Summary

This work describes results obtained on the study of charge density waves (CDW) in strongly correlated systems with a new experimental method: resonant soft x-ray scattering (RSXS).

The basic motivation is the 1986 discovery by Bednorz and Müller of a new type of superconductor, based on Cu and O (generically called “cuprates”), with a critical temperature of approximately 30 K. Their discovery was one of the most important in condensed matter physics. Interestingly, the high-$T_c$’s occur only upon doping a Mott Hubbard insulator with holes or electrons. So that the cuprates show not only high-$T_c$ but also in the vicinity of half filling a controlled Mott metal-insulator transition. Since then, the cuprates have been under an extraordinary intensive, both experimental and theoretical, investigation.

After more than 20 years of research, however, the cuprates are far from understood. Despite the variation in chemical compositions, the cuprate superconductors have many common characteristics, and it is natural to assume that these characteristics determine the basic physics. The high-$T_c$ superconductors are layered materials, containing quasi-two-dimensional CuO$_2$ planes sandwiched between block layers. The electronic states close to the Fermi level are contained in the CuO$_2$ planes. The block layers play the role of charge reservoirs, controlling the number of carriers in the conduction planes upon chemical doping. Consequently, theoretical models designed to describe the physics of a single CuO$_2$ plane for different electronic concentrations were proposed for the cuprates. However, there is no general agreement on what should be the minimal model that captures the basic physics of a CuO$_2$ plane.

The cuprates drastically change their behavior with small changes of the electron density in the CuO$_2$ plane. The basic behavior of the CuO$_2$ plane is common to all the cuprates superconductors. The undoped materials as in La$_2$CuO$_4$ are antiferromagnetic insulators. Replacing La$^{3+}$ by Sr$^{2+}$ in La$_{2-x}$Sr$_x$CuO$_4$, the insulating CuO$_2$ plane may be regarded as hole doped. Upon hole doping $\delta = x$ in this particular case ($\delta$ is the concentration of the doped holes) the three-dimensional antiferromagnetic order is rapidly destroyed and a transition from the insulator to superconductor takes place in the range of $\delta = x = 0.05$ to 0.30. The optimal doping is around 0.15 which is the doping value where $T_c$ is maximum. In the overdoped region ($\delta > 0.20$), and above $T_c$, the system behaves like a Fermi-liquid metal while in the underdoped region ($\delta < 0.20$) and in the normal state strong deviations from Fermi liquid behavior are observed leading to the characterization of anomalous metals. The majority of physicists believe that an understanding of the
underdoped phase would provide the key for elucidating the mechanism of superconductivity.

X-ray absorption (XAS) experiments have shown that the first electron removal states have O $p$ character, placing the cuprates in the charge-transfer category of the Zaanen-Sawatzky-Allen (ZSA) scheme. It is believed that the only Cu orbital which participates in the low-energy physics is the $d_{x^2−y^2}$ one. It is coupled to the in-plane oxygen $p$ orbitals, and therefore the first models contained all these degrees of freedom ($d$ and $p$). However, based on the strong Cu-O hybridization, many physicists believe that one step further can be taken and a reduction to a one-band Hamiltonian which contains only the $d_{x^2−y^2}$ orbitals can be made. If the system is doped the added holes are believed to mainly occupy the Oxygen sites. In particular, Zhang and Rice (ZR) proposed that Cu-O hybridization strongly binds a hole on each square of O atoms to the central Cu $2^+$ ion to form a local singlet, which is a coherent superposition of the $2p_x$ orbitals of the four nearest-neighbour oxygen atoms. This so-called Zhang-Rice singlet moves through the lattice in a similar way as a hole in the single band effective Hamiltonian of the strongly interacting Hubbard model, and has been used as the building block in the construction of an effective microscopic Hamiltonian for the cuprates. Because the low energy excitations are mainly in the Zhang-Rice-Singlet band, it is also called the effective lower Hubbard band (LHB) in the literature.

