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Quasiparticle Coherence, Collective Modes, and Competing Order in Cuprate Superconductors

By

James Patrick Hinton

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Joseph Orenstein, Chair
Professor James Analytis
Professor Tanja Cuk

Spring 2014
Quasiparticle Coherence, Collective Modes, and Competing Order in Cuprate Superconductors

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James Patrick Hinton
Abstract

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University of California, Berkeley

Professor Joseph Orenstein, Chair

In recent years, the study of cuprate superconductors has been dominated by the investigation of normal state properties. Of particular interest is the nature of interactions between superconductivity and other incipient orders which emerge above the superconducting transition temperature, $T_c$. The discovery of charge density wave (CDW) correlations in YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) and HgBa$_2$CuO$_{4+d}$ (Hg-1201) has established that some form of charge order is ubiquitous in the cuprates. In this work, we explore the non-equilibrium dynamics of systems which sit near the boundary between superconductivity and competing orders.

Ultrafast pump-probe spectroscopy is ideally suited to the study of competing order. Exciting the sample with an optical pulse perturbs the system from equilibrium, altering the balance between the co-existing orders. The return to equilibrium is then monitored by a time-delayed probe pulse, revealing multiple decay processes as well as collective excitations. We first apply this technique to Hg-1201, conducting a detailed study of the phase diagram. At temperatures near $T_c$, the pump pulse induces a non-equilibrium quasiparticle population. At $T_c$ we observe a doping-dependent peak in the relaxation time of these quasiparticles which we associate with a divergence in the coherence time of the fluctuating CDW. Using heterodyne probing in the transient grating geometry, we are able to disentangle the transient
reflectivity components associated with superconductivity and the pseudogap, demonstrating competition across the phase diagram. We also discuss the observation of a sharp transition in the nature of the pseudogap signal at $\sim 11\%$ doping.

In YBCO, we explore the temperature and doping dependence of coherent oscillations excited by the pump pulse. We associate these oscillations with the excitation of the CDW amplitude mode, and model their temperature dependence within the framework of a Landau model of competing orders.

We conclude with an investigation of pseudogap dynamics in the electron doped compound Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ as a function of temperature and doping. Near optimal doping, we observe the impulsive excitation of a critically damped mode, with time-temperature scaling consistent with quantum-critical fluctuations. This mode competes with superconductivity in a dynamical fashion, such that the suppression of this mode below $T_c$ can be lifted via photo-evaporation of the superconducting condensate.
For my grandparents.
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Chapter 1

Introduction

The search for high temperature superconductivity in transition-metal oxides was begun in earnest by J. Georg Bednorz and K. Alex Müller in late 1983 [11]. Working at the IBM research laboratory in Zurich, Switzerland, they synthesized the first polychristaline samples of hole-doped Ba$_x$La$_{5-x}$Cu$_5$O$_{5(3-y)}$ in the fall of 1985. In late January of 1986, they discovered that this material displayed superconductivity below a record high transition temperature ($T_c$) of approximately 30 K [12], for which they were awarded the 1987 Nobel Prize in physics. This sparked an explosion of research on the synthesis of copper-oxide superconductors, culminating in the so-called "Woodstock of Physics" at the APS March Meeting in 1987. Within a few years the highest achievable transition temperature sky-rocketed to 135 K under ambient conditions and over 150 K at high pressures in HgBa$_2$Ca$_2$Cu$_3$O$_{1+x}$. Unfortunately, this rapid rise in $T_c$ was not accompanied by a complete understanding of the physics governing high $T_c$ superconductivity.

The Cuprate superconductors are characterized by a quasi-two-dimensional structure of weakly coupled Cu-O planes. The undoped parent compound is an antiferromagnetic Mott insulator, which acquires a superconducting ground state when doped with charge carriers. The emergence of superconductivity from a parent state dominated by Coulomb repulsion between electrons necessitates that any theory of high $T_c$ superconductivity must be grounded in an understanding of the behavior of strongly-correlated electrons [60]. In this spirit, theories were developed which emphasized the roles of interactions between electrons in localized Cu states [5] and interactions between hybridized Cu-O orbitals [97, 31].
However, over the next decade and a half a number of refined experimental probes, including neutron scattering [94], angle-resolved photo-emission spectroscopy (ARPES) [86], and scanning-tunnelling microscopy (STM) [49], revealed a rich variety of phenomena which proved resistant to description within a single theoretical framework. This situation still persists, with the discovery of new phenomena in the cuprates occurring with regularity.

1.1 Recent Developments in the Study of Cuprate Superconductors

There have been two areas of intense focus in recent cuprate research. One is the properties of the pseudogap, an ill-defined yet ubiquitous region of the phase diagram which separates the "strange metal" phase at high temperatures from the superconducting phase at low temperatures. There has been a long standing debate over the nature of this state, which some advocating for a "pre-formed pairs" scenario of phase-incoherent Cooper pairs, while others argue that the pseudogap represents a distinct thermodynamic phase. Recent observations of broken symmetries accompanying the formation of the pseudogap have shifted the consensus towards the latter.

Perhaps the most compelling piece of evidence for a thermodynamic phase transition comes from ultrasound attenuation measurements [85]. In these experiments, the frequencies and line-widths of absorption resonances are tracked as a function of temperature, revealing discontinuities at thermodynamic phase transitions. In YBa$_2$Cu$_3$O$_{6+\delta}$ (YBCO), these measurements revealed a line of phase transitions at the pseudogap onset temperature $T^\ast$ which penetrate into the superconducting dome, terminating at a quantum-critical point near optimal doping.

In addition to this evidence of a phase transition, there is mounting evidence for the breaking of time-reversal symmetry at $T^\ast$. In spin-flip neutron scattering, the diffraction of a beam of polarized neutrons can be divided into two channels: spin-flip and spin-preserving. By comparing the temperature dependence of the diffraction peaks in these two channels, the onset of magnetic order can be identified. In a variety of cuprate compounds [101, 22, 32], this experiment revealed the onset of a spin flip neutron scattering signal at the Bragg
peak, corresponding to \( q = 0 \) magnetic order. This has been interpreted as evidence for intra-unit cell current loops or antiferromagnetism. Time-reversal symmetry breaking is also suggested by the onset of optical non-reciprocity in polar-Kerr rotation measurements [102]. A direct comparison of polar Kerr, ARPES, and time-resolved reflectivity was made in single layer Pb\(_{0.55}\)Bi\(_{1.5}\)Sr\(_{1.6}\)La\(_{0.4}\)CuO\(_{6+\delta}\) (Bi-2201), indicating that optical non-reciprocity is accompanied by the opening of a particle-hole asymmetric gap and the onset of a photo-induced reflectivity transient at \( T^* \) [47].

The other recent area of focus has been the existence of various forms of charge order which compete with superconductivity in the underdoped cuprates. In YBCO, measurements of the Hall resistance [59] and quantum oscillations [26] indicated the existence of electron-pockets at low temperatures and high magnetic fields. This observation suggests that the Fermi surface is reconstructed by translation symmetry-breaking order. Nuclear magnetic resonance revealed that this symmetry breaking involved static charge ordering at magnetic fields strong enough to destroy superconductivity [101]. Finally, an unambiguous detection of fluctuating charge order which competes with superconductivity in YBCO was reported using both elastic X-ray scattering [17] and resonant-inelastic X-ray scattering (RIXS) [38]. These observations, combined with previous observations in other cuprate compounds [49, 94], indicate that some form of charge order is a universal feature of the cuprate superconductors. Various theoretical proposals have been presented which attempt to unify the pseudogap and charge-order phenomenology within a single theoretical framework involving antiferromagnetic correlations [21, 46, 99].

