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X-ray diffraction studies of charge density waves in cuprate superconductors: A brief review

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ABSTRACT

High temperature superconductivity in the cuprates has fascinated scientists for more than 25 years, but there is still no consensus on the pairing mechanism. Soon after the discovery of high temperature superconductivity, it was suggested that the cuprates have an incipient tendency towards spatial electronic order – spin and charge order. In this paper, I will review X-ray diffraction studies of charge density waves in the cuprates. These results, by a number of different groups, indicate that short-range charge correlations exist across the cuprate family, and in many cases are clearly competing with the superconductivity.

1. Introduction

The cuprate superconductors were discovered almost 30 years ago by Bednorz and Müller [1], and have remained a perennial subject of interest for condensed matter physicists ever since. It is known that the electrons form Cooper pairs [2], but, unlike the BCS superconductors, the superconducting gap displays *d*-wave symmetry, and the origin of the pairing mechanism remains a subject of debate.

The common feature of the cuprate superconductors, as the name indicates, is that they contain copper and oxygen. More specifically, all of the cuprates contain a CuO_2 plane. In this 'plane' layer, each copper is surrounded by four oxygens in the plane, with two apical oxygen atoms above and below it. These CuO_2 planes are thought to be the primary source of superconductivity, and the eventual origin of the *d*-wave nature of the superconductivity. To gain insight into the instabilities of these planes, numerous studies have been carried out on materials with similar arrangements; see Ref. [3] for a review of some of this work.

Simply having a CuO_2 plane is not *necessarily* sufficient for superconductivity to occur. Often, the number density of charge carriers per Cu has to be tuned to give rise to superconductivity. This is most commonly done by chemical doping, but can also be achieved by, e.g. applying pressure. Here, I concentrate on doping, and in particular on hole doping. Electron-doped cuprate superconductors are well known, but are not the focus of this review.

Charge carrier doping may be done by substitutional means, as in $La_{2-x}Sr_xCuO_4$ (LSCO), or by altering the oxygen content, as in $YBa_2Cu_3O_{6+x}$ (YBCO). By altering the number of charge carriers, one can then map out a phase diagram that is common across all of the hole-doped cuprate superconductors. With a low number density of charge carriers (extremely underdoped), a Mott insulating state forms, eventually giving way to a superconducting dome. The appearance of domes like these is often considered to be related to an underlying quantum critical point [4]. Above this dome is a normal state that displays a rich array of phenomena. When overdoped, Fermi liquid behaviour is seen. On reducing the number density of charge carriers this shifts to non-Fermi-liquid behaviour, and then in the underdoped region, it is dominated by the 'pseudogap' state [5]. It has been evident for some time that the normal state of the cuprates is susceptible to electronic and magnetic instabilities, as indicated by the extensive literature on charge and magnetic stripes, although such instabilities had not been observed in all members of the family. For a brief review, see Ref. [6].

Driven by improvements in sample quality in this region [7] by multiple groups, a number of experimental studies, using many different techniques, have investigated the pseudogap region in more detail. It has become clear from the ensemble of results that *inside* the pseudogap region, incommensurate charge correlations develop, and that this is a common feature of the cuprate superconductors. This paper will focus on the X-ray diffraction measurements in this region, up to August 2014.

2. Charge density waves and superconductivity

Before discussing the recent results, a short consideration of charge density waves (CDWs) is appropriate. The usual starting

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point for this is the 1-D Peierls instability, where the energy of a 1D electron gas is lowered by the introduction of a gap at the Fermi surface, by introducing a real space modulation with the appropriate wavevector. Ref. [8] provides a good review of this topic.

In this picture, the lattice is coupled to the electrons, through electron–phonon coupling, and so distorts. In practice, it is not possible to decouple the lattice and the electrons, and the electronic distortion [9].

This means that the electron–phonon coupling plays a very important role in the development of a charge density wave state, and two regimes exist: strong and weak coupling. An accessible approach to this may be found in Ref. [10]. The weak coupling case strongly resembles the original Peierls argument, with electronic energy gain occurring primarily at the Fermi surface. In the strong coupling case, the electronic energy gain is spread across the Brillouin zone, due to strong distortions of the electron dispersion.

In a superconductor, a gap forms when the electrons at the Fermi surface pair up in momentum space, rather than real space. For BCS superconductors, this pairing is driven by the electron–phonon coupling, as the phonons provide the glue for the formation of the Cooper pairs. There are several materials where the Fermi surface is gapped by charge density wave formation, and then subsequently develops a superconducting gap – the most well known is $NbSe_2$. Here, the typical observation is of competition between the superconductivity and the charge density wave state. For the cuprate superconductors, the nature of the pairing mechanism is not so clear, but one can still map out the electron–phonon coupling.