It is clear that the character of the ground state of an antiferromagnetic insulator is fundamentally altered by addition of a small amount of charge or holes. At present, in the two-dimensional Cu-O system, it is unclear whether the interaction between the doped holes is driven by short-range exchange, long-range Coulomb, or a combination of both. So far, there is no direct experimental evidence that favors either scenario.

In two-dimensional Cu-O systems one of the candidate ground states, which has been proposed to compete with superconductivity, is the so-called “stripe” phase. Stripe phases were predicted to arise in doped antiferromagnets through competition between magnetism and the kinetic energy of mobile carriers (typically holes). In copper-oxides the main experimental evidence for stripes is neutron scattering from La$_{1.48}$Nd$_{0.4}$Sr$_{1.12}$CuO$_4$ (LNSCO) and La$_{1.875}$Ba$_{0.125}$CuO$_4$ (LBCO) which reveals coexisting static spin and charge order whose wavelengths differ by a factor of two, reminiscent of charged rivers separating regions of oppositely-phased antiferromagnetism. A neutron is electrically neutral object, however, so does not detect charge order but rather its associated lattice distortion; it is not known if the “stripe” phase in LNSCO and LBCO actually involves ordering of the doped holes.

In quasi-two-dimensional Cu-O systems, the existence of hole crystallization was also studied intensively, starting from 1992 when Dagotto et al. proposed an electronic
model for ladder-like structures in which the Copper and Oxygen ions are ordered in two parallel $t$-$J$ chains forming the legs of a ladder and $t'$-$J'$ coupling along the rungs. In their model, a pair of holes should exist along the rung, and depending upon the parameters chosen, a doped ladder can exhibit either exchange-driven superconductivity or an insulating “hole crystal” ground state in which the carriers crystallize into a static, Wigner lattice, forming a Wigner crystal (WC). Moreover, in a recent calculation by White et al., using the dynamic matrix renormalization group (DMRG) method, the charge density wave (CDW) is also a WC and it is stabilized at a filling of $n = 3/4$. The competition between these two phases is similar to that believed to occur between ordered stripes and superconductivity in two-dimensional Cu-O systems.

The only known doped ladder in Cu-O systems is Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ (SCCO). Superconductivity has indeed been found by Uehara et al. in Sr$_{0.4}$Ca$_{13.6}$Cu$_{24}$O$_{41}$ when the sample is subjected to a hydrostatic pressure of $P > 3$ GPa, above which the resistivity drops to zero at ~ 12 K. A more complex phase diagram showed that SCCO is insulating for all $x$, however it undergoes an insulator to metal transition under pressure at 7 GPa for $x = 0$ and at 3 GPa for $x > 9$. At intermediate values $1 < x < 9$ the system remains insulating at all attainable pressures.

SCCO, however, exhibits all the transport signatures of a CDW, including a screening mode in impedance measurements, a pinning mode in microwave conductivity, a giant dielectric constant, and a nonlinear current–voltage ($I$–$V$) curve, which together indicate that the carrier density is modulated in real space. These observations are typical of conventional Peierls CDW materials like NbSe$_3$ or K$_{0.3}$MoO$_3$ in which the carrier density is modulated by a distortion in the crystal structure, driven by the electron–lattice interaction. However a charge density wave could also be driven by effective long-range interactions such as the WC as predicted and would have the same transport signatures.

The most direct way to study hole crystallization or WC is x-ray scattering from which one can determine (1) its wavelength, (2) coherence length, (3) form factor (deviation from sinusoidal, for example), and (4) the temperature dependence of its order parameter, $\eta(T)$. It is difficult to detect a WC with hard x-ray scattering or non-resonant scattering for the following reasons. First, one needs to measure the structure factor at finite $q$. Second, x-ray scattering is more sensitive to structural distortions in crystals than to the charge modulation itself. The distortion in crystals can occur not only due to the charge modulation but also from other phenomena such as “misfit” between two different layers. SCCO is an adaptive misfit material consisting of ladder and chain subsystems with incompatible periods $c_l/c_c = 10/7$. So it is very difficult to distinguish these two effects only with hard x-ray scattering.