In this work, we will provide evidence of the interplay between superconductivity, charge order, and the pseudogap in both hole-doped and electron-doped cuprates using time-resolved reflectivity measurements.

1.2 Organization of this Thesis

This thesis is organized as follows: In Chapter 2, a brief history of ultrafast laser technology and an overview of its applications is provided. This is followed by a discussion of the basic theory of pump-probe reflectivity, focusing on the relationship between observed changes in reflectivity and the underlying modification of the dielectric function.
1.2. ORGANIZATION OF THIS THESIS

Chapter 3 contains begins with a discussion of the phenomenology of pump-probe experiments in the cuprates. We then move on summarize the features of the HgBa$_2$Cu$_1$O$_{6+\delta}$ material system, and the advantages of studying this especially simple cuprate superconductor. The pump-probe reflectivity data is presented and used to construct a phase diagram of the ultrafast optical response, which we then compare to that obtained from transport measurements. We observe the onset of a quasiparticle excitation coincident with the emergence of low energy Fermi-liquid conductivity, and a modification of the Drude conductivity upon entering the pseudogap phase. The pseudogap transition temperature $T^*$ obtained from reflectivity runs tangent to the superconducting dome, in contrast to DC transport measurements, which terminate near optimal doping. We then present the phase-resolved transient grating data and use it to derive an understanding of the physical processes underlying the multi-component signals that we observe. These measurements demonstrate that the discrepancy between reflectivity and transport measurements of $T^*$ is due to the different energy scales accessed by these two probes. Lastly, we present the relaxation dynamics of photo-excited quasiparticles as a function of doping, temperature, and magnetic field, and we propose that their behavior can be described by a crossover from fluctuating charge density wave to superconducting coherence.

In chapter 4 we report the observation of coherent oscillations associated with charge density wave (CDW) order in the underdoped cuprate superconductor YBa$_2$Cu$_3$O$_{6+x}$ by time-resolved optical reflectivity. Oscillations with frequency 1.87 THz onset at approximately 105 K and 130 K for dopings of $x = 0.67$ (ortho-VIII) and $x = 0.75$ (ortho-III), respectively. Upon cooling below the superconducting critical temperature ($T_c$), the oscillation amplitude is enhanced, the phase shifts by $\pi$, and the frequency softens by $\delta \nu / \nu \approx 7\%$. A bi-quadratically coupled Landau-Ginzburg model qualitatively describes this behavior as arising from competition between superconducting and CDW orders.

We use pump-probe spectroscopy to measure the time-dependence of the photoinduced reflectivity $\Delta R$ in the electron-doped cuprate superconductor Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$ as a function of doping, temperature, and laser fluence in Chapter 5. We observe a strong doping dependence in the dynamics of the pseudogap signal. Focusing on the lightly overdoped sample with $x = 0.156$, we observe the onset of a negative $\Delta R$ signal at $T^* \approx 75$ K, above the superconducting transition temperature, $T_c$, of 23 K. The relatively slow decay of $\Delta R$, compared
to analogous signal in hole doped compounds, allows us to resolve time-temperature scaling consistent with critical fluctuations. A positive $\Delta R$ signal onsets at $T_c$ that we associate with superconducting order. We find that the two signals are strongly coupled below $T_c$, in a manner that suggests a repulsive interaction between superconductivity and another fluctuating order.
Chapter 2

Pump-Probe Reflectivity and Phase-Resolved Transient Grating Spectroscopy

Optical spectroscopy is perhaps the oldest quantitative probe of the microscopic properties of matter [98], and is ubiquitous in the natural sciences [15]. For many years, various forms of reflectance spectroscopy have been deployed with great success in the study of basic condensed matter systems including metals [30], semiconductors [80], and superconductors [40]. The invention of the dye laser in 1966 [83] enabled the use of sub-nanosecond pulses in applications such as nonlinear [61] and time-domain [79] spectroscopies. The major breakthrough which led to the proliferation of ultrafast optical techniques was the development of the Ti:Al₂O₃ (Ti:Sapph) laser in the mid 1980’s [76]. This led to an explosion of technological development in femtosecond optics such as time-domain THz and multidimensional spectroscopy techniques.

Femtosecond optical techniques are widely used in the study of the cuprates, with important results obtained via THz [18], pump-probe reflectivity [34], and pump-probe ARPES experiments [87]. In this work, we present the results of time-resolved reflectivity (TRR) and phase-resolved transient grating spectroscopy (TGS). The principles underlying these two techniques will be discussed below, but we will first give a brief summary of the mechanism of ultrashort pulse generation in Ti:Saph oscillators.
2.1 Ultrashort Pulse Generation in Ti:Sapph Oscillators

The key ingredient in the operation of any laser is population inversion, whereby an external energy source produces a higher population in the excited states of the lasing medium than in the ground state. This leads to a rate of stimulated emission of radiation which is higher than the rate of absorption, and the medium then acts as an optical amplifier. In the case of our KLM Ti:Sapph laser, population inversion is induced by a Spectra Physics Nd:YVO₃ pump laser. A cavity of length $L$ resonates at frequencies given by $\omega_n = n\pi c / L$. The other important properties of the laser are then $g(\omega - \omega_0)$, the frequency dependent gain of the Ti:Sapph crystal, and $l$, the roughly frequency independent loss of the cavity.

As shown in Figure 2.1(a), the emission spectrum of the laser is then given by a comb of frequency spikes with spacing $\Delta \omega = \pi c / L$ an amplitude envelope $E_0(\omega - \omega_0) = g(\omega - \omega_0) - l$, which cuts off when $g(\omega) < l$. These spikes have independent phases which vary randomly in the absence of other interactions, so the net electric field at a fixed point in the light path is given by

$$E(t) = \sum_n E_0(\omega - \omega_0) e^{i\omega_n t - \phi_n}$$  \hspace{1cm} (2.1)

In the random phase case, the laser intensity is constant. This is known as continuous-wave (CW) operation. If the phase of all of the frequency components can be made to match and the spacing $\Delta \omega$ is small, then this expression reduces to

$$E(t) = \sum_n E_0(t - n\Delta t) e^{i\omega_0 t}$$  \hspace{1cm} (2.2)

where $E_0(t)$ is the Fourier transform of $E_0(\omega)$ and $\Delta t = 2\pi / \Delta \omega = c / L$. This expression describes the series of optical pulses shown in Figure 2.1(b), which have a temporal width inversely proportional to the bandwidth, $\delta t = 1 / \delta \omega$.

