Unveiling the role of the Mott-like electronic excitations in high-temperature superconductors by time-resolved photoemission

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Introduction

Thirty years after the discovery of high-temperature superconductivity (HTSC) in copper-based oxides, a microscopic theory of the mechanism underlying this phenomenon is still missing. Among the many issues that defy an explanation in the conventional Bardeen-Cooper-Schrieffer (BCS) framework, we focus on the interplay between the low-energy physics (superconductivity) and the high-energy electronic properties. While in the BCS theory, the superconducting phase transition is accompanied by a modification of the electronic density of states over a frequency range of the order of the superconducting gap (<10 meV), in copper oxides the condensate formation strongly affects the high-energy scale physics (>1 eV) [1].

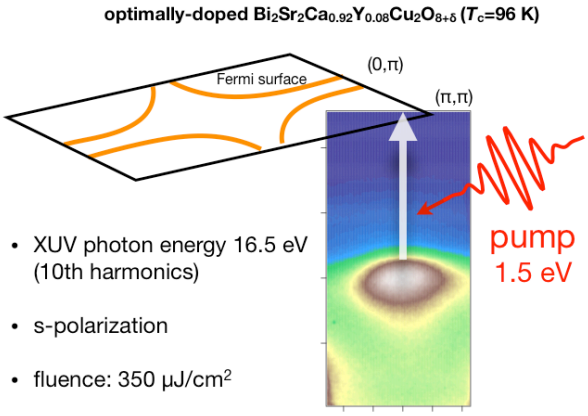

Figure 1. Cartoon of the experimental configuration. The pump excitation at 1.5 eV photon energy creates a non-thermal electronic distribution characterized by an excess of holes in the O-2p_π oxygen bands and of electrons in the conduction band. Snapshots of the relaxation process are taken by XUV probe pulses (hν=16.5 eV) that photoemit electrons at a kinetic energy E_{kin}=hν-Φ, where Φ is the work-function of the material.

A step forward in the understanding of this phenomenon was the recent development of time-resolved broadband spectroscopies. Pump-probe multicolour techniques finally demonstrated the interplay between specific many-body electronic excitations in the range of 1.5-2 eV, which corresponds to the energy scale of the Mott physics, and the onset of superconductivity [2]. More specifically to the case of cuprates, these transitions constitute the lowest-energy electronic excitations, that is the charge-transfer (CT) process of a localized Cu-3$d_{x^2-y^2}$ hole to its neighbouring O-2$p_{x,y}$ orbitals. However, many questions are still to be answered, since the rate of the optical transition is regulated by the strength of the matrix element and by the density of states of both the initial and final states. As a consequence, the superconductivity-induced variation of optical transitions at 1.5-2 eV can be attributed to any of these three causes, without any clue to unambiguously solve the problem.

Here we tackle this problem by directly investigating the dynamics of the occupied oxygen bands at 1.5-3 eV binding energy, after the excitation with an intense 1.5 eV pump pulse. The main goal is to relate the ultrafast modification of the oxygen bands in copper oxides to the optical transitions at 1.5 and 2 eV and, eventually, to the onset of superconductivity.

Results

In order to explore, for the first time, the dynamics of the oxygen bands in copper oxides we performed time-resolved photoemission spectroscopy (TR-ARPES) measurements, with high temporal resolution and XUV photon energy, at the beamline ARTEMIS of the Central Laser Facility.

The experiments were performed on high-quality $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$ single crystals (Y-Bi2212) at the optimal hole concentration to attain the maximum critical temperature (T_c=96 K). The sample was excited by ultrashort (<50 fs) pump pulses, with 1.55 eV photon energy, 1 kHz repetition rate and 350 μJ/cm^2 intensity. The electrons were photomitted by the 10th harmonics, produced in a gas jet, of the fundamental radiation of an amplified Ti:sapphire laser. The central energy of the XUV probe pulses was set to 16.5 eV, while the polarization was perpendicular to the plane of incidence. The photoemitted electrons were collected by a