To study such electronic ordering, we have used a new experimental method RSXS which is sensitive to small changes in electronic structure. RSXS is a combination of
X-ray diffraction and spectroscopy in the energy range of about 200-2000 eV and provides a powerful means to investigate charge ordering phenomena.

The sensitivity of resonant soft x-ray scattering (RSXS) to charge modulations has been tested on various systems which are La$_2$CuO$_{4+y}$ films, Yba$_2$Cu$_3$O$_{6.5}$ and underdoped single crystals of Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$. In La$_2$CuO$_{4+δ}$ films we observed an inhomogeneous distribution of oxygen doping. We have also observed a superstructure at the (0,0,1.054) reflection in doped films. In YBa$_2$Cu$_3$O$_{6.5}$ (ortho-II YBCO) we observed direct evidence for modulation of low energy electronic states of Cu in both the CuO$_2$ chain and the CuO$_2$ plane. A huge polarization-dependent enhancement of the (1/2,0,0) superstructure Bragg peak is observed when the photon energy is tuned to the Cu $L_2,3$ absorption edge. The ordering in the CuO$_2$ plane discovered here sheds new light on how the one dimensional Cu-O chains affect the CuO$_2$ plane, and why many normal and superconducting state properties of this system exhibit strong anisotropy. It is also important that, with this technique, we can also see the incommensurate structural modulation in Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ as seen by others technique. We have confirmed that there is no observable charge modulation in the CuO planes in this super structure. We also learned that the interference between regular scattering and resonance scattering could lead to a complicated shape of the resonance profile, which strongly depends on the relative phase of these scattering processes. These are all described in Chapter 3.

In Chapter 4 is described our discovery of a Wigner crystal in the ladders and a 4$k_F$ charge density wave (CDW) in the chains Sr$_{14}$Cu$_{24}$O$_{41}$. In Chapter 6, the WC in the ladders and the charge density waves (CDW) in the chains of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ are studied as a function of the number of doped holes per ladder Cu site. Our results demonstrate that commensuration is critically important for the formation of the hole crystal in SCCO. Interestingly, the WC in the ladders appears only with odd wavelength (i.e. $\lambda = 5c_L$ or $3c_L$, not for $4c_L$). We try to explain the behavior of the ladders with an RVB-type model. The CDW in the chain turns out to be more complicated. It seems that the strong modulation which arises from the atom displacement in the chain is driving the hole modulation in the chain.

In Chapter 5, the distribution of holes in the spin ladder compound Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ (SCCO) is revisited using polarization-dependent XAS and RSXS. A new interpretation is proposed which results in a strongly modified hole density distribution. Based on this new interpretation, for $x = 0$ the density of holes in the ladders, $n_L$, and chains, $n_c$, are found to be 2.8 and 3.2, respectively. This is strongly modified from previous estimates of 0.8 and 5.2 respectively. The ladder hole density increases almost linearly with $x$ as was found previously. For example $x = 11$, the $n_L$ and $n_c$ are 4.4 and 1.6, respectively. These new densities are shown to be consistent with experiment and with models of hole crystallization in the ladder provided that the holes are paired as suggested by White et. al.
In Chapter 7, we present a study of the static “stripe” phase in La$_{15/8}$Ba$_{15/8}$CuO$_4$ (LBCO) with RSXS. The charge scattering exhibits giant resonances at the doped hole and upper-Hubbard band features below the O$K$ edge. We estimate a peak-to-trough valence amplitude of 0.063 holes and, using a model for the stripe form factor, an integrated area of 0.59 holes under one stripe. The results demonstrate a direct participation of the holes in this phase and are consistent with half-filled stripes.