This phase configuration is known as mode-locking, and can be achieved in a number of ways. In the case of our laser system, mode-locking stems from saturable absorption via the nonlinear Kerr effect. A quantitative description of this effect is complicated and beyond the scope of this summary. However, the basic physical concepts are relatively simple. The discussion in the previous paragraph neglected the effect of saturation on the gain medium, whereby the number of excited state electrons decreases as the rate of stimulated emission increases. This leads to a decrease in optical gain as the laser intensity in the cavity increases,
2.2. THEORY OF PHOTO-INDUCED REFLECTIVITY

Figure 2.1: (a) The frequency dependence of the gain $g(\omega)$ (red dash) and the loss $l$ (blue dash) is plotted, with the frequency dependent laser output shown as vertical black spikes. (b) The mode-locked output of the laser is shown in the time domain.

with equilibrium reached when the gain is equal to the loss. The nonlinear Kerr effect occurs when a material has an intensity-dependent index of refraction. This effect occurs in the Ti:Sapph crystal, and leads to a self-focusing of an intense laser beam within the crystal. The arrangement of the pump beam and the cavity beam in the Ti:Sapph crystal is such that the self-focusing improves the overlap between the two, effectively increasing the optical gain. Since the intensity of the mode-locked pulse is $\sim 2 \times 10^5$ times higher than that of the CW beam, this configuration favors mode-locking, causing the phase to self-align [100].

2.2 Theory of Photo-induced Reflectivity

We will now discuss the phenomenological framework for understanding the data collected by TRR and TGS measurements. In reflectivity experiments, the measured quantity is a real number $R$, where the reflected intensity $I_R = RI_0$. This reflectivity is the square of the modulus of the complex reflectance amplitude $\tilde{r}$. In TRR measurements, a pump pulse excites the sample and alters the dielectric function. In the limit of weak excitation, the
change in reflectivity after excitation can be written

\[ \Delta R = |\tilde{r} + \delta \tilde{r}|^2 - |\tilde{r}|^2 = |\tilde{r}| |\delta \tilde{r}| \cos(\phi_s) \]  

(2.3)

where \( \phi_s = \phi_r - \phi_{\delta r} \) is the phase angle between the equilibrium and photo-induced reflectances. This fundamentally limits traditional two-pulse pump probe experiments, which are insensitive to changes in reflectivity out of phase with the equilibrium reflectivity.

\[ \text{Figure 2.2: The four-beam boxcar geometry used to perform phase-resolved transient grating measurements. The LO is the probe beam whose phase is directly modulated in the experiment.} \]

This deficiency can be overcome via heterodyne detection of the probe electric field. This necessitates the spatio-temporal overlap of the reflected probe pulse with a local oscillator pulse with an adjustable phase. This is difficult to achieve in general, but emerges naturally in a TGS geometry \([42, 69]\). Figure 2.2 shows the four-beam "boxcar" geometry used in phase-resolved TGS measurements. In this experiment, the sample is pumped with a pair of identical pulses with a fixed phase relationship and relative angle. These pulses produce a sinusoidal grating of optical intensity at the surface of the sample, leading to a periodic grating of excitations. The sample is then probed by a pair of pulses with adjustable relative phase, and relative angle identical to the pump-pair. Each of the probe pulses is both diffracted and specularly reflected from the excitation grating. The boxcar geometry ensures that the first-order diffracted component of each beam emerges colinear with the reflected component of its partner. After interacting with the sample, the electric fields of these two
refracted-reflected pairs can be written as follows.

\[ E'_1 = (\tilde{r} + \delta \tilde{r})E_1 + \tilde{\eta} \delta \tilde{r} E_2 \]
\[ E'_2 = (\tilde{r} + \delta \tilde{r})E_2 + \tilde{\eta}^* \delta \tilde{r} E_1 \]  

(2.4)

\( E_1 \) and \( E_2 \) are the fields of the incident probe pulses, and \( \eta \delta \tilde{r} \) is the diffraction amplitude of the grating. The complex conjugate of \( \eta \) in the lower equation is due to the diffraction of the two beams into opposite orders. If \( E_1 \) is diffracted into the +1 order, then \( E_2 \) is diffracted into the −1 order. We explicitly write all parameters in terms of amplitudes and phases \( (\tilde{r} = re^{i\phi}) \), and keep only terms linear in \( \delta r \). The intensities recorded at a square law detector can be written

\[ I_1 = |E'_1|^2 = E_1^2 r \delta r \cos(\phi_s) + E_1 E_2 \eta r \delta r \cos(\phi_{LO} - \phi_\eta + \phi_s) \]
\[ I_2 = |E'_2|^2 = E_2^2 r \delta r \cos(\phi_s) + E_1 E_2 \eta r \delta r \cos(\phi_{LO} - \phi_\eta - \phi_s) \]  

(2.5)

where \( \phi_{LO} \) is the relative phase of the two incident probe beams and \( \phi_s = \phi_r - \phi_{\delta r} \), as defined previously. By comparing the dependence of each intensity on \( \phi_{LO} \), the phase of the sample can be determined unambiguously [37]. A detailed example of this analysis is given in Appendix B. This allows us access to the phase of the underlying photo-induced change of the optical conductivity.

The underlying quantity which is usually of interest in reflectivity measurements is the dielectric function \( \epsilon = n^2 \). In equilibrium reflectivity measurements, \( \epsilon(\omega) \) can be obtained from \( R(\omega) \) by way of Kramers-Kronig transformation, given that \( R \) is measured over a broad enough frequency range. At normal incidence, the Fresnel equation gives the reflectance \( \tilde{r} \) in terms of the dielectric function as

\[ \tilde{r} = \frac{1 - \sqrt{\epsilon}}{1 + \sqrt{\epsilon}} \]  

(2.6)

We can then expand for small changes in \( \epsilon \), writing

\[ \delta \tilde{r} = \frac{\partial \tilde{r}}{\partial \epsilon} \delta \epsilon = \frac{-1}{\sqrt{\epsilon} (1 + \sqrt{\epsilon})^2} \delta \epsilon \]  

(2.7)

In terms of the measured quantities \( \delta r \) and \( \phi_s \), the change in dielectric function can be written as

\[ \delta \epsilon = \sqrt{\epsilon} (1 + \sqrt{\epsilon})^2 \delta r e^{i(\phi_r - \phi_s)} \]  

(2.8)
With knowledge of the real and imaginary parts of $\epsilon$ from equilibrium optical measurements, the full amplitude and phase of $\delta \epsilon$ can be recovered. This can then be related to the optical conductivity $\sigma(\omega)$ by relation

$$
\epsilon(\omega) = 1 + \frac{4 \pi i \sigma(\omega)}{\omega}
$$

$$
\delta \sigma = -\frac{i \omega}{4 \pi} \delta \epsilon
$$

(2.9)
Chapter 3

Optical Dynamics in Cuprates: A Detailed Study of HgBa$_2$CuO$_{4+\delta}$

3.1 Ultrafast Reflectivity in the P-type Cuprates

Each material material system within the cuprate family of high temperature superconductors has unique behaviors, many of which are evident in time-resolved reflectivity measurements. However, all of these systems share basic phenomenology in common. The $\Delta R/R$ response in cuprates can be roughly divided into three temperature regimes. These three prototypical signals are plotted in 3.1. The initial increase in reflectivity at high temperatures is related to the heating of the electron gas by the pump pulse. This is followed by cooling of the electronic system into quasi-equilibrium with the lattice via coupling to low energy bosons. This coupling has been studied in detail using both single color and spectrally-resolved ultrafast reflectivity. Broadband time-resolved reflectivity measurements in room temperature BSCCO [20] have revealed rich physics contained within this relaxation, suggesting that the bosons governing this thermalization have both electronic and phononic components. For the most part, this work will ignore the high temperature thermal signal, treating it as a background.

