Resonant x-ray scattering explorations of charge order and broken symmetries in underdoped cuprates

The spontaneous self-arrangement of electrons into periodically modulated patterns, a phenomenon commonly termed as charge order or charge-density-wave, has recently resurfaced as a prominent, universal ingredient for the physics of high-temperature superconductors. Its antagonist coexistence with superconductivity, together with its possible connection to a quantum critical point beyond optimal doping, are symptomatic of a very fundamental role played by this symmetry-broken collective electronic state. Resonant x-ray scattering (RXS) has rapidly become the technique of choice for the study of charge order in momentum space, owing to its ability to directly identify a breaking of translational symmetry in the electronic density. Here we will review our RXS work on underdoped Bi2201 and electron-doped NCCO to detect charge-density-waves even in presence of short-ranged order, exploring a realm previously accessible using real-space probes. In addition, we will discuss how the information available from the full two-dimensional momentum space can be used to demonstrate the presence of charge stripes in YBCO. Finally, we will review our explorations of polarization-dependent scattering intensities to uncover the local symmetry in the charge distribution around the Cu atoms, which was found to be predominantly of a $d$-wave bond-order type.

Keywords: charge order; superconductivity; cuprates; resonant x-ray scattering

Introduction

Recently, the study of charge order and its competition with superconductivity has resurged as a prominent topic of research for the physics of cuprate high-temperature superconductors [1]. An outpouring of experimental results in the last 2-3 years enabled a rapid and unprecedented advancement in our characterization of charge order across several cuprate families. Resonant soft x-ray scattering has represented a key experimental probe of charge order in these materials, leveraging the peculiar nature of the resonant light-matter interaction process and its unique sensitivity to reveal the universality of charge order in cuprates, as well as its orbital symmetry and local structure.

Revamped by the recent discovery of charge order in YBCO [2–5], the presence of this instability has now been confirmed in all cuprate families – Bi2201 [6], Bi2212 [7], Hg1201 [8], and including electron-doped cuprates [9], a situation which is summarized in Fig. 1(a,b). At last, charge order can be qualified as a universal, defining instability of the doped copper-oxygen planes. Most importantly, resonant x-ray scattering, owing to its peculiar sensitivity to the electronic degrees of freedom, has enabled further investigations of the microscopic structure of charge order in the cuprates [10–13]. These studies revealed different manifestations of the charge order symmetry across different cuprate families, thus exposing a variegated but essential phenomenology for the physics of copper-based high-temperature superconductors.
Figure 1. (a,b) Charge order onset temperature (a) and wavevector (b) vs. doping chart for hole-doped (b) cuprates. The shaded areas in (a) denoting the antiferromagnetic (AF), superconducting (SC), and pseudogap (PG) regions define the phase diagram of YBCO. Shaded lines and areas in (b) are guides-to-the-eye to highlight different regimes in the doping-dispersion of the wavevector. From [1].

Methods

Resonant x-ray scattering is a photon-in, photon-out diffraction technique, where the excitation is performed at element-specific x-ray resonances. With this method, it is possible to look for the fingerprints of ordered structures in reciprocal space, while enhancing the sensitivity to selected species. In the context of charge order, RXS has established itself as a prime experimental probe to detect weak, static oscillations of the charge density with unprecedented sensitivity, and has been applied to several families of charge-ordered materials, especially transition metal oxides [14–16]. The enhanced sensitivity of RXS to charge and spin is directly inherited from the nature of the resonant scattering process, which involves a high-energy intermediate state with a core-hole and a valence electron. Such process corresponds to a second-order transition in linear perturbation theory from the nonrelativistic minimal coupling Hamiltonian, and
in general its cross section is proportional to the quantum-mechanical probability \( w_{i\rightarrow f} \) to start from a many-body ground state \( |i\rangle \) with zero energy and momentum and leave the system in a final state \( |f\rangle \) with finite energy \( E \) and momentum \( \mathbf{Q} \):

