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Stephen Edkins

Visualising the Charge and Cooper-Pair Density Waves in Cuprates

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Stephen Edkins

Visualising the Charge and Cooper-Pair Density Waves in Cuprates

Doctoral Thesis accepted by
the University of St Andrews, St Andrews, Scotland, UK

Springer

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In memory of my father, David John Edkins (1947–2007), who fostered my interest in science and technology.

Supervisor's Foreword

It was a great pleasure to co-supervise Stephen Edkins for his Ph.D. studies. We have collaborated for over a decade now and are always on the lookout for exceptionally talented graduate students. Our joint projects are very demanding both technically and because they require splitting the student's Ph.D. time between the UK and the USA. Stephen had an exemplary record as an undergraduate at the University of Cambridge, so when he applied to work on a joint project that we were offering to do spectroscopic imaging scanning tunneling microscopy (SI-STM) of cuprate and ruthenate superconductors, we were delighted to invite him to join the team. He first excelled on his graduate courses at the Scottish Centre for Doctoral Training in Condensed Matter Physics in St Andrews, and there he also performed useful finite element calculations that helped with the design of novel uniaxial pressure apparatus.

After that first year at St Andrews, Stephen moved to Cornell to begin working on the SI-STM projects. Atomically resolved visualization of electronic structure using standard single-electron tunneling allowed him to obtain important results on the symmetry of the famous density wave state that is the wide focus of studies in lightly doped cuprate superconductors. Stephen played a key role in establishing that this density wave has a *d*-symmetry form factor, a state that has never been observed in any other system or material. He showed that this exotic form factor exists not just at zero magnetic field but also in the density wave that can be induced within vortex cores. Not content with this, he also obtained excellent data from the superconductor Sr_2RuO_4 at dilution refrigerator temperatures.

In spite of the quality of the data obtained in all three of the above projects, in the end Stephen elected not to include the vortex core or Sr_2RuO_4 work in his thesis. This is because of a serendipitous development. During the project on the cuprates, he and his collaborator Mohammed Hamidian managed to pick up a nanoscale flake of high-temperature superconductor and have it terminate the standard tungsten STM tip. They recognized that this situation allowed them to form Josephson tunnel junctions with nanometer resolution so that, if such tips can be scanned stably, visualization of the superconducting condensate based on Cooper-pair tunneling would become possible for the first time. This discovery opened the way to an entirely new class of instrument, a scanned Josephson tunneling microscope (SJTM). But this unanticipated project came with all the challenges associated with pursuing unprecedented research directions. With no literature comparisons to work from, the team had to understand what regime the Josephson junctions were operating in, and establish what classes of information the new SJTM could yield. Stephen's contributions to this were pivotal, and the comprehensive and didactic description that he has provided in this thesis will, we believe, underpin this new field as it moves forward.

As well as describing and developing the new instrument, Stephen's measurements revealed a periodically modulated superconducting condensate with a wavelength of a few nm in cuprates. Spatially modulated superconductivity was first postulated theoretically half a century ago, and also features prominently in coupled order parameter theories of high-temperature superconductivity; the data presented in Chap. 7 of this thesis are the first experimental observation of its existence.

We have both been privileged to supervise many outstanding graduate students, but few achieve something as novel and substantial as Stephen did on this project. This is one of the best PhD theses that we have supervised or read, and we are delighted to see it recognized in this way by Springer.

St Andrews, Scotland, UK

Prof. J.C. Davis
Prof. A.P. Mackenzie

Abstract

The study of cuprate high-temperature superconductors has undergone a recent resurgence due to the discovery of charge order in several families of cuprate materials. While its existence is now well established, little is known about its microscopic origins or its relationship to high-temperature superconductivity and the pseudogap. The aim of the research presented in this thesis is to address these questions.

In this thesis, I will report on the use of spectroscopic imaging scanning tunneling microscopy (SI-STM) to visualize the short-ranged charge density wave (CDW) in $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Na_xCa_{2-x}CuO_2Cl_2$. Building on previous measurements of the intra-unit-cell electronic structure of cuprates, I introduce sub-lattice segregated SI-STM to individually address the atomic sub-lattices in the CuO_2 plane with spatial phase sensitivity. Using this technique, I establish that the CDW in $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Na_xCa_{2-x}CuO_2Cl_2$ has a previously unobserved *d*-symmetry form factor, where a breaking of rotational symmetry within the unit cell is modulated periodically in space.