The negative reflectivity transient, plotted in magenta in 3.1, is associated with the onset of the pseudogap (PG) phase. At low dopings, this onset is very broad in temperature, though it sharpens with increasing doping as this work will demonstrate. We have performed
transient reflectivity measurements on an optimally doped Pb$_{0.55}$Bi$_{1.5}$Sr$_{1.6}$La$_{0.4}$CuO$_{6+\delta}$ (Bi-2201) crystal. ARPES and polar Kerr measurements were performed on crystals from the same growth, demonstrating the opening of both a particle-hole asymmetric gap and a non-reciprocal polarization rotation coincident with the onset of the PG $\Delta R/R$ signal \cite{47}. This provides strong evidence that the pseudogap is not merely a precursor to superconductivity, but is a distinct electronic phase in its own right. Supercontinuum optical measurements have demonstrated that this signal can be understood as a transient modification of the low energy Drude parameters \cite{19,39}.

At low temperatures a long lived positive signal emerges which we will refer to as the quasiparticle (QP) signal. This signal onsets at a temperature roughly coincident with superconducting transition, $T_c$. The QP response shrinks and eventually changes sign upon hole doping past the apex of the superconducting dome \cite{36}, and is understood to be a result of the photo-induced breaking of Cooper pairs into superconducting quasiparticles. It displays strongly fluence dependent decay rates at low temperatures and excitation densities due to the bimolecular nature of quasiparticle recombination as described within the framework of the Rotwarf-Taylor equations \cite{84,35}. In order for the system to return to equilibrium, all
3.2. HG-1201: The Model Cuprate Superconductor

While there are many behaviors which are universal to the hole-doped cuprates, each material system also has its own individual quirks. The best example of this is in YBCO, which has one-dimensional Cu-O chains interspersed between the two-dimensional Cu-O planes where superconductivity resides. The distribution of electronic order in these chains has a strong doping dependence and displays interesting physics in its own right, leading to a variety of unusual behaviors including optical anisotropy. In order to identify the properties which are intrinsic to cuprate superconductivity, it is important to study a material system that is relatively free from unwanted complexity. The single layer cuprate Hg-1201 can be considered a model cuprate system, as it has a simple and highly symmetrical crystal structure, a high maximum $T_c$ of 97 K, and can be synthesized relatively defect free [8]. The major stumbling blocks impeding the development of this material have been the toxicity and high vapor pressure of mercury oxide, which demand careful handling and high pressure growth, respectively [106]. These obstacles have been largely overcome in recent years, allowing the growth of extremely high quality samples which have been studied by a multitude of experimental probes.

Intense study over the last several years has shown that many interesting effects observed in other cuprate systems are also manifest in Hg-1201. These include observations of quantum oscillations [9], intra-unit cell magnetic order [62, 63], and fermi-surface reconstruction via Hall and Nernst measurements [27]. This system has also revealed the strongest evidence for low temperature Fermi liquid behavior in both optical spectroscopy [71] and DC
transport [10]. Finally, charge ordering, similar to that reported in YBCO, has recently been observed in X-ray scattering experiments in underdoped Hg-1201 [90]. Here we report the first comprehensive time-domain reflectivity survey of the single-layer cuprate Hg-1201.

3.3 Methods

These measurements presented here were performed on a series of high quality single crystals of Hg-1201 ranging from underdoped to overdoped with \( T_c \)’s of 55 K, 65 K, 71 K, 79 K, 81 K, 91 K, 94 K, 92 K, 90 K, and 85 K. These samples were grown by the self-flux method and annealed to achieve different oxygen concentrations, with \( T_c \) determined within \( \sim 1 \) K by magnetic susceptibility measurements. As Hg-1201 is especially hygroscopic, sample surfaces degrade rapidly upon exposure to air. Samples were therefore immersed in Fluorinert for long term storage, and stored in a nitrogen-purged dry-box after mounting. Samples were mounted on copper by a thin layer of TORseal and allowed to cure overnight. In order to obtain reproducible results, it was necessary to polish samples before every measurement, due to small changes in surface doping which occur over time-scales on the order of days. Samples were polished after mounting using a series of 3M polishing films with sequentially decreasing grain size of 3, 0.3, and 0.05 \( \mu \)m.

Zero-field optical measurements were performed in a continuous helium flow Oxford Instruments Microstat optical cryostat. A KM Labs Ti-Sapph oscillator at 800 nm wavelength and 80 MHz rep rate was used for all pump-probe measurements. Pump fluences of \( \sim 1 \) and \( 2 \mu J/cm^2 \) were used for two-beam pump-probe and four-beam transient grating measurements, respectively. Because of the poor c-axis thermal conductivity and variable sample thickness, the laser induced heating near \( T_c \) ranged from \( \sim 4 - 8 \) K in these measurements. However, the peak in relaxation time was measured as a function of laser intensity and observed to approach \( T_c \) as the incident power was lowered, indicating that we can reliably associate it with \( T_c \). Magnetic field measurements were performed in an Oxford Instruments superconducting magnet cryostat, with a maximum achievable field of 6 T.
3.4. The Optical Phase Diagram of Hg-1201

The time and temperature dependence of the $\Delta R/R$ in lightly underdoped Hg-1201 with $T_c = 91$ K is shown as a false color image in Figure 3.2(a). The three prototypical signals are all evidenced, with a thermal response at high temperature, PG response for $T_c < T < T^*$, and a quasiparticle response at low temperatures. This behavior can be simply encapsulated by integrating $\Delta R(t)/R$ at each temperature over the first picosecond after photo-excitation. This quantity, which we call $\Delta R_I$, is shown in Figure 3.2(b). This procedure suppresses information about the relaxation dynamics, allowing us to focus on the temperature dependence of the initial excitation amplitude. In Figure 3.3(a) we repeat this analysis for all of the dopings that were measured, ranging from 55 K underdoped to 85 K overdoped, and study the doping-dependent transition temperatures.

Figure 3.2: a) False-color image showing $\Delta R/R$ as a function of time-delay and temperature for an underdoped Hg-1201 sample with $T_c = 91$ K. b) Signal from a) averaged over the first picosecond after photo-excitation, indicated by the transparent grey bar in a).
Figure 3.3: a) The temperature dependence of $\Delta R_I$ for each doping, with curves arbitrarily offset for clarity. (b)-(e) Detail of $\Delta R_I$ vs. $T$ for select dopings. The transparent red and blue bars correspond to $T^*$ and $T^{**}$, respectively. Straight lines indicate transitions identified with deviations from linear temperature dependence, while the curved blue lines are polynomial fits were used to determine $T^{**}$. The Inset to (e) shows the out phase TG/R signal, indicating a QP onset at $\approx T_c$.