3. Diffraction studies

Charge density modulations were initially observed in YBCO by diffraction using two primary techniques:

- resonant soft X-ray scattering at the Cu *L*-edge [11–14]. This technique is particularly sensitive to the displacements associated with the Cu ions, but can only examine a limited portion of reciprocal space, due to the wavelength of the X-rays at the Cu *L*-edge (~ 15 Å). Achkar et al. [12] use this sensitivity to localize the charge density modulation on the planar Cu ions only.
- hard X-ray diffraction, at X-ray energies equal to or greater than 80 keV [15–17]. With this technique, a much larger region of reciprocal space is experimentally accessible, but the observed scattering is dominated by the more massive elements in the material.

Similar evidence for a charge density wave state has been observed in $Bi_2Sr_{2-x}La_xCuO_{6+x}$ (Bi2201) [18], $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi2212) [19], $Bi_{1.5}Pb_{0.6}Sr_{1.54}CaCu_2O_{8+\delta}$ [20], LSCO [21], $HgBa_2CuO_{4+d}$ (Hg1201) [22], using Cu *L*-edge resonant X-ray scattering, and in LSCO using high energy X-rays [23–25]. Tabis et al. report no sign of the charge density wave in Hg1201 using hard X-ray diffraction [22]. Charge density waves have also been seen in related weakly- or non-superconducting cuprates such as $La_{2-x}Ba_xCuO_4$ (LBCO) [26,27] and $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ (Eu-LSCO) [11,28].

The charge density wave state discussed here has been observed in multiple STM measurements; a direct comparison is made in Ref. [29], and further references can be found therein.

Inelastic X-ray and neutron scattering studies have probed the electron–phonon coupling at the wavevectors associated with the charge density wave. The work by Le Tacon et al. [30] provides a good introduction to this work.

In the following sections, I will concentrate primarily on the diffraction studies, with YBCO as the primary subject, as it has been the most densely studied material.

3.1. Short range ordered charge density wave state

Both soft and hard X-ray techniques observe the same broad features in all materials: two ordered electronic modulations with ordering wavevectors $\mathbf{q}_1 = (q_h, 0, 0.5)$ and $\mathbf{q}_2 = (0, q_k, 0.5)$, where $q_{h/k} \sim 0.3$ and is incommensurate, with no evidence for a lock-in transition. The Bragg peaks associated with these modulations are of the order of 1×10^{-6} of a typical strong structural Bragg peak in the relevant compound. High-resolution inelastic X-ray scattering indicates that the energy width of the Bragg peak is < 0.3 meV [31].

3.2. Temperature dependence

The Bragg peak associated with the modulation appears at a temperature below the onset of the pseudogap, but above T_C, and grows in intensity smoothly with a concave upwards shape to a maximum amplitude at T_C in zero field. This means that the actual onset temperature can be difficult to identify, and this presumably arises because of the fluctuating nature of the charge density wave observed. Below T_C, the Bragg peak intensity disappears as the superconductivity order parameter grows, although this effect is significantly less pronounced in Hg1201, Bi2201 and Bi2212. It is clear that the charge density wave state is competing with the superconductivity. When a magnetic field is applied, the maximum Bragg peak intensity is observed at the onset of the vortex liquid state [15,23]. The onset temperature varies with doping, with a maximum close to 1/8th doping [14,17,24].

3.3. Correlation lengths

The Bragg peak width can be used to extract the correlation lengths. The in-plane correlation length increases as the Bragg peak intensity increases, and so is maximal at T_C in zero field. For YBCO, this is ~ 70 Å, whereas for LSCO, Hg1201 and Bi2201 it is ~ 20–30 Å. As the superconductivity is destroyed by magnetic field, this correlation length decreases.

The out-of-plane correlation length is very short in all cases, indicating that the scattering is 'rod-like' rather than 'peak-like'. Where directly measured (YBCO [15], LSCO [23,24]), this correlation length is of the order 5–10 Å.

3.4. The CDW wavevector and the Fermi surface

The in-plane component of the CDW wavevector decreases monotonically as the hole doping is increased (the *L* component remains unchanged). For overdoped single-layered cuprates, the Fermi surface consists of a large cylindrical sheet; the volume is set by the doping of the CuO_2 plane [32–34].

YBCO is a bilayered cuprate, and so this sheet is split into bonding and anti-bonding surfaces, and further complicated by the existence of 1-D sheets from additional Cu–O layers. Nonetheless, the same principles regarding the volume change with doping apply. Using band-structure calculations of the in-plane Fermi surface by Carrington and Yelland [35], and ignoring any potential reconstruction due to the pseudogap, $q_{h/k}$ appear to be nesting vectors linking the squared-off sides of the cylinder. The length changes observed by experiment match with the expected changes due to the doping level. This is backed up further by the recent work on the single-layered Hg1201 by Tabis et al. [22], where the observed in-plane wavevector for Hg1201 fits the same