Orbital selective dynamics in Fe-based systems using time-resolved ARPES

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Abstract. Exoticity in material properties is often linked to the complex interplay of spin, charge, orbital and lattice degrees of freedom that makes the study of the origin of such exoticity difficult. The outstanding issue is to disentangle parameter space and reveal the underlying physics. We propose a unique method to excite electrons of a selected symmetry without significant effect on other electrons using polarized pump light pulse in a pump-probe experiment. Using this technique, we show that the relaxation of itinerant electrons occurs faster than the local electrons; the first experimental identification of the orbital selective electron dynamics in a complex correlated system, EuFe$_2$As$_2$. In another experiment, we discover that the magnetic order in CaFe$_2$As$_2$ can be melted selectively without significant effect on electrons in the other energy bands. These results provide two important conclusions; (i) magnetism in Fe-based systems may not be linked to the phase space occupied by other electrons and (ii) polarized pump excitation in a pump-probe experiment is a novel method to study orbital selective dynamics.

Introduction

Discovery of superconductivity [1] in Hg in 1911 nucleated a new field of research that has been growing continuously and rapidly even after more than a century is over. Most of the materials found in the early years have superconducting transition temperature, $T_c$ very low and the underlying physics could be captured by the condensation of cooper pairs formed due to electron-phonon coupling. The theory that captures these features is called BCS (Bardeen-Cooper-Schrieffer) theory [2]. In 1986, a new class of materials based on Cu-oxides found to show superconductivity at significantly high temperatures [3]. Extensive research in the cuprate superconductors led to finding of $T_c$ much higher than liquid nitrogen temperature of 77 K which enabled emergence of advanced technology. The properties of these so-called high $T_c$ superconductors cannot be captured by the BCS theory and are known as unconventional superconductors while the BCS superconductors are termed as conventional superconductors. In 2006, another new class of superconductors discovered which are Fe-based compounds [4]; there are several other classes of superconductors discovered in the meantime which are not mentioned here. The discovery of superconductivity in Fe-based systems led to significant puzzle as Fe is a highly magnetic element and superconductors are perfect diamagnets. There are several interesting common features and differences among these two classes of materials. For example, the parent compounds in cuprates are antiferromagnetic Mott insulators, where the insulating property arises due to the strong electron-electron Coulomb repulsion, $U$ compared to the width, $W$ of the conduction band. The charge carrier doping suppresses antiferromagnetic order and superconductivity emerges beyond a critical doping. It appears that the antiferromagnetic interaction and Coulomb repulsions are important to derive superconductivity in these materials. While
origin of superconductivity in these systems remains an unresolved problem, major attention has been paid in understanding the puzzles found in the normal phase of these materials, such as, pseudogap phase, strange metallicity etc.

On the other hand, the parent Fe-based compounds are metallic and show spin density wave (SDW) phase in the ground state. These materials show structural transition from tetragonal to orthorhombic phase along with a magnetic transition to a spin density wave (SDW) ground state. Charge carrier doping in these systems suppresses both the structural and magnetic transitions and superconductivity appears at a critical doping. Interestingly, many materials show coexistence of magnetic order and superconductivity in these systems. One can achieve superconductivity via application of pressure too. The structural transition from the tetragonal phase having $C_4$ rotational symmetry to orthorhombic phase having $C_2$ symmetry often renormalizes the energy band dispersions and lifts the band degeneracies \[5,6\]. The lower symmetric phase is termed as nematic phase. It is observed that emergence of superconductivity in these materials also accompanies significant structural reorganizations. Thus, the superconductivity in Fe-based systems appears to be significantly more complex and involves fluctuations of spin, charge and nematic degrees of freedoms. It is a formidable task to disentangle these degrees of freedom and study their underlying physics. Here, we propose a method based on time- and angle-resolved photoemission spectroscopy (trARPES) which can be used to probe various degrees of freedom selectively.

**Experimental method:**

The experimental results presented here are based on the experiments carried out at CITIUS, University of Nova Gorica, Slovenia as reported elsewhere \[7-9\]. The time- and angle-resolved photoemission study was done using a mode-locked Ti:sapphire laser (photon energy 1.5 eV, pulse duration 40 fs and repetition rate 5 kHz). The laser beam was split into two parts using a beam splitter; the major part was used to generate higher-order harmonics to be used as a probe pulse. The other part was used as a pump pulse which goes through a polarizer to produce linearly polarized light and a delay stage for tuning the pump-probe time.

![Fig. 1](image-url)  
(a) Schematic of the band structure of 122 materials in the paramagnetic phase. (b) SDW phase due to the nesting of the Fermi surfaces. (c) Schematic representation of trARPES.
delay, Δt. The photoemission measurements were performed using a R3000 electron analyzer and a closed cycle helium cryostat. The pressure during the measurements were maintained below 1 × 10^{-10} Torr. The energy resolution was set to 100 meV to get adequate signal to noise ratio. Single crystalline CaFe$_2$As$_2$ samples were grown by the Sn-flux method at TIFR, Mumbai, India. The samples were cleaved in-situ to generate a clean surface before every measurement. The dynamics of the photoexcited electrons is studied by varying the time delay between the pump and probe.