\[
w_{i\rightarrow f} \propto \sum_{\mathbf{R}} \sum_{m} \left| \frac{\langle \mathbf{f} | \mathbf{e}' \cdot \mathbf{p} | m \rangle \langle m | \mathbf{e} \cdot \mathbf{p} | i \rangle}{E - E_n + \hbar \omega_{in} - i\Gamma_m} \right|^2 e^{i\mathbf{QR}} \times \delta (\hbar \omega_{in} - \hbar \omega_{out} - E) \tag{1}
\]

where \( \mathbf{R} \) denotes the set of atomic positions, \( \mathbf{p} \) is the momentum operator, \( \mathbf{e}(\mathbf{e}') \) represents the polarizations of incoming (outgoing) photons with energy \( \hbar \omega_{in} \) (\( \hbar \omega_{out} \)) and momentum \( \hbar \mathbf{k}_{in} \) (\( \hbar \mathbf{k}_{out} \)), \( |m\rangle \) is a set of intermediate states with a core hole and an excited valence electron above the Fermi energy. Note that energy and momentum conservation laws applied to the scattering process impose that \( \hbar \omega_{in} = \hbar \omega_{out} + E \) and \( \hbar \mathbf{k}_{in} = \hbar \mathbf{k}_{out} + \mathbf{Q} \); the case of elastic scattering, which is the subject of this article, corresponds to \( E = 0 \). For a more comprehensive review of the foundations of RXS theory, see also [17–21].

In the case of cuprates, the maximum sensitivity is attained at the oxygen and copper soft x-ray resonances (at 530 eV and 930 eV, respectively), where the RXS intermediate involves an excited electron in a Cu-3d or O-2p orbital within the CuO\(_2\) planes. The experimental results presented hereafter have all been measured at the Cu-L\(_3\) resonance.

**Results**

*Charge order in Bi2201 and confirmation of real space – reciprocal space duality*

Our first study of charge order aimed at elucidating the connection between scattering probes, which are bulk-sensitive and operating in reciprocal space, and microscopy techniques, which are surface-sensitive and access the real space domain. Our first RXS study was performed on underdoped single crystals of the single-layered Bi-based cuprate compound Bi\(_2\)Sr\(_2\)La\(_x\)CuO\(_{6+d}\) (Bi2201), with La content \( x \) of 0.8, 0.6, and 0.5, corresponding to hole doping \( p \) of 0.11, 0.13, and 0.14, respectively [6]. In particular, by comparing deep-penetrating scattering probes to surface-based scanning tunnelling microscopy (STM), we sought to disclose the connection between signatures of charge order in the bulk of the crystal and at its surface, where static modulations of the local density of states had been reported since the early 2000’s [22]. Figure 2(a) shows RXS scans of the momentum axis parallel to the Cu-O bond direction, taken at the Cu-L\(_3\) resonance in the most underdoped sample \((p-0.11)\), where the emergence of a diffuse peak at low temperature can be clearly discerned, despite the weak scattered intensity atop the large fluorescent background. This broad feature signals the presence of a short-ranged electronic density wave in the CuO\(_2\) planes at low temperature. Notably, the scattering signal vanishes when the photon energy is tuned away from the resonance [Fig. 2(b)], as the scattering process becomes insensitive to the states carrying the modulating charge. Figure 2(d) shows the STM tunnelling conductance map on the very same samples, with corresponding Fourier transform in Fig. 2(c). The equivalence between bulk and surface probes becomes self-evident, thus demonstrating the connection and unity between these two complementary techniques in this field of research.
Figure 2. (a,b) Charge-density-wave peak in cuprate compound Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+d}$ as seen in reciprocal space at low temperatures (20 K) using resonant scattering (a); and corresponding intensity profile across the copper resonance (b). (c,d) Charge-density oscillations in the same samples from STM conductance map (d) and corresponding Fourier transform (c), showing the equivalence with the momentum space representation from scattering (a). From [6].