Toward identifying a mechanism of CDW formation, I establish that the amplitude of CDW modulations in the electronic structure is maximal at the pseudogap energy scale and that these modulations exhibit a spatial phase difference of π between filled and empty states. Together with the doping evolution of the CDW wave vector, this highlights the role of the low-energy electronic structure of the pseudogap regime in CDW formation.

To elucidate the relationship between the CDW and the superconducting condensate, I will introduce nanometer resolution scanned Josephson tunneling microscopy (SJTM). In this approach, the Cooper-pair (Josephson) tunneling current between a $Bi_2Sr_2CaCu_2O_{8+\delta}$ sample and a scannable $Bi_2Sr_2CaCu_2O_{8+\delta}$ nano-flake STM tip is used to directly visualize the superconducting condensate. I will report the observation of a periodic modulation in the Cooper-pair condensate at the same wave vector as the CDW, the first direct detection of a periodically modulating condensate in any superconductor.

Acknowledgements

I would first and foremost like to thank my supervisors Séamus Davis and Andy Mackenzie for their support and guidance, as well as teaching me a great deal. I have benefited greatly from the research environment in both of their groups, of which membership has been a privilege.

The research presented in Chap. 4 of this thesis was carried out in close collaboration with Mohammad Hamidian and Kazuhiro Fujita to whom I extend my gratitude for sharing their expertise in spectroscopic imaging STM. The research presented in Chaps. 5 and 7 was conducted in collaboration with Mohammad Hamidian and Andrey Kostin. I thank Mohammad for his tutelage in the operation of a cryogenic STM.

The idea of examining the difference between the oxygen sub-lattices of the CuO_2 plane in SI-STM spectroscopic maps to reveal a *d*-symmetry form factor CDW was originally suggested by Subir Sachdev. I would like to thank him for sharing this with us as well as for useful discussions. I would also like to thank Andrey Chubukov for his very useful comments in the preparation of Chap. 6.

Finally, I would like to thank all of my colleagues past and present for their help, advice, and friendship, as well as my family for their love and support.

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Contents

Chapter 1
Introduction to Unconventional Superconductivity and Density Waves in Cuprates

Superconductors, known for their ability to conduct electricity without resistance, are fairly common in nature. This is a result of the fact that, despite the strong interactions between their electrons, most of the metals we know can be described by a liquid of electron-like quasi-particles. This liquid, known as a Fermi liquid, is intrinsically unstable to the formation of superconductivity. The vast majority of these superconductors only superconduct below a transition temperature which is within a few degrees of absolute zero, limiting their widespread commercial exploitation.

This thesis concerns a family of superconductors whose superconducting transition temperatures were unprecedentedly high upon their discovery by Bednorz and Muller in 1986 [1]. These materials, known as cuprates because their common constituents are copper and oxygen, won Bednorz and Muller the 1987 Nobel Prize for Physics for their discovery [2]. Although the cuprates lost their status as the highest temperature superconductors in the past couple of years to hydrides at ultra-high pressures, they retain the name "high temperature superconductors" and are still a system of unparalleled interest [3]. The high transition temperatures of the hydrides seems to be well understood in terms of extensions of traditional theory, but the mechanism of the more exotic superconductivity in cuprates is still the subject of active debate.

In addition to superconductivity, the cuprates also exhibit what is called a charge density wave (CDW). In a CDW the charge density in the material modulates with a periodicity that is different from that of the material's crystal structure. In this thesis I utilise recent developments in scanning tunnelling microscopy (STM), and develop nanometer-resolution scanned Josephson tunnelling microscopy (SJTM) with the aim of elucidating the role of CDW in the physics of these materials.

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1.1 Superconductivity

1.1.1 What Is a Superconductor?

The concept of spontaneous symmetry breaking is a cornerstone of 20th century physics [4]. In condensed matter physics we have chosen to classify different phases of matter by the symmetries they break. If the state of a system is not invariant under an element of the symmetry group of the Hamiltonian to which it is a statistical solution, then it is said to break the corresponding symmetry.

As an example take a macroscopic number of particles in free space which interact with each other. The Hamiltonian which governs these particles is invariant under spatial translations. However, the particles could condense into a crystal. This is clearly a state which breaks translational symmetry as depicted in Fig. 1.1 in one dimension.

The crystal has broken translational symmetry by "choosing" where to fix the jth particle in space, the positions of the others following directly from the lattice constant a_0 in a perfect crystal. Any choice of position for this first particle would have resulted in a state with the same free energy. The crystal has spontaneously broken translational symmetry by its choice of a position for the jth particle from a degenerate manifold.