In Fig. 1(a), we show a schematic diagram of a hole band around Γ (0,0)-point and an electron band around X (π,π)-point of 122 class of materials which satisfy nesting condition and are responsible for the SDW ground state. The band structure in the SDW phase is shown in Fig. 1(b) exhibiting an energy gap due to the supercell of the magnetically ordered phase. The pump pulse shown in Fig. 1(c) excites electrons of selected momentum shown by a box in Fig. 1(b). The excited electrons gain an energy of 1.5 eV and occupy unoccupied states above the Fermi level. These hot electrons will relax fast by dissipating their energies via electron-electron scatterings. This process occurs at a very fast time scale and cannot be probed by the time scale of our measurements. In this process, the unoccupied bands above the Fermi level gets populated which are probed by the probe pulse coming at a time delay, Δt as shown in Fig. 1(d). Since the photoemission process occurs at an extremely fast time scale (~ attosecond), much faster than the relaxation time of various degrees of freedom in solid, the probe pulse essentially provides a snapshot of the electronic structure before the system relaxes via various dissipation processes. Thus, change in band structure and how it reconstructs can be probed by this process efficiently.

**Results and discussions**

![Fig. 2: (a) trARPES data of EuFe$_2$As$_2$ collected at 210 K using p-pol pump and p-pol probe pulse.](image)

(b) Integrated spectral intensity between -0.1 to -0.2 eV as a function of pump-probe delay.
Photoemission spectroscopy is a powerful and arguably the only tool to probe the electronic structure directly. The basic process involves the photo-electric effect, in which the sample under investigation is irradiated with a photon beam. The intensity of the excited electrons depends on the photoexcitation cross section which can be derived using Fermi’s Golden rule; the photoemission cross section can be expressed as $\sigma(\epsilon) = |\langle \psi_f | H' | \psi_i \rangle|^2 \delta(\epsilon_f - \epsilon_i - \hbar \nu)$. Here, $\epsilon_f$ and $\epsilon_i$ are the energy of the final state, $|\psi_f\rangle$ and initial state, $|\psi_i\rangle$, respectively. $H'$ ($= \hat{A}, \hat{p}$) is the perturbation due to the incident light. If we assume that the detector is placed on the z-axis and the xy-plane is the photoemission plane which contains incident light, the final state, $|\psi_f\rangle$ will be even with respect to the mirror reflection on xy-plane. $\sigma(\epsilon)$ will be nonzero when the integral, $\langle \psi_f | A \cdot p | \psi_i \rangle = \int \psi_f^* A \cdot p \psi_i d\tau \neq 0$ that requires $A \cdot p | \psi_i \rangle$ to be even. In Fe-based systems, the hole pockets around the $\Gamma$-point are constituted by $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals. The orbitals, $d_{xy}$ and $d_{xz}$ are odd with respect to the $xz$-mirror plane, and $d_{yz}$ will be even. Therefore, if linear polarization of the incident light is perpendicular to the $xz$-plane (here defined as s-polarization or ‘s-pol’), it will be an odd function and will provide contributions for $d_{xy}$ and $d_{xz}$ electron excitations. On the other hand, the in-plane light polarization (defined as p-polarization or ‘p-pol’) will give $d_{yz}$ contributions. Such symmetry selection rule is often used to derive the symmetry of the initial states in various photoexcitation processes.

To verify the applicability of this selection rule to study orbital selective dynamics, we show a typical excitation spectrum in Fig. 2(a) where the sample, EuFe$_2$As$_2$ is excited with p-pol pump pulse at the sample temperature of 210 K and probed by p-pol probe pulse. The color scale represents the intensity of the momentum-integrated spectral functions along the ΓX line. The figure shows significant population of electrons much above the Fermi level due to pump-excitations. The modulation of intensities occurs due to lattice vibrations leading to a time-dependent change in hybridization. In order to probe the decay process, we have integrated the intensities between 0.1 and 0.2 eV above the Fermi level. This energy range will have negligible contributions due to Fermi-Dirac distribution functions. The integrated intensities for both ‘p-pol’ and ‘s-pol’ probe pulse is shown in Fig. 2(b) as a function of pump-probe delay. The relaxation dynamics is found to be identical in both cases. This suggests that either the electron dynamics is not symmetry dependent or the technique is not sensitive to the detection of selective excitations.

