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Report on Doctoral Dissertation of mgr inż. Izabela Biało

General remarks

The dissertation submitted by Izabela Biało in partial fulfilment of the requirements for the degree of Doctor of Philosophy in physics is entitled *'Role of the charge correlations in the mechanism of high temperature superconductivity'*. The presented work is contributing to the solution of one of the most important problems in the condensed matter physics: the pairing mechanism of the high temperature superconductivity in copper-oxides (cuprates). The main goal of the thesis was to study the impact of the electronic correlations on the properties of the cuprates, in particular on superconductivity.

Number of synchrotron X-ray scattering techniques, in combination with uniaxial pressure and high-magnetic fields, were employed to study the delicate balance between various broken symmetry states and superconductivity. Particular attention was paid to understanding the key parameters leading to the suppression of superconductivity. One of such parameters explored in the thesis was breaking the symmetry of the crystallographic lattice, which affects the central building block of the cuprates - the CuO_2 planes. This symmetry breaking can be achieved by uniaxial pressure, or it emerges naturally (in a particular region in the cuprate phase diagram) in the form of the charge-density-wave (CDW) order that coexists, yet competes with superconductivity. Thus, systematic studies by carefully selected experiments at synchrotron sources of the CDW order and its impact on the electronic properties were carried out in a number of cuprate compounds.. Furthermore, the standard X-ray scattering and diffraction techniques were combined with the application of uniaxial pressure and high magnetic fields. The presented experimental results provide evidence that the short-range CDW order is a universal phenomenon in cuprates, which exists in a limited range of temperatures and doping, and, although very weak, has a detrimental influence on superconductivity. The local distortion of the lattice caused by uniaxial pressure does not influence the strength of these charge correlations. Moreover, CDW does not significantly impact the lattice dynamics observed through the optical phonons. However, under magnetic field and at sufficiently low temperatures, these charge correlations reconstruct the Fermi surface into a small electron pocket. Notably, the presented results are consistent with the empirical model of superconductivity proposed in 2019 by Pelc *et al.* (Science Adv., 5(1), 4538), where the pairing is associated with an excitation of *one* localized carrier per CuO2 unit cell.

Content of the thesis

The dissertation consists of 8 chapters, including the Appendix. The document contains the introduction to the research area, including a compact description of the motivation, presentation of the experimental results, and summary. Each chapter starts with a description of the experimental technique(s) relevant for the chapter.

In chapter 1, the main concepts related to high-temperature superconductivity are presented. The chapter summarises selected experimental results which were reported over the past years, and which yielded the empirical model for the cuprates, according to which a gradual charge carrier localization is responsible for the strangeness of these compounds, including superconductivity. Here, also the motivation and main objectives of the work are presented.

The experimental part of the thesis begins in chapter 2 with a detailed characterization of the CDW order in the normal and superconducting states. This includes the temperature and doping dependence of the CDW order in the model hole-doped cuprate $HgBa_2CuO_{4+\delta}$ (Hg1201) studied by means of Cu *L*-edge resonant elastic X-ray scattering technique at synchrotron BESSY II in Berlin. The basic properties of this charge order, i.e., correlation length, amplitude, or wavelength are discussed. In particular, the regime where the CDW order coexists with superconductivity is of particular interest as it helps to understand the interplay between the two.

The studies presented in chapter 3 are aimed to resolve the debate regarding the mechanism of the Fermi surface reconstruction in cuprates at intermediate dopings (around 10%). On one hand, the short-range CDW order was proposed in the literature to be responsible for the Fermi surface reconstruction when superconductivity is suppressed by sufficiently high magnetic fields and the charge correlations are sufficiently enhanced. This scenario was contradicted after the discovery of a new type, also magnetic field induced three-dimensional (3D) CDW order. To resolve this dispute and to shed light on the formation of the 3D CDW order, hard X-ray absorption studies of Cu *L*-edge in double-layered $YBa_2Cu_3O_{6+d}$ (YBCO) are presented. They are complemented by measurements performed on other single-layer compounds. These studies were performed under pulsed magnetic field up to 30 T at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The studies presented here support to the scenario where the initially short-range CDW order is enhanced as superconductivity is suppressed by the magnetic field, but at sufficiently high fields it causes the reconstruction of the Fermi surface.