We can expand the density of particles in Fourier components,

$$\langle n(x)\rangle = n_0 + Re\{n_Q(x)e^{iQx}\} + \dots\ , \tag{1.1}$$

where $Q = 2\pi/a_0$. The complex field $n_Q(x) = |n_Q(x)|e^{i\,\arg\{n_Q(x)\}}$ is a sensible choice of order parameter for our crystalline phase. It will be zero above the melting temperature of the crystal and non-zero below. In this language, choosing a particular position for the jth particle corresponds to choosing a particular phase of $n_Q(x)$, $\phi(x) = \arg\{n_Q(x)\}$. This corresponds to spontaneously breaking a U(1) symmetry. The concept of spatial phase in a crystal will be a key theme in this thesis which I will return to in Chaps. 3 and 4, where the spatial phase sensitivity of spectroscopic-imaging STM (SI-STM) will be used to probe the intra unit cell electronic structure of cuprates.

Part of the utility of the classifying phases of matter by their broken symmetries is that the broken symmetry has an attendant generalised rigidity [4], i.e. a stiffness to

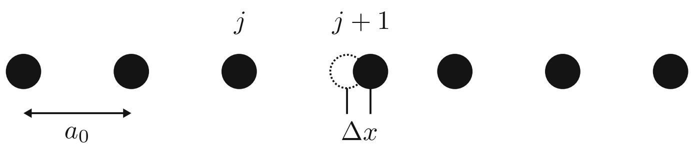

Fig. 1.1 Cartoon one-dimensional crystal with lattice constant a_0. The distance between the jth and $j+1$th particle is stretched by a distance Δx

spatial gradients in the order parameter. For the crystal there is a very tangible rigidity to changing the separation between any two atoms, akin to stretching a spring. If we consider the order parameter description of this crystal then we can recast this as a phase rigidity. To change the distance between two particles, j and $j+1$ by an amount Δx requires a phase gradient $\phi(x_{j+1}) - \phi(x_j) = Q\Delta x$, for which there is an energy cost.

If we make the constraint that the order parameter amplitude is spatially uniform so that $n_Q(x) = |n_0|e^{i\phi(x)}$ we can make the following expansion of the free energy

$$F[\phi(x)] = F_0 + \int dx K\,(\nabla\phi(x))^2 + \ldots \quad (1.2)$$

where K is a positive constant and F_0 is the energy of the uniform crystal. Here there is a clear energy cost to gradients in $\phi(x)$; a phase rigidity. Viewed this way, that fact that crystals behave like rigid bodies is a natural consequence of their phase stiffness, which in turn is a direct consequence of breaking translational symmetry.

For a superconductor the relevant broken symmetry of the Hamiltonian is a global phase symmetry. This is the invariance of the Hamiltonian under a transformation of the quasi-particle operators of the form $\hat{\psi}^{\dagger}(\vec{r}) \rightarrow e^{i\theta}\hat{\psi}^{\dagger}(\vec{r})$, as must be the case if the number of particles is conserved. What are the consequences of breaking this symmetry?

An order parameter describing this phase would be a complex scalar field of the form $\Psi(\vec{r}) = |\Psi(\vec{r})|e^{i\phi(\vec{r})}$. If this order parameter is non-zero then everywhere this state breaks the U(1) phase symmetry of the Hamiltonian. We can construct a Ginzburg–Landau expansion of the Helmholtz free energy functional in this order parameter

$$F[\Psi(\vec{r})] = \int d^3\vec{r}\alpha(T-T_c)|\Psi(\vec{r})|^2 + \frac{\beta}{2}|\Psi(\vec{r})|^4 + \frac{1}{2m}|\left(-i\hbar\nabla - 2e\vec{A}\right)\Psi(\vec{r})|^2 + \frac{|\vec{B}|^2}{2\mu_0} + \ldots \quad (1.3)$$

where $\vec{A}$ is the magnetic vector potential and $\vec{B} = \nabla \times \vec{A}$ [5]. This is the simplest expansion of an electrically charged complex scalar field that is gauge invariant. In anticipation of the microscopic description of a superconductor in terms of Cooper-pairs of electrons I have given the field a charge $2e$ where e is the electron charge. That the field is scalar implies that these Cooper-pairs are in a spin-singlet state. Below a critical temperature T_c the order parameter Ψ will become non-zero to minimise this free energy.