Figure 3.3(b)-(e) we examine the temperature dependence of four characteristic dopings. In samples near optimal doping, we can clearly see the onset of both PG and QP signals. We estimate $T^*$, the onset of the PG signal, as the temperature at which $\Delta R_I$ deviates from a linear temperature dependence. Upon further cooling, $\Delta R_I$ shows an inflection point, followed by an upturn. We identify this inflection point with the onset of the QP response, and see that the signal evolves smoothly through $T_c$ upon further cooling. In heavily underdoped samples we see a PG response at high temperatures which persists up to room temperature. Transport measurements in these samples measure $T^*$ to be above room temperature, which is inaccessible to our apparatus. The PG signal in these samples is only weakly temperature dependent, so we can find the onset of the QP signal simply by looking for the deviation from linear temperature dependence. In the heavily overdoped sample we can clearly see $T^*$ in $\Delta R_I$. However, the upturn associated with QP excitations is notably
absent in this sample, as has been observed in other cuprate systems [36].

![Optical phase diagram](image)

*Figure 3.4:* Optical phase diagram assembled from the transition temperatures determined in 3.3, with $T^*$ (red) and $T^{**}$ (blue). The temperatures determined by TRR (squares) are compared with those obtained from transport (triangles) [10]. Onset of charge order from RIXS is also plotted (green dot) [90]. The solid lines give the $T^*$ and $T^{**}$ transitions indicated by TRR, while the dashed red line gives the $T^*$ line suggested by Transport measurements.

These onset temperatures are compiled into a phase diagram in Figure 3.4. In underdoped samples, our measurement of $T^*$ is roughly consistent with the values obtained from transport and neutron scattering experiments [10, 62]. $T^*$ is defined in transport as the temperature at which the resistivity deviates from linear temperature dependence, where the onset of a spin-flip neutron scattering signal indicates broken time-reversal symmetry. However, we clearly observe a $T^*$ transition in the overdoped part of the phase diagram, indicating that $T^*$ runs tangent to the superconducting dome, in conflict with transport and neutron scattering which suggest that $T^*$ terminates near optimal doping.

The onset of the QP component occurs well above $T_c$ and is coincident with $T^{**}$, the
temperature below which Fermi liquid-like resistivity as well as a peak in thermopower are observed [10]. In the underdoped sample with \( T_c = 71 \) K, this temperature correlates to the recently-observed onset of fluctuating CDW order [90]. In YBCO \( T^{**} \) also coincides with the emergence of a non-reciprocal optical polarization rotation [102], thought to be related to the breaking of time-reversal symmetry. With this detailed phase diagram in hand we will now discuss the physical origin of the transient reflectivity in these different temperature regimes.

3.5 Transient Grating and the PG and QP Response

In conventional superconductors, the onset of superconductivity is accompanied by a depletion of free-carrier Drude spectral weight from energies below the gap. This spectral weight is deposited in the delta function at zero frequency [92]. The interband transitions in these systems are largely unaffected by the opening of the superconducting gap. The concentration of electron density above and below the superconducting gap does lead to small shifts of interband spectral weight which show up as narrow resonances with widths comparable to the lifetime of interband electronic excitations [29]. Notably, conservation of the total spectral weight dictates that the interband spectral weight is conserved, as the condensate weight is pulled entirely from the Drude peak [91].

By contrast, the behavior of the optical conductivity in the cuprate superconductors is far more complicated. The opening of the pseudogap at \( T^{*} > T_c \) depletes spectral weight from energies below \( \Delta_{PG} \) [51]. Cooling below \( T_c \), spectral weight flows from energies below \( \Delta_{SC} \) into the zero frequency delta function, much as in a the conventional BCS picture. However, this low energy redistribution is accompanied by a flow of interband spectral weight into the Drude peak [73]. This behavior is inexplicable within the BCS framework, and is thought to be strong evidence for the unconventional nature of superconductivity in the cuprates.

In order to address the nature of the excitations we observe, it is advantageous to use phase-resolved transient grating spectroscopy (TGS). This allows us to directly measure the real and imaginary parts of the photo-induced change in dielectric function at the probe energy of 1.5 eV [37]. In cuprates, this technique has two significant advantages over traditional pump-probe reflectivity measurements. The ability to compare the relaxation dynamics
Figure 3.5: The real (a) and imaginary (b) components of TG/R in the UD 91K sample at 10 K. The fits from Equation 3.1 are shown in black dash, with the QP and PG components shown in blue and red dash, respectively. (c-e) Phase of the the photoinduced reflectivity change $\delta r$ for the QP (blue arrows) and PG (red arrows) signals extracted from the fits for UD 71K, UD 91K, and OD 85K. The horizontal and vertical axes correspond to changes in phase and out of phase with the equilibrium reflectivity, respectively. The dashed arrows give the reflectivity phases which correspond to changes in $\epsilon_1$ and $\epsilon_2$ at 1.5 eV. (f-h) The temperature dependent amplitude of fits to the QP and SC components are plotted for the same three dopings. The blue and red lines are guides to the eye for the QP and PG signals, respectively.

both in and out of phase with the equilibrium reflectivity enables us to separate the multi-component signals with relative ease and significantly less ambiguity than merely fitting a single-phase $\Delta R/R$ curve. Additionally, identifying the phase of the different components of the change in dielectric function provides information about the physical processes associated with photo-excitation.

Figure 3.5 summarizes the result of our transient grating measurements on Hg-1201. The real and imaginary components of $\delta r$ clearly relax on different timescales, suggesting that at low temperature the PG and QP components coexist. In order to separate these components we fit with a function of the form

$$
(1 - e^{-\frac{t-t_0}{\tau_r}}) \times (A_0 e^{i\phi_0} + A_{QP} e^{i\phi_{QP}} e^{-\frac{t-t_0}{\tau_{QP}}} + A_{PG} e^{i\phi_{PG}} e^{-\frac{t-t_0}{\tau_{PG}}})
$$

where $A_0$, $A_{QP}$, and $A_{SC}$ are the amplitudes of the long time offset, QP, and PG components, respectively, with phases and exponential time constants given by $\phi$ and $\tau$. $\tau_r$ is a tempera-
ture and phase-independent rise time, which is $\approx 200$ fs for all dopings. The high quality of these fits can be seen in 3.5 (a) and (b), with a clear separation into QP and PG components. This fit can be performed for temperatures below $T^*$ in the underdoped samples. In the overdoped sample, the room temperature thermal signal is of comparable amplitude to the PG and QP components, so we treat this component as a linearly temperature-dependent background and subtract it off, leaving behind curves which can be fit with Equation 3.1. The results of this fit are shown in Figure 3.5.

The phase of each signal is temperature independent to within $\sim 10^\circ$ for each doping, yielding an unambiguous optical phase for the QP and PG excitations. The peak amplitude of the PG and QP signals is plotted in Figure 3.5 (f)-(h), with behavior similar to what has been observed in optimally doped BSCCO [19]. The two signals coexist at all dopings, and they display evidence of phase competition, as the PG signal is suppressed as the QP signal grows. This suppression is weakest in the overdoped sample, suggesting that the competition weakens as the two onset temperatures become comparable. These fits demonstrate that the QP signal onsets near $T^{\star\star}$ and evolves smoothly upon cooling through $T_c$. Notably, the PG signal in the 71 K UD sample turns down upon cooling below $\sim 100$ K, well above $T_c$. This indicates that the PG signal is competing with phase-fluctuating superconductivity or a different order parameter, rather than with long-range superconductivity.