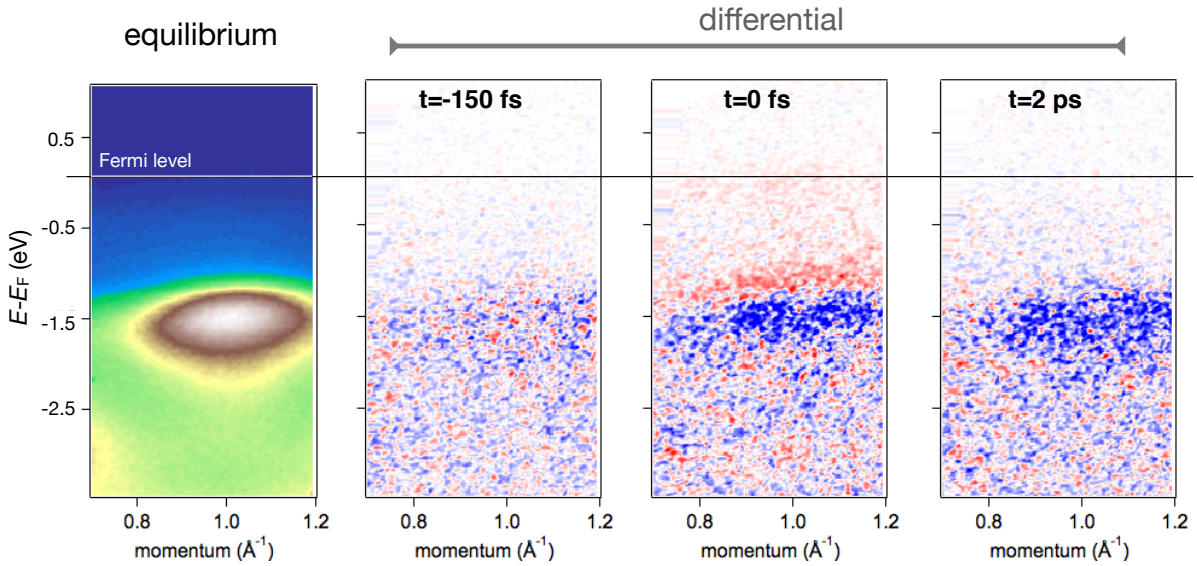

Figure 2. Equilibrium photoemission spectrum, I(**k**, E_{kin}, *t*), as a function of the momentum (**k**) and the energy difference from the Fermi level ($\varepsilon=E-E_F$) of the photoemitted electrons. Differential photoemission spectra of the O-2p_π bands. The red(blue) colour scale indicates a positive(negative) variation of the differential spectra, defined as $\Delta I(\mathbf{k}, \varepsilon, t)=I(\mathbf{k}, \varepsilon, t)- I(\mathbf{k}, \varepsilon, t=-500\ fs)$.

SPECS Phoibos 100 detector. The total energy resolution, which was mainly limited by the bandwidth of the XUV probe, was about 130 meV.

Preliminary ARPES measurements on the same Y-Bi2212 crystals were performed at the University of British Columbia in order to characterize the oxygen bands and identify their position in the energy-momentum space. As shown in Figure 1, the photoemission spectrum is characterized by a strong peak at 1.5 eV binding energy and at parallel momentum $\mathbf{k}_{\parallel}=(\pi,\pi)$. This feature has been previously assigned to the O-2p_π oxygen band which is non-bonding with the Cu-3$d_{x^2-y^2}$ orbitals that form the conduction band [3]. The pump excitation kicks the electronic distribution out of equilibrium, leaving an excess of holes in the oxygen bands and an excess of electrons in the conduction band, which relax toward the equilibrium condition on the fs-ps timescale.

Figure 2 shows the differential ARPES spectra measured at T=30 K, obtained by subtracting the equilibrium spectra, I(**k**, ε), to the spectra measured at a given delay *t*. The effect of the pump excitation is clearly observed at zero time-delay, i.e., when the pump and probe pulses completely overlap. The signal changing from positive to negative about the maximum value of the peak is characteristic of a small shift in the binding energy of the O-2p_σ bands. The dynamics of this shift is rather fast and the initial position of the peak is recovered within 200 fs. We ascribe this fast dynamics to the relaxation of the non-thermal electronic population created by the pump pulse. More interestingly, a significative signal persists on the ps timescale. As shown in the right panel of Fig. 2, a homogeneous negative variation is measured up to several picoseconds after the excitation. This variation is related to a loss of spectral weight of the O-2p_σ band, which is eventually recovered before the arrival of the next pulse (1 ms). This unexpected result, suggests that a fraction of the holes initially photoinjected by the pump pulse gets trapped in a long-lived metastable state characterized by an excess of holes on the non-bonding O-2p_π oxygen bands. This behaviour can be understood by recalling that the O-2p_π wavefunctions do not overlap with those forming the conduction-band. Therefore, while the holes photoinjected in the bonding O-2p_σ oxygen bands can inelastically decay into the conduction band via scattering with phonons and magnetic fluctuations [4,5], the holes in the O-2p_π bands remain trapped for a longer time. These results open intriguing perspectives: the charge unbalance on the oxygen atoms can lead to a local deformation of the lattice, eventually driving the formation of long-lived localized polarons.

Conclusions

In conclusion, we have demonstrated that XUV time-resolved ARPES can be used to track the dynamics of the occupation of the oxygen bands at the binding energy of the order of the charge-transfer transition, which is strongly affected by the onset of superconductivity. These results unveil a non-trivial excitation pathway which results in the long-lived trapping of holes in the oxygen O-2p_π bands, probably under the form of localized polarons. Whether the observed polaron formation is related to the onset of superconductivity will be subject of further investigations in which the relevant parameters, such as the temperature and the hole doping, will be varied throughout the cuprate phase diagram.

Our results underscore the crucial role of the excitation process and of the formation of long-lived non-thermal states in pump-probe experiments on copper oxides. The present time-resolved XUV photoemission experiment paves the way to the new era of time-resolved ARPES on cuprates, in which the ultrafast electron dynamics will be mapped over the entire Brillouin zone.

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