Since the pump pulse excite electrons at the ground state, we planned to study the polarization dependence of the pump pulse while probe pulse probes the excited intermediate states. The process can be understood as follows. The intensity of the excited states due to pump pulse excitations will be nonzero if and only if

![Fig. 3: Excitation dynamics using p-pol (solid circles) and s-pol (open circles) pump pulse. Sample temperature 210 K and probe energy 29 eV.](image-url)
\[ \langle \psi_f | A \cdot p | \psi_i \rangle = \int \psi_f^* A \cdot p \psi_i d\tau \neq 0 \] for pump excitations. Now, in the case of s-pol light, \( \vec{A} \) is perpendicular to the \( \text{zx} \)-plane that makes \( A \cdot p \psi_i \) zero for \( d_{xz} \) orbital excitation as \( \vec{p} \psi_i \) will be essentially lying in the \( \text{zx} \)-plane. Similarly, ‘p-pol’ light will provide major contribution from \( d_{zc} \) orbital for an incidence angle close to 45°. Such qualitative arguments, consistent with dichroic effect, indicates that polarized pump pulse is a good tool to excite electrons of selected symmetry. The experimental results are shown in Fig. 3 exhibiting significant differences in the relaxation time for ‘p-pol’ and ‘s-pol’ cases.

Utilizing the above scenario, we have probed the excitation dynamics of EuFe\(_2\)As\(_2\) and CaFe\(_2\)As\(_2\). The results for EuFe\(_2\)As\(_2\) are shown in Fig. 4. Experimental data at a sample temperature of 30 K shown in Fig. 4(a) exhibit significantly different decay time for two polarizations of the pump pulse. The temperature evolution of the decay time is shown in Fig. 4(b). While the decay time for \( d_{xz} \) electrons is about 500 fs at room temperature that for \( d_{xy}/d_{yz} \) electrons is close to 2000 fs. From the band structure calculations and ARPES studies, it is well known that the width of the \( d_{xy} \) band is significantly narrower than \( d_{xz}/d_{yz} \) bands [10]. Since the local electrons will be less exposed to the crystal lattice, it will be less favorable to dissipate energy by electron-phonon coupling. With the onset of antiferromagnetic order, there will be a gap in the

Fig. 4: (a) trARPES response of EuFe\(_2\)As\(_2\) after ‘s-pol’ and ‘p-pol’ pump excitation at a sample temperature of 30 K. (b) Decay time constants of hot electrons for both cases.

Fig. 5: (a) trARPES response of CaFe\(_2\)As\(_2\) after ‘s-pol’ and ‘p-pol’ pump excitation at a sample temperature of 200 K and 150 K. (b) Energy distribution curves at \( \Gamma \) at 50 fs delay after pump excitations.
$\beta$-band which participate in the magnetic ordering. We observe an enhancement of decay time across the antiferromagnetic transition as expected from the behavior at higher temperatures.

We now investigate the electron dynamics close to the excitation threshold ($\Delta t \sim 0$). The results for CaFe$_2$As$_2$ are shown in Fig. 5. The trARPES response collected at sample temperatures of 200 K and 150 K are shown in Fig. 5(a). While the ‘p-pol’ and ‘s-pol’ excitations provide identical description at 200 K, the data at 150 K (below Neel temperature) are very different. The peak at 50 fs is intense in ‘p-pol’ case while it is almost absent in the ‘s-pol’ case. From the ARPES studies it is well known that SDW phase leads to a gap in the $d_{xz}/d_{yz}$ band while $d_{xy}$ band remains unaffected [11,12]. From the above results, it appears that s-pol pump pulse response becomes different across the magnetic transition while p-pol pump excitations look very similar to the paramagnetic phase. In order to probe this scenario further, we show the energy distribution curves (EDC) at the $\Gamma$-point collected from the spectra at 50 fs delay time. The spectra in the ‘s-pol’ case show signature of SDW gap while the ‘p-pol’ data looks very similar to the paramagnetic phase. This suggests that ‘p-pol’ light melted the magnetic order but ‘s-pol’ light could not do so. This is outstanding and demonstrate that one can selectively melt the magnetically ordered phase and that the magnetic order and structural order may not be linked.

**Conclusion**

In summary, we present here a method to selectively excite electrons using a time- and angle-resolved photoemission spectroscopy. We demonstrate that polarized probe pulse is unable to distinguish the symmetry of the electrons in the ground state presumably due to the fact that electron-phonon coupling mixes up the symmetries at the intermediate states of the pump-probe process. On the other hand, polarized pump pulse selectively excites electrons from the ground state of the material and hence is able to manifest the orbital selective signal. We have shown the excitation dynamics of EuFe$_2$As$_2$ and CaFe$_2$As$_2$ using this technique. The results in EuFe$_2$As$_2$ show that local electrons have significantly longer decay time compared to the itinerant ones [7]. The order in CaFe$_2$As$_2$ could be melted selectively using this technique which also suggests that the magnetic and structural order in these systems may not be linked [8].

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