Now consider the case where the order parameter amplitude is everywhere constant so that $\Psi(\vec{r}) = |\Psi_0|e^{i\theta(\vec{r})}$. We can write the free energy functional as,

$$F[\theta(\vec{r})] = F_0 + \rho_s \int d^3\vec{r}\left(\nabla\theta(\vec{r}) + \frac{2e}{\hbar}\vec{A}\right)^2 + \ldots, \quad (1.4)$$

with F_0 the free energy of the uniform superconducting state and ρ_s, the superfluid stiffness, given by

$$\rho_s = \frac{\hbar^2}{2m}|\Psi_0|^2 \, . \tag{1.5}$$

It is informative at this point to revisit the discussion of crystallisation and the analogies that can be drawn between that process and the formation of the superconducting condensate. The 1D crystal considered above breaks a global U(1) symmetry by choosing a lattice phase. This broken symmetry results in a generalised rigidity, a rigidity against deforming the inter-particle separation from its equilibrium value. This can be expressed as a phase stiffness. This phase stiffness essentially defines this 1D crystalline state of matter.

The same is true of the superconductor. It breaks a U(1) phase symmetry resulting in a stiffness, ρ_s, to gradients in the phase of the order parameter $\theta(\vec{r})$. Below I will show that the physical properties of a superconductor follow immediately from this broken phase symmetry and its resultant phase stiffness. This phase stiffness is the defining property of a superconductor.

Making a Legendre transformation, $g = f - \mu_0 \vec{H} \cdot \vec{B}$, of Eq. 1.4 to the Gibbs free energy and minimising with respect to variations $\delta\vec{A}$ yields a current

$$\vec{j}_s = -\frac{2e}{\hbar}\rho_s \left(\nabla\theta(\vec{r}) + \frac{2e}{\hbar}\vec{A} \right) \, . \tag{1.6}$$

This expression has profound consequences.

The first is that superconductors should expel magnetic flux from their bulk: the Meissner effect [6]. To see this we can take the curl of both sides resulting in the following differential equation for the magnetic field

$$\nabla^2 \vec{B} = \frac{\vec{B}}{\lambda^2} \, , \tag{1.7}$$

where $\lambda = \sqrt{\hbar^2/4\mu_0 e^2 \rho_s}$ is a phenomenological constant called the penetration depth. This implies that magnetic fields must exponentially decay into the bulk of a superconductor over a length scale λ. Thus superconductors expel magnetic fields from their bulk.

To act as perfect diamagnets and expel magnetic fields from their bulk, superconductors must produce screening currents that oppose an applied magnetic field. These must be equilibrium currents, implying that they experience zero resistance. These zero resistance equilibrium currents suggest the possibility of non-equilibrium currents with zero resistance which are a hallmark of superconductivity and give it its name.

A zero resistance transport current, the passing of current without any voltage dropped, was measured by Kamerlingh Onnes in mercury in 1911, heralding the discovery of superconductivity [7]. Clearly this property is remarkable and of great technological importance. However, it is not fundamental to superconductivity in the way that the equilibrium screening currents of the Meissner effect are.

1.1.2 BCS Theory of Superconductivity

Having considered what a superconductor is from a phenomenological point of view, I now turn to a microscopic description of such a state. Key insight into this came in 1957 with a paper from Bardeen, Cooper and Schrieffer, the exposition of what is now called the BCS theory of superconductivity [8].

Prior to this Cooper had shown that, in the presence of a Fermi surface and arbitrarily weak attractive interactions, two quasi-particles with opposite momenta are unstable to the formation of a bound state or Cooper pair. One way of demonstrating this instability of the Fermi liquid is to calculate the particle-particle (pairing) susceptibility within the random phase approximation (RPA),

$$\chi_{pp}(\vec{q},\omega) = \frac{\chi^0_{pp}(\vec{q},\omega)}{1 + g\chi^0_{pp}(\vec{q},\omega)}\,, \tag{1.8}$$

which measures the response to a field that acts to pair particles [9]. Here g is an effective point-like interaction between Fermi liquid quasi-particles with spin σ of momentum $\vec{k}$ and energy $\epsilon_{\sigma,\vec{k}}$. χ^0_{pp} is the bare (non-interacting) susceptibility,

$$\chi^0_{pp}(\vec{q}=0,\omega) = \frac{1}{\Omega}\sum_{\vec{k}} \frac{f(\epsilon_{\sigma,\vec{k}}) - f(-\epsilon_{\sigma-\vec{k}})}{\hbar\omega - \epsilon_{\sigma,\vec{k}} - \epsilon_{-\sigma,-\vec{k}} + i0^+}\,, \tag{1.9}$$

where $f(\epsilon_{\sigma,\vec{k}})$ is the occupation factor of a quasi-particle state labelled by $\vec{k}$ and σ and Ω is the volume of the system.