Motivated by the discovery of a high-temperature dynamic precursor of the CDW order, inelastic X-ray scattering studies of lattice dynamics in electron-doped $Nd_xCe_{1-x}CuO_4$ (NCCO) were performed and presented in chapter 4. The measurements of phonon dispersion along the direction parallel to Cu-O bonds were performed with the aim to understand the impact of the charge correlations on the lattice dynamics. The presented analysis resolves the controversy regarding, in the literature suggested, softening of the optical phonons caused by the CDW order in NCCO. These presented results implies that the static CDW order has no considerable impact on the phonons, however the dynamical charge correlations cause a broadening of the optical phonon modes. Furthermore, the impact of the oxygen-copper-oxygen fluctuation on the phonons is discussed in the context of the carrier localization.

Chapter 5, summarises the study of the impact of uniaxial pressure on the ordered states in cuprates. Resonant X-ray scattering technique was employed (at BESSY II in Berlin) in combination with uniaxial pressure to study the influence of the lattice distortion on the strength of the CDW order in NCCO. In parallel, electronic transport measurements were performed to determine the impact of the lattice symmetry breaking on superconducting transition temperature. These studies were aimed to test the delicate balance between the CDW order and superconductivity. The application of uniaxial pressure allowed also to establish that the CDW order in NCCO is biaxial, in agreement with the study presented for Hg1201 in chapter 2. The experiments were performed alongside the extensive development of the uniaxial pressure apparatus.

In chapter 6, the impact of the uniaxial pressure on the relative occupancy of the doped holes within $2p_x$ and $2p_y$ oxygen orbitals is analyzed and discussed. Soft X-ray absorption studies of O *K*-edge and Cu *L*-edge in $La_{2-x}Sr_xCuO_4$ (LSCO) in combination with uniaxial pressure were performed at synchrotron SOLARIS in Kraków. The details of the near-edge absorption fine structure are analyzed as a function of the applied uniaxial strain, with the particular focus on two spectroscopic features; the mobile hole peak and the upper Hubbard peak. The main idea was to induce, via controllable strain, an asymmetry between initially equivalent lattice directions, and test if such distortion can induce relative changes in the electron density within $2p_x$ and $2p_y$ oxygen orbitals and, hence, establish if the oxygen-oxygen charge transfer within these orbitals is possible. The preliminary results presented in this chapter suggest that the carrier distribution within the hybridized O and Cu orbitals can be tuned by an orthorhombic distortion. To perform these studies the PhD candidate designed a uniaxial pressure cell, which can be adopted to various experiments in commercially available vacuum chambers.

Finally, the main results and the conclusions of this work are summarized in chapter 7.

Additionally, detailed information about the growth and characterization of the single crystals of cuprates used in this work are presented in the Appendix.

Main achievements

Izabela Biało conducted has chosen a very ambitious project for her PhD topic: the understanding of the unconventional superconductivity in cuprate superconductors. Needless to say, that this subject has been a great challenge to scientists for over three decades, without finding the solution. In this optics, the objective of the thesis is timely and the problems are well formulated. The work presented here contains a wide collection of experimental results obtained using complementary techniques, mainly synchrotron-based methods. The research was conducted not only at home laboratories (AGH-UST and TU WIEN) but also at three large-scale facilities (ESRF, BESSY II, and SOLARIS). The experimental results are well presented and discussed. The most important achievements of the thesis may be summarised as follows:

- Characterization of the CDW order across the temperature-doping phase diagram of the model cuprate Hg1201. This includes the estimation of the order's basic parameters such as correlation length, amplitude, or wavelength. The results allowed the author to establish the destructive influence of the CDW order on superconductivity, presumably by breaking the oxygen symmetry within the CuO_2 layer. Analysis of the evolution of the CDW order's wave vector with doping allowed to make a link between these charge correlations and the reconstruction of the Fermi surface observed previously in quantum oscillation and Hall effect measurements.
- Experimental demonstration that the emergence of the three-dimensional field-induced charge order in YBCO is linked to the presence of the Cu-O chains, specific to the crystal structure of this compound. Consequently, the results implies that these additional charge correlations are not generic to the cuprates, and thus cannot be responsible for the Fermi surface reconstruction that is also present in underdoped Hg1201.
- Establishing the phonon dispersion in NCCO and connecting it with the CDW correlations. The presented results demonstrate that the CDW correlations do not cause anomalous softening of the optical phonon modes, contrary to what was suggested in the literature. Instead, the local minimum in the dispersion is a result of two modes anticrossing, only coincidentally, close to the wave vector of the CDW order. However, a broadening of the optical mode, associated with the oxygen atoms vibrating along the Cu-O bonds, appears to be resulting from the electron-phonon interactions caused by the dynamical CDW order.
- Determination of the impact of the uniaxial pressure applied along the Cu-O bonds on the critical temperature, on *c*-axis resistance, as well as on the lattice distortion in selected cuprates. It was shown that the uniaxial pressure applied as a symmetry-breaking field successfully suppresses superconductivity in tetragonal NCCO. Importantly, the experiments conducted under uniaxial pressure revealed that the CDW order in NCCO is bidirectional *i.e.*, the periodic charge modulations span equally along the *a* and *b* crystallographic directions.
- Observation of the uniaxial pressure-induced transfer of the spectral weight from the O2*p* band to the upper Hubbard band, an effect which in some aspects is similar to the changes induced by decreasing the doping level. The preliminary results suggest that the carrier distribution within the hybridized O and Cu orbitals can indeed be tuned by a slight orthorhombic distortion, potentially influencing the process of Cooper pair formation.
- Finally, from the engineering point of view, the development of the various uniaxial pressure cells for electronic transport and X-ray scattering experiments is a great achievement. Four uniaxial pressure cells were developed and tested; three of them were designed adapted for resonant X-ray scattering experiments at BESSY II (one driven by a piezoelectric element, one driven by mechanical spring, and one driven by

pressurized He gas. Furthermore, an additional spring-driven cell was designed to perform XAS studies at SOLARIS, due to its universal design, it can be used in other X-ray facilities as well.

Criticism and questions

The PhD candidate performed a large number of experiments using state-of-the-art setups which cover several important aspects of cuprates superconductors. The obtained results are robust, well documented and the analysis are convincing. I highly appreciate them. Nevertheless, I have the impression, that the candidate is not proud enough of her results in order to clearly spell out the consequences (which are there) for the newly proposed model for superconductivity un this class of materials. But I guess, this is due to her character and not to her knowledge of the topic.

I understand, that the referee should ask specific questions of the candidate in written form which she should answer during the defence. Here are they:

- Why studying the CDW phenomenon is important to understanding the unconventional superconductivity in cuprates?
- How the obtained results can be placed in the broader context of the physics associated with the "localized carrier"? How are those connected with the superconductivity?
- Does the indicated model explain the properties of the cuprates across the phase diagram, or is it applicable only to the region where the CDW order is observed?
- Do the model and the obtained results imply the existence of a quantum critical point within the superconducting phase?
- Why the CDW correlations are reflected as anomalies of particular phonon branches?

Concluding remarks

The thesis submitted to the Faculty of Physics and Applied Computer Science of the AGH University of Science and Technology and the Institute of Solid State Physics of the TU Wien by Izabela Biało represents scientific work conducted at a very high level. It contains a large collection of experimental data which will certainly be of benefit for the scientific community that is working on the problems related to unconventional superconductivity. All experiments are well selected to address a set of well-defined scientific questions. The measurement techniques and methods are correctly applied. Thesis is generally well written and interesting to read.

In my opinion, the presented thesis fulfils all the requirements for obtaining a PhD degree. Hereby, I strongly recommend the dissertation of Izabela Biało to the Scientific Discipline Board for Physical Sciences of the AGH University of Science and Technology, and to the PhD Examination Committee of the Institute of Solid State Physics of the TU Wien for the public defense without any reservation.

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