### 3.5.1 Analysis of QP Signal

Before further exploring the temperature dependence of the two components, we will focus on the physical implications of their distinct optical phases. As a guide, we will use the extensive broadband pump-probe reflectivity data collected on double-layer BSCCO. These measurements show that the QP signal involves a change of spectral weight over a broad frequency range which is attributed to a modification of interband transitions. Using the detailed ellipsometry data from [64], we attempt to model the doping dependence of the QP phase that we observe.

We first consider what sorts of modifications we expect photo-excitation to make to the interband transitions in the presence of low energy gap. Optical spectroscopy experiments have demonstrated that the onset of superconductivity depletes spectral weight from the inter-
band transitions, as mentioned previously. This suggests that we should see an enhancement in the real part of the interband conductivity, which naively matches the observation that the QP signal is positive. However, this leads to the wrong sign of the imaginary part of $\Delta R$ and does not account for the sign change of the QP signal in overdoped samples. There are two interband transitions that are proximate to the probe energy: one low energy oscillator which ranges in center frequency from 1.9 eV to 1.3 eV, and a high energy oscillator which ranges from 2.2 eV to 2.7 eV. In the 71 K underdoped sample, the high energy transition at 2.4 eV dominates the NIR response. An enhancement of this oscillator leads to an increase in $\epsilon_1$ which is much larger than the increase in $\epsilon_2$, contradicting the observation that these two quantities are approximately equal. In the overdoped sample, where the oscillators at 1.3 and 2.6 eV have comparable strength, enhancement leads to a positive change in $\epsilon_1$ and $\epsilon_2$, the opposite of what is actually observed.

Having demonstrated that restoring spectral weight to the interband oscillators does not sufficiently reproduce our observations, we consider energy shifts that may be associated with quasiparticle excitation. Although, as previously mentioned, the interband spectral weight redistribution due to gap opening in conventional superconductors happens over a very narrow frequency range, there are important differences in cuprate superconductors which must be considered. The d-wave superconducting gap in cuprate superconductors is highly anisotropic, with a maximum value as much as ten times larger than that of conventional superconductors. The peaks in the visible to NIR part of the optical conductivity are known to stem from transitions from states near the Fermi energy into higher energy that emerge from the charge transfer band on hole doping. Excitation of quasiparticles leads to a redistribution of occupied electronic states to higher energy, red shifting the transitions between these states and the higher energy bands.

In order to fit the amplitude and phase of the QP response, we performed a simultaneous fit of the UD 71 K, UD 91 K, and OD 85 K samples using two Lorentz oscillators of the form

$$\epsilon(\omega) = \frac{\omega_p^2}{(\omega_0^2 - \omega^2) - i\gamma\omega}$$

The equilibrium parameters of these oscillators are all doping dependent. We allow the plasma frequencies to rescale by a doping independent amount, and the center frequencies
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Figure 3.6: (a) Simulation of $\Delta R(\omega)/R(\omega)$ for the QP signal based on the model involving interband oscillators presented in the text. (b) Schematic illustration of the shift in interband transitions induced by the excitation of quasiparticles. Both of the oscillators proximate to the 1.5 eV probe energy are shifted down in energy. The lower energy oscillator loses weight, while the upper energy oscillator gains weight.

To shift in the same manner. Changes in interband spectral weight must compensated by an opposite change in the Drude peak. For simplicity, we assume that this weight shifts to energies far below the probe frequency. From the Kramers-Kronig relations, one can demonstrate that this leads to a shift in the real part of the dielectric function proportional to the change in interband spectral weight which is given by $\delta \epsilon_1 = (8/\omega^2)\delta SW$. This fit yields a decrease in oscillator strength $\delta \omega_p/\omega_p \sim -2.6 \times 10^{-2}$ for the lower energy peak and an increase of $\delta \omega_p/\omega_p \sim 1.2 \times 10^{-2}$ for the higher energy peak, with redshifts of 1.6 meV and 1.4 meV, respectively. A schematic of this process is shown in Figure 3.6(a). The phase of the 71 K underdoped and 85 K overdoped samples are captured quite well by this fit. This demonstrates that the change in sign of the signal can be explained by the emergence of the strong interband transition below 1.5 eV, and is not a result of any change in nature of the coupling between the quasiparticles and the interband transitions. The fit to the 91 K underdoped sample is poor. However, this sample is in the part of the phase diagram where the low energy and high energy transitions have a comparable effect on the reflectivity at 1.5 eV. The amplitude and phase of $\delta r$ produced by shifting these oscillators is therefore
3.5. TRANSIENT GRATING AND THE PG AND QP RESPONSE

extremely sensitive to their equilibrium values, which may not precisely match those obtained from ellipsometry on similar samples. In addition to matching our phase-resolved data, this model qualitatively reproduces the broadband reflectivity results obtained in BSCCO. The simulated $\Delta R(\omega, t)/R(\omega)$, plotted in Figure 3.6(b), can be compared to Figure 4 in [39].

3.5.2 Analysis of PG Signal

We now turn to our analysis of the PG signal. The broadband response of the PG signal is well fit by modifications of the Drude peak. We will therefore model our signals accordingly. The free carriers in the cuprates are poorly described by the non-interacting Drude model, which assumes frequency independent carrier mass and scattering rate, due to their strong coupling to a spectrum of low energy bosons. The extended Drude model remedies this limitation by introducing the optical self-energy $\Sigma_{\text{op}}(\omega)$, which is related to a momentum average of the quasiparticle self-energy. $\Sigma_{\text{op}}(\omega)$, which is a function of the frequency dependent mass and relaxation times, is given by

$$2\Sigma_{\text{op}}(\omega) = \omega \left(1 - \frac{m^*(\omega)}{m}\right) - \frac{i}{\tau(\omega)} \tag{3.3}$$

The optical conductivity is then

$$\sigma_D(\omega) = \frac{i}{4\pi} \frac{\omega_p^2}{\omega - 2\Sigma_{\text{op}}(\omega)} \tag{3.4}$$

In the cuprates, the frequency and temperature dependence of $\Sigma_{\text{op}}(\omega)$ has been studied extensively. As this quantity is modified significantly on cooling through the pseudogap phase, we will now consider what sorts of modifications are consistent with our observations.

The plasma frequency is a property of the non-interacting electron population, and therefore cannot be altered by pumping. This means that we must only consider changes in $\Sigma_{\text{op}}(\omega)$ when modelling the observed $\delta \epsilon_D$. In general, we can express changes in the dielectric constant as

$$\delta \epsilon_D(\omega) = \left(\frac{\partial \epsilon_D(\omega)}{\partial \Sigma_{\text{op}}(\omega)}\right) \delta \Sigma_{\text{op}}(\omega)$$

$$= -2\epsilon_D^2(\omega) \frac{\omega}{\omega_p^2} \delta \Sigma_{\text{op}}(\omega) \tag{3.5}$$

This expression indicates that changes in the real and imaginary parts of $\Sigma_{\text{op}}(\omega)$ will produce values of $\delta \epsilon_D$ which are, respectively, in and out of phase with $-\epsilon_D^2$. In Figure 3.7(b) we
illustrate the phase of $\delta \epsilon$ associated with changes in $(m^*/m)$ and $\tau^{-1}$. The Drude component of the dielectric constant is obtained by subtracting the interband peaks and an estimate from the literature of $\epsilon_\infty \approx 3.5$. In the underdoped samples, $\delta \epsilon_{pg}$ is primarily related to an increase in the effective mass at 1.5 eV. This situation abruptly shifts as optimal doping is approached; the dominant effect switches to a decrease in the scattering rate.