In the limit where $\omega, \vec{q} \to 0$

$$\chi^0_{pp}(\vec{q}=0,\omega=0) \sim N(\epsilon=0)\log(\Lambda/T)\,. \tag{1.10}$$

Here $N(\epsilon=0)$ is the density of states of the Fermi energy and Λ is an ultra-violet cut-off [9]. Equation 1.10 shows that $\chi^0_{pp}(\vec{q}=0,\omega=0)$ is positive and logarithmically divergent with decreasing temperature. This results from the fact that, in the presence of time reversal symmetry, $\epsilon_{\sigma,\vec{k}} = \epsilon_{-\sigma,-\vec{k}}$. Examination of Eq. 1.8 then shows that for any arbitrarily small attractive interaction ($g < 0$) the particle-particle susceptibility will diverge at non-zero temperature. This signals an intrinsic instability of the metal towards forming Cooper pairs.

In the simplest case, the wave-function of the Cooper-pair can be written as a product of orbital and spin parts. Anti-symmetry under exchange then dictates that if the pair is in a spin-singlet state it must have an even parity orbital wave-function. If the pair is a spin-triplet state it must have an odd parity orbital wave-function. If we were to expand the orbital wave-function in spherical harmonics (which is valid in free space), spin-singlet pairs will have angular momentum quantum number $l = 0, 2, \ldots$ which we call *s*- and *d*-wave respectively, by analogy with the orbitals of the hydrogen atom. Likewise, spin-triplet superconductors will have $l = 1, 3, \ldots$ corresponding to p- and f-wave respectively.

With the insight that the Fermi liquid is unstable to the formation of Cooper-pairs in the presence of an attractive interaction, Bardeen, Cooper and Schrieffer considered the equivalent of the Hamiltonian,

$$\hat{H} = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}\sigma} + \sum_{\vec{k}\vec{q}} V_{\vec{k}\vec{q}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} \hat{c}_{-\vec{q}\downarrow} \hat{c}_{-\vec{q}\uparrow}, \tag{1.11}$$

where

$$V_{\vec{k}\vec{q}} = \begin{cases} -V & \text{if } |\epsilon_{\vec{k}}| \text{ and } |\epsilon_{\vec{q}}| \leq \hbar\omega_c \\ 0 & \text{otherwise} \end{cases} \tag{1.12}$$

so that there is an attractive interaction between quasi-particles up to a energy cut-off $\hbar\omega_c$ away from the Fermi energy. It is manifest in the form of the interaction chosen that any Cooper pairs formed will be of the spin-singlet type and thus must have an even parity orbital wave-function.

Anticipating the formation of a condensate of Cooper-pairs BCS introduced the variational wave-function,

$$|\Psi_{BCS}\rangle = \prod_{\vec{k}} \left(|u_{\vec{k}}| + |v_{\vec{k}}| e^{i\theta} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} \right) |0\rangle \ , \tag{1.13}$$

where $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$, θ is an arbitrary phase factor and $|0\rangle$ corresponds a sea of Fermi liquid quasi-particle states filled up to the Fermi wave-vector $\vec{k}_F$ [8]. This many-body wave-function takes the form of a superposition of a filled Fermi surface plus a Fermi surface with 0, 1, 2,…Cooper pairs. Making a connection with the previous section, this is a coherent state of Cooper pairs, with minimum uncertainty in the phase and indefinite particle number. It thus manifestly breaks phase symmetry and we can associate θ with the phase of the condensate.

BCS went on to find the parameters $u_{\vec{k}}$ and $v_{\vec{k}}$ of the ground state by the variational method. In Chap. 2 we will need to calculate the single-particle tunnelling current between a superconductor and either a normal metal or another superconductor. For this we will need to know the single-particle excitation spectrum of the superconductor. To calculate this one can follow Bogoliubov [10] who considered the following mean-field decoupling of Eq. 1.11

$$\hat{H} = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}\sigma} + \sum_{\vec{k}\sigma} \Delta_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} + \Delta^{*}_{\vec{k}} \hat{c}_{-\vec{k}\downarrow} \hat{c}_{-\vec{k}\uparrow} \ , \tag{1.14}$$

with mean-field $\Delta_{\vec{k}}$ given by the self-consistency condition

$$\Delta_{\vec{k}} = \sum_{\vec{q}} V_{\vec{k}\vec{q}} \langle \hat{c}_{-\vec{q}\downarrow} \hat{c}_{\vec{q}\uparrow} \rangle \ . \tag{1.15}$$