**The other side of the phase diagram: Charge order in electron-doped NCCO**

As mentioned in the introduction, charge order has been rapidly found in all cuprate families over a few years of intensive quest, however the electron-doped side of the phase diagram has remained long unexplored. The scientific question that arises in this context is a fundamental one for this phenomenology: what is the driving force behind charge order, and is it affected by the nature of the electronic states near the Fermi energy? To address this important point, we investigated charge order in electron-doped compounds, whose electronic states are predominantly of Cu-3d character, as opposed to the O-2p orbitals which form the valence band in hole-doped compounds [9]. Figure 3(a) and 3(b) show a series of low-temperature RXS scans at different photon energies for a 0.14 and 0.15 superconducting electron-doped Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) samples, respectively. In both cases, a broad charge order peak becomes apparent when the photon energy is tuned right at the Cu-$L_3$ resonance, and disappears completely less than 1 eV away from it. This finding demonstrates the persistence of charge order...
across the extended phase diagram and confirms the centrality of this instability for the low-energy electronic states in the copper-oxygen planes in cuprate superconductors.

The microscopic texture of charge order: stripes and d-wave form factor in YBCO

While being a powerful technique in revealing the momentum-space signatures of weak electronic modulations, RXS has been used to mostly extract the wavevector, strength, and correlation length (inverse peak width) of charge order in cuprates. The resonant process and its cross-section however provide additional information on the local symmetries (at the Cu site, in the case of the Cu resonance) that are imprinted on the form factor tensor which reflects the quantum-mechanical amplitudes for the x-ray transition from core to valence. This information cannot be readily retrieved from a single RXS measurement, however a partial reconstruction of the form factor entries by applying a procedure well-known for magnetic scattering, named azimuthal scan. The schematics of this configuration are shown in Fig. 4(a), and essentially require measuring momentum scans for different angular orientations of the crystallographic axis around an axis (the azimuthal axis) collinear with the probed wavevector \( \mathbf{Q} \). The corresponding momentum scans vs. azimuthal angle are shown in Fig. 4(b). Using this method on charge-ordered, underdoped YBa_2Cu_3O_{6+y} (YBCO) crystals, a modulation of the scattered intensity as a function of the azimuthal angle could be observed [Fig. 4(f)], whose shape was best reproduced by using a general model for the form factor assuming a local orbital symmetry of the kind depicted in Fig. 4(g) (red pattern), also known as \( d \)-wave bond order \([11]\).
Figure 4. (a) Special scattering geometry used for the tomographic reconstruction of the charge-density-wave peak in reciprocal space [11]. (b) Corresponding momentum scans of charge order peak vs azimuthal angle (α) in YBa2Cu3O6.75. (c) Reconstruction of peak shape from the azimuthal angle dependence of the momentum broadening. (d,e) The resulting peak shape reveals asymmetries that are only compatible with a stripe scenario (b) and not with a checkerboard pattern (c) [10]. (f,g) Azimuthal dependence of RXS intensity (f) and corresponding fit to a multicomponent form factor demonstrating a $d$-wave type orbital pattern of O-2p orbitals (g). From [11].

Lastly, we have adopted a similar approach, again in YBCO but this time focusing on the momentum structure of the RXS scans (as opposed to the scattered intensity) in order to perform a circular reconstruction of the two-dimensional profile of the charge order peak [Fig. 4(c)], which revealed inner anisotropies incompatible with preservation of fourfold rotational symmetry [10]. The latter, which imposes certain constraints on the shape of the charge order peak, is associated with a rotationally-invariant checkerboard state [Fig. 4(e)]. The violation of fourfold symmetry in the RXS two-dimensional peak profiles thus provided support for locally unidirectional modulations of the electronic density, much alike charge stripes [Fig. 4(d)].

**Conclusion**

To summarize, the phenomenology of charge order in cuprates has been explored to an unprecedented level in recent years, leading to tremendous advancements of our understanding and description of the related phenomenology, on both theoretical and experimental grounds. Recent works have further clarified the connection between charge order and other coexisting and competing phases, such as antiferromagnetism and superconductivity, but more work lies ahead to fully uncover the fundamental role of this instability and the ultimate extent of its relevance for the physics of cuprates and of unconventional superconductors in general.

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