**Figure 3.7:** (a) The phase of the change in optical self-energy $\delta \Sigma_{op}$ associated with the PG signal plotted as a function of doping. This phase abruptly shifts by $\pi/2$ at $\sim 11\%$ doping, indicating a transition from modulation of $m^*$ to modulation of $\tau^{-1}$. The phase of the PG signal (red arrow) is compared to the phases associated with changes in the real (cyan arrow) and imaginary (magenta arrow) parts of $\Sigma_{op}$ for (a) 71 K underdoped and (b) 85 K overdoped samples.

In order to understand the cause of this sharp transition, we will now consider the conditions required for spectral weight to be conserved. Each component of the photoinduced change in $\sigma(\omega)$ must individually conserve spectral weight in order to display a delay-independent phase. This condition imposes constraints on $\delta \Sigma_{op}$ which be written as
follows.
\[
\int \delta \sigma_1 (\omega) \, d\omega = \Re \{ \int \frac{\partial \sigma(\omega)}{\partial \Sigma_{\text{op}}(\omega)} \, \delta \Sigma_{\text{op}}(\omega) \, d\omega \} = 0
\]  
(3.6)

This expression takes on a relatively simple form when written in terms of the relaxation time and effective mass.

\[
\int \frac{\left( m^*/m \right) \left( \frac{1}{\tau} \right)}{\left| (\omega - 2\Sigma_{\text{op}})^2 \right|} \delta \left( \frac{m^*}{m} \right) \omega^2 \, d\omega = -\frac{1}{4} \int \frac{\left[ \left( \frac{m^*}{m} \right)^2 \omega^2 - \left( \frac{1}{\tau} \right)^2 \right]}{\left| (\omega - 2\Sigma_{\text{op}})^2 \right|} \delta \left( \frac{1}{\tau} \right) \, d\omega
\]  
(3.7)

Quantitatively relating $\delta m^*$ to $\delta \tau^{-1}$ requires knowledge of the full frequency dependence $\Sigma_{\text{op}}$, which is unfortunately unavailable to us. We can still obtain interesting physical information from this expression by noting that the denominator in both integrals is positive definite. The numerator in the expression on the right is generally negative at low frequency, where $(m^*/m)\omega < \tau^{-1}$. Therefore, a low energy increase in scattering rate would lead to a large increase in effective mass at higher energy scales. A low energy decrease in scattering rate is observed as a result of density of states depletion accompanying the onset of the pseudogap [52]. In Hg-1201, this has been related to the onset of Fermi-liquid behavior below $T^*$ as observed in both DC and IR conductivity measurements [71, 10]. The $\Delta R_{\text{PG}}$ signal we observe in the underdoped samples is consistent with a filling in of the pseudogap at low energies. Above a doping of 11 – 12%, we see the onset of a decrease in the high energy scattering rate which we estimate to be of order 10 cm$^{-1}$. It is notable that the transition between low energy and high energy shifts in $\Sigma_{\text{op}}$ occurs at the same doping where the values of $T^*$ obtained from transport and $\Delta R$ deviate, as shown by the dashed and dotted lines in Figure 3.4. Additionally, equilibrium reflectivity experiments observe no evidence of low-energy decrease in scattering rate associated with pseudogap formation in the optimal and overdoped cuprates [52]. This suggests that the interactions which lead to the pseudogap in the underdoped part of the phase diagram persist above $T_c$ on the overdoped side, where they couple to the high energy scattering rate rather than opening up an observable pseudogap.

In the underdoped samples, the change in $\Sigma_{\text{op}}$ at low energy is consistent with thermally-induced filling in of the pseudogap. However, the high energy decrease in scattering rate observed at higher dopings is the opposite of what one would expect from heating of the electron gas. Additionally, the temperature-dependent relaxation time in both doping regimes is manifestly non-thermal. This is illustrated in Figure 3.8, which shows the temperature
dependence of the PG relaxation time $\tau_{PG}$ for three different dopings. This time does not match either of the two termal relaxation times observed at high temperatures, which have roughly temperature and doping independent values of $1.2 \pm 0.1$ ps and $0.35 \pm 0.05$ ps. The PG signal must then be a result of excitation into an electronic non-equilibrium state. As we have shown, the excitation of quasiparticles results in a qualitatively different signal, so it is doubtful that excitation of electrons across the pseudogap could be responsible for this signal. It is possible that the PG response reflects an alteration of the scattering rate via the excitation of an as-yet unidentified low energy collective mode, as has been observed in the optimally electron-doped cuprate NCCO (see Chapter 5).

Figure 3.8: The relaxation time of the PG signal for 79 K underdoped, 94 K underdoped, and 92 K overdoped samples is compared as a function of temperature. The 79 K underdoped sample shows a roughly temperature independent $\tau_{PG}$. The temperature dependence in the more heavily doped samples is roughly linear, with a high temperature extrapolation to zero consistent with $T^*$. An example of the fits to the thermal and PG signals is shown in the inset.
3.6 Quasiparticle Coherence and Recombination

The analysis to this point has neglected the relaxation dynamics of the QP signal. This subject has been studied extensively in the cuprates \cite{35, 84, 23}, with the majority of data interpreted within the framework of the Rotwarf-Taylor (RT) equations \cite{53}. These are equations describing the recombination of non-equilibrium quasiparticles with the simplifying assumption that the rate of recombination depends only on the quasiparticle population, ignoring their momentum distribution \cite{82}. These equations provide an effective quantitative description of reflectivity dynamics in cuprates, despite the fact that their assumptions are certainly not valid d-wave superconductors. The two differential equations which couple the quasiparticle population $n$ and the phonon population $N$ as follows

$$\dot{n} = I_{qp} + 2N\gamma_{pc} - \beta n^2$$

$$\dot{N} = I_{ph} + \beta n^2/2 - \gamma_{pc}N - (N - N_{eq})\gamma_{esc}$$

where $I_{qp}$ and $I_{ph}$ are the external generation rates of quasiparticles and phonons. Pairs of quasiparticles recombine to produce phonons at a rate $\beta n^2$, while phonons produce pairs of quasiparticles at a rate $\gamma_{pc}N$. Only phonons with an energy of at least $2\Delta$ can produce quasiparticles, so the effective population of pair-breaking phonons decreases as they scatter inelastically to lower energies, a process represented by the term $(N - N_{eq})\gamma_{esc}$.

In the case of pump probe reflectivity measurements, we study the behavior of the system after an impulsive injection of quasiparticles at $t = 0$. The quasiparticle population is the sum of thermally excited and photo-injected components, $n = n_{th} + n_{ph}$. At low temperatures the thermal population vanishes and the recombination rate scales linearly with $n_{ph}$. In this work we will focus instead on the high temperature regime, where $n_{th}$ is much larger than $n_{ph}$. If we ignore pair breaking by phonons, we obtain $\dot{n} = -2\beta n_{th} n_{ph}$. This yields an exponentially decaying photo-injected population with a decay rate $1/\tau_d = 2\beta n_{th}$ which we use to fit our data. Figure 3.9(a) shows the temperature dependence of $\Delta R/R$ in the underdoped sample with $T_c = 55$K. The exponential fits to the data are shown, and are of uniformly high quality. It is clear upon inspection that the exponentially decaying QP signal extends well above $T_c$ at this doping, so it must not be associated with the onset of phase-rigid superconductivity. Furthermore, the onset temperature of phase-fluctuating superconductivity, $T_\phi$, has been shown by microwave and DC transport measurements to be less than 100 K across the
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Figure 3.9: (a) Temperature dependence of $\Delta R(t)/R$ in the 55 K underdoped sample, with exponential fits shown in black dash. Curves are arbitrarily offset for clarity. Amplitude (a) and time constant (b) of the positive component of the exponential fits, with the temperature axis normalized to $T_c$. Curves are arbitrarily offset for clarity, with zero values marked by dashed lines.

The phase diagram [43]. As seen in Figure 3.9(b) The QP component we observe can be successfully extracted at temperatures of up to 140 K, with the initial onset of a positive $\Delta R$ component occurring at $T^{**}$ (3.3). We therefore conclude that the QP signal is sensitive to the excitation of quasiparticles across a gap of non-superconducting origin.

The decay time-constant $\tau_d$ of $\Delta R_{QP}$ is plotted for a series of underdoped samples in Figure 3.9(c). The quasiparticle relaxation time decreases upon warming from low temperature, levels off upon approaching $T_c$, and then increases by $\sim 0.5 - 1$ ps, peaking near $T_c$. $\tau_d$ then decreases again, leveling off above $T_c$ at a value comparable to that just below $T_c$. The amplitude of the $T_c$ peak in $\tau_d$ grows with hole doping, reaching a local maximum at $T_c = 71$ K, then shrinks by a small amount before rapidly growing near optimal doping. In the deeply underdoped samples this peak appears on top of a smoothly evolving background. As optimal doping is approached, the QP signal above $T_c$ becomes impossible to separate from the large PG signal. Features of this sort have been observed before in pump-probe experiments on Hg-1223 [24], and the shape of this peak is reminiscent of other cusp like features observed at $T_c$ in YBCO [38, 17] and BSCCO [105].

We chose to study the $T_c = 71$ K underdoped sample in more detail due to its combination
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Figure 3.10: (a) The temperature dependence of the relaxation time $\tau_d$ is plotted in zero field and 6 T applied normal to the sample surface. The peak vanishes completely with application of the magnetic field, and the relaxation time is slightly suppressed at all temperatures. (b) The field dependence of $\tau_d$ at 35 K, $T_c = 71$ K, and 80 K. The peak at $T_c$ is suppressed exponentially with increasing magnetic field.

of a prominent peak and a broad temperature range above $T_c$ where the QP dynamics can be resolved. We studied the temperature dependence of this peak in magnetic fields of up to 6 Tesla, with the results plotted in Figure 3.10. In (a) we plot the temperature dependence of $\tau_d$ at 0 field and 6 T. The peak in $\tau_d$ is entirely washed out in a magnetic field of 6 T, with a small decrease in the relaxation time at all temperatures. In Figure 3.10(b) the field dependence of the relaxation time is plotted for temperatures below, above, and at $T_c$. At high and low temperature, $\tau_d$ decreases very slightly with increasing field, in contrast to its behavior at $T_c$. The peak in $\tau_d$ falls off exponentially with a characteristic field of $2.6 \pm 0.5$ T, a small field on the scale of $H_{C2} \approx 50 T$. Our observations regarding the cusp in the quasiparticle relaxation time at $T_c$ are not easily explicable within the heavily simplified framework of the RT equations. A significant feature of broken-symmetry ground states which is ignored by the RT equations is the effect of quasiparticle coherence. We will now demonstrate that our observations emerge naturally from consideration of quasiparticle coherence in mixed state of superconductivity and fluctuating density wave order.
3.6. QUASIPARTICLE COHERENCE AND RECOMBINATION

3.6.1 Coherence Factors

The fundamental premise of BCS theory is that the SC condensate is made up of Cooper pairs, which are coherent combinations of two electrons with opposite momentum and spin [92]. An important consequence of this ground state is that SC quasiparticles are coherent combinations of electrons and holes, and cannot be treated independently when calculating the effects of interactions with external perturbations. This necessitates the calculation of paired-state coherence factors, which have observable consequences for the temperature dependence of measurable quantities including nuclear magnetic resonance and electromagnetic absorption. These predictions were confirmed experimentally in conventional superconducting systems, providing strong support for BCS theory. Although BCS-like coherence factors have been also been observed in STM quasiparticle interference at low temperatures in the cuprates [50, 45], the effect of coherence factors has been neglected in the analysis of ultrafast quasiparticle dynamics. In this section we will show that coherence factors can have dramatic consequences in systems with mixed superconducting-density wave ground states.

When electrons in a non-interacting metal are excited out of their ground state, they leaves behind holes. A particular electron and hole recombine with a rate given by Fermi’s golden rule, which is proportional to the matrix element between the initial and final states and the density of final states. In order to determine the overall electron recombination rate, the matrix elements for different processes must be summed in quadrature. In a superconductor, a single electronic transition involves multiple quasiparticle transitions, which necessitates that one sum the matrix elements for these connected transitions before squaring. This leads to a modification of the transition rates which can be obtained simply by multiplying the bare transition rate by a coherence factor. In a superconductor, this coherence factor is a function of the Bogoliubov coefficients $u$ and $v$ given by

$$F^{SC}_S = (uu' \mp vv')^2 = \frac{1}{2} \left( 1 \pm \frac{\Delta \Delta'}{EE'} \right)$$

$$F^{SC}_R = (vu' \mp uv')^2 = \frac{1}{2} \left( 1 \pm \frac{\Delta \Delta'}{EE'} \right)$$

(3.9)

for quasiparticle scattering and recombination, respectively. $\Delta$ is the SC gap, $E$ is the quasiparticle energy, the upper (type I) and lower (type II) signs in each equation refer to
3.6. QUASIPARTICLE COHERENCE AND RECOMBINATION

Figure 3.11: (a) Doping dependence of the peak value of 1-F, assuming a smooth background temperature dependence with $F \approx 0$. The black line is a double lorentzian fit to the data, with the two peaks at $\delta = 8.8$ and 12.1 given by dashed lines. The form of the condensates for the incoherent normal state (b), the CDW state (c), the SC state (d), and the CDW-SC mixed state (e). The mixed state condensate is built from coherent combinations of SC and CDW pairs.

Quasiparticle recombination after photo-excitation is mediated by interaction with phonons, a process which depends only on the net momentum absorbed by the emitted phonon. It is therefore appropriate to consider coherence factors of the first type, corresponding to the upper sign in Equations 3.9 and 3.10. For simplicity, we will assume that quasiparticles participating in recombination have thermalized to the gap edge. This assumption approximately matches pump-probe ARPES observations, which demonstrate that thermalization occurs on a timescale much faster than recombination [87]. Under this assumption, the coherence factors simplify to $F