $x^2 − y^2$ and $xy$ orbitals, respectively, which in turn results in an orbital selective spectral weight transfer as seen from figure 3. The occupancy of $xz/yz$ and $x^2 − y^2$ orbitals reduces at $E_F$ with a simultaneous increase in occupancy of $3z^2 − r^2$ orbitals at a higher binding energy. This change in the orbital occupancy is reflected in the spectral weight shifts which in turn result in the formation of a pseudogap with the doping of Se. It should be noted from figure 1(c) that the spectral weight transfer is weak in the case of FeTe while FeSe$_{0.5}$Te$_{0.5}$ exhibits a significant shift.

A comparison of the figures 1(d) and (e) will reveal that the doping dependent spectral weight transfer is similar to the temperature dependent transfer in their energy positions. It was shown earlier that lowering the temperature results in a reduction in the Fe-chalcogen height [Z shown in figure 1(a)] in the case of FeTe and FeSe$_{0.5}$Te$_{0.5}$ but a slight increase in the case of FeSe [26]. The magnitude of this decrease is greater in the case of FeSe$_{0.5}$Te$_{0.5}$ compared to FeTe. Thus, at 77 K, FeSe$_{0.5}$Te$_{0.5}$ has the shortest chalcogen height while FeTe has the longest. The reduced chalcogen height at low temperature in the case of FeSe$_{0.5}$Te$_{0.5}$ leads to the strongest hybridization between the orbitals. This is reflected in the maximum spectral weight transfer to higher binding energy in comparison to both of the parent compounds. As mentioned before in an analogy with the doping dependent case discussed earlier, the reduction in the Fe-Chalcogen height shifts the electron occupancy from the $xz/yz$ and $x^2 − y^2$ to the $3z^2 − r^2$ orbitals resulting in the temperature dependent spectral weight transfer and thereby the pseudogap. This is a temperature induced crossover from a metallic state in which all the $t_2g$ orbitals are depleted, signifying a Mott transition. This kind of spectral weight transfer which is a characteristic of Mottness [27], was identified earlier as Orbital Selective Mott Transition (OSMT) [8].

Our study presents the first observation of a temperature induced crossover to a low temperature OSM phase in the family of Fe chalcogenides although such phenomena were observed earlier in $\text{A}_x\text{Fe}_{2−x}\text{Se}_2$ ($\text{A} = \text{K, Rb}$) where a high temperature OSM phase was identified [28]. Such spectral weight redistributions with a lowering of temperature were ascribed earlier to the spin
Figure 3. The individual contributions of (a) $xy$, (b) $yz/zx$, (c) $3z^2-r^2$ and (d) $x^2-y^2$ orbitals to Fe 3d partial DOS for FeTe, FeSe$_{0.5}$Te$_{0.5}$ and FeSe. The inset of (b) represents the expanded PDOS near $E_F$ for $yz$ (solid lines) and $zx$ (dotted green line, for FeSe$_{0.5}$Te$_{0.5}$) orbitals. The reduced symmetry in the case of FeSe$_{0.5}$Te$_{0.5}$ lifts the degeneracy of $zx$ and $yz$ orbitals, thus the PDOS contribution splits which is otherwise the same in the case of FeTe and FeSe.

density wave transition (SDW) in FeTe by Zhang et al [15] who concluded that the suppression of the SDW is the cause of the reduction in the near $E_F$ spectral weight at low temperatures. But our observation of a stronger spectral weight shift in the case of FeSe$_{0.5}$Te$_{0.5}$ compared to that of FeTe shows that the spectral weight shift in this case is not related to the SDW transition. A recent ARPES study [29] has reported the evolution of the spectral feature (a hump which corresponds to feature A in our data) as a function of $x$. The intensity of the hump was found to reduce with decreasing Se content. This study points to the role of electronic correlations driving the system close to the Mott metal insulator transition. Another ARPES study, temperature dependent, by Liu et al [30] has reported a peak-dip-hump line shape in the case of Fe$_{1.02}$Te across its antiferromagnetic transition at 70 K. This study has shown the hump to become broader as the temperature is lowered below 50 K and explained the results in terms of the strength of polarons. It should be noted that the spectral weight shifts observed by us are all above the Neel temperature. Nevertheless, these results together highlight the intricate electron correlation in the near $E_F$ states over a broad range of temperature. In figure 4 we have compared...
the spectra collected using the HeI and HeII photons for FeTe, FeTe$_{0.5}$Se$_{0.5}$ and FeSe respectively. The black and red spectra correspond to data taken at 300 K and 77 K respectively. There is an enhancement of Fe 3d derived states in the case of He II for all the compositions due to the higher cross section of Fe 3d at the He II energy. The spectral weight shifts and thereby the pseudogap that arises, as described above, also follows the same trend in the case of He II but with a lower magnitude compared to He I.

In conclusion, we studied the temperature and doping dependent spectral changes in the near $E_F$ valence states in FeSe$_{1-x}$Te$_x$. The strong orbital dependent spectral weight transfer at low temperature suggests that these compounds are in close proximity with Mottness. Using theoretical band structure calculations, we have shown that the spectral weight transfer is due to the shifting of the electron occupancy from the $xz/yz$ and $x^2 - y^2$ orbitals to the $3z^2 - r^2$ indicating a temperature induced crossover from a metallic state to an Orbital Selective Mott (OSM) Phase.

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