Doping induced band renormalization in 122-type Fe-based superconductor

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Abstract. We study the electronic structure of a superconducting composition of 122-type Fe-based pnictide material, CaFe1.9Co0.1As2 employing high resolution angle resolved photoemission spectroscopy technique. The experimental results exhibit three bands close to Fermi level at Γ-point of the Brillouin zone among which only one band crosses the Fermi level. In the parent compound, CaFe2As2, all the three bands cross the Fermi level and form three hole pockets. While the destruction of Fermi pockets due to electron doping (Co-substitution dopes electrons into the system) is expected, we observe significant orbital selective band renormalization with respect to the parent compound. It appears that the effect of spin-orbit coupling is stronger in the doped compound.

Introduction

The parent compounds of Fe-based superconductors (FeScs) usually forms in tetragonal paramagnetic structure at room temperature. With cooling, the system undergoes both structural and magnetic transitions; a long range anti-ferromagnetic (AFM) ordering in a two fold-symmetric orthorhombic crystal structure appears at low temperature [1]. Chemical doping in the parent FeScs at different sites suppresses the ground state orders and superconducting (SC) phase appears within a critical range of doping concentration. Although, the phase diagram obtained with doping in FeScs are similar to that observed in Cu-based superconductors, the electronic properties of FeScs are more complex due to the presence of multiple bands close to Fermi energy, complex pressure-temperature phase diagram, coexistence of mutually exclusive magnetic order and superconductivity, etc [1, 2]. Chemical doping is usually expected to affect the charge carrier concentration, structural distortion and electron impurity scattering due to different atomic sizes and valence electrons of the dopant atoms. Evidently, Fe-based systems are highly complex. The angle resolved photoemission spectroscopy (ARPES) studies of these materials suggest interesting doping induced effects renormalization of band dispersion, spin-orbit coupling (SOC) strength, etc [3, 4].
In order to probe the doping induced effects in 122-type Fe-based pnictide compounds, we studied the electronic structure of CaFe$_{1.9}$Co$_{0.1}$As$_2$ (CaCo122) employing high resolution ARPES. Similar to other FeScs parent compounds, CaFe$_2$As$_2$ (Ca122) undergoes both structural and magnetic transitions at 170 K from its room temperature paramagnetic-tetragonal structure to AFM-orthorhombic structure [5, 6]. Doping of transition metal elements such as Co, Ni, Rh etc at the Fe-site suppresses the phase transitions and at a critical doping range, SC ground state appears. The compound, CaCo122 shows SC phase with transition temperature of $T_c \sim 15$ K which is the highest in this class of materials [1]. The electronic structure studies of both the parent and doped compounds suggest weak doping induced effects in the momentum integrated spectral density of states [8, 9]. Evidently, the role of Co-doping at the Fe-sites leading to superconducting state is complex and subtle changes close to the Fermi level needs to be studied carefully. We have investigated the electronic band structure of CaCo122 employing ARPES and find significant orbital selective band renormalization which might be a reason for the exotic ground state of this material.

Experimental Method
High quality single crystals of the CaCo122 were prepared using flux grown method [7]. No signature of magnetic or structure transition was observed in temperature dependent magnetic susceptibility and x-ray diffraction measurements. A sharp diamagnetic response was observed below 15 K indicating onset of the superconducting phase of the compound [9]. The crystallinity of the as grown samples were studied using Laue x-ray diffraction (XRD) technique. The (001)-aligned Laue XRD pattern collected on the sample is shown in the Fig. 1(b). Sharp and bright spots suggests very good quality of the single crystals.

The ARPES measurements were performed at Electron Spectroscopy Lab, TIFR, India, using GammaData Scicnta DA30L detector and a monochromatized UV lamp, VUV5k. The energy and angle resolutions were set to 10 meV and 0.3°. The ARPES measurements using 48 eV photon energy were carried out at VUV beamline of Elettra, Trieste, Italy. In the later case, the photoemission signals were detected using a Scienta R4000 WAL electron analyzer with energy and angle resolution of $\sim 15$ meV and $\sim 0.3°$, respectively [10]. The electronic band structure calculations were carried out following the density functional theory approach implemented in Wien2k-software using standard convergence criteria used for such systems.

Results
The experimental geometry used for the ARPES measurements is shown in Fig. 1(a). In both the ARPES measurements, the (110)-crystal axis of the sample is aligned along the slit, which allowed us to probe the electronic structure of compound along $\Gamma(0,0) - X(\pi,\pi)$ direction. The incidence angle ($\theta$ shown in Fig. 1(a)), was 60° and 45° in the lab based He-I$\alpha$ and synchrotron radiation source measurements, respectively. In Fig. 1(c), we show the ARPES spectra of CaCo122 collected using He-I$\alpha$ source at 25 K. Due to the matrix cross section element effect, only one band is observed which crosses the Fermi energy ($\epsilon_F$) at $k_F \sim 0.2$ Å$^{-1}$, in contrast to the expected no of bands close to $\epsilon_F$ [10, 11, 12]. Intense and broad feature at binding energy $\sim 300$ meV have partial contribution from the surface-band; this is verified by the rigid energy shift of the band with time delay after cleaving (not shown here). To observe the dispersion of the other expected bands at the $\Gamma$-point, the ARPES spectrum was also collected using 48 eV photon energy which represents the similar $k_z$-value (see Fig. 1(d)) [13].

The observed dispersion of the bands are shown by the dashed lines (smooth hand drawn curves) and labelled by Greek letters. While, the $\alpha_1$-band crosses the Fermi level at $k_F \sim 0.2$ Å$^{-1}$ close to that observed in the He-I$\alpha$ ARPES spectrum, the top of the $\alpha_2$-band just touches the Fermi level and does not form a finite size Fermi surface. The $\alpha_3$-band appears $\sim 140$ meV
from the $\epsilon_F$ which can be seen in the EDC shown in the Fig. 1(f). The $\kappa$-band crossing at $k_F \sim -0.79\AA^{-1}$ is the electron-pocket centred at the X-point.

To understand the effect of Co-doping in Ca122, in Fig. 1(f), we show the theoretically calculated band structure of the Ca122 obtained with inclusion of the spin-orbit coupling (SOC) term and compare it with the experimental results discussed above. The calculated band structure is consistent with the ARPES spectra of the parent compound considering that there is some additional band renormalization effects due to electron-electron correlation [13, 10]. However, a significant deviation in the relative energy position of the bands in Ca122 ARPES spectra is observed with respect to the band structure results shown in Fig. 1(f) and earlier ARPES studies. The calculated band structure results show a large energy difference between the $\alpha_1$ and $\alpha_2$ bands, and a relatively smaller gap between $\alpha_2$ and $\alpha_3$-bands at the Γ-point which was also observed in the experimental electronic studies carried out using ARPES technique [13, 10]. However, the ARPES spectra of CaCo122 exhibit an opposite trend; the gap between $\alpha_1$ and $\alpha_2$ bands is about 50 meV while the gap between $\alpha_2$ and $\alpha_3$ is about 140 meV. The Co-doping at Fe-site effectively adds an extra electron per atomic substitution. This will shift the energy bands; the vanishing of two hole pockets can be attributed to such effective electron doping. However, it fails to explain the change in the relative band energy difference at Γ-point with Co-doping indicating that the rigid band description is not applicable in this case.

In contrast to the shift of $\alpha$-bands with the charge carrier doping, the $\delta$-band having dominating $d_{z^2}$-character, appears at slightly low binding energy in comparison to the parent compound case [10]. The unequal positive energy shifts of the $d_{xy}$, $d_{yz}$ and $d_{zx}$ bands as well as the negative energy shift of the $e_g$-symmetric $\delta$-band suggests orbital-dependent band renormalization in addition to a simple charge carrier doping. We observed that the energy gap
between the $\alpha_2$ and $\alpha_3$-bands at the $\Gamma$ point depends on the SOC; the gap appears only with inclusion of the SOC term in the band structure calculations. Thus, the increase in the energy difference between the bands observed above suggests significant increase in SOC strength with doping which is unusual as both Co and Fe atoms have very similar atomic weights. It is worth to note here that the changes observed in the near $\epsilon_F$ electronic structure of the parent compound with doping will enhance the total density of states close to $\epsilon_F$, which explains the doping induced effects observed in earlier bulk electronic structure studies carried out using hard x-ray photoemission spectroscopy and x-ray absorption spectroscopy techniques [9, 8]. Clearly, the evolution of the electronic structure with Co-doping at Fe-site is complex and calls for more theoretical and experimental studies.

Conclusions
In summary, we have studied the electronic structure of CaFe$_{1.9}$Co$_{0.1}$As$_2$, a superconducting composition in the CaFe$_2$As$_2$ family using high resolution ARPES technique. Experimental results show signature of destruction of two hole pockets near $\Gamma$ point due to electron doping via Co-substitution. In addition, we observe orbital dependent band renormalization due to Co-substitution; the band renormalization suggests role of strong spin-orbit coupling. These results reveals an unusual scenario due to electron doping in Ca122 that leads to superconductivity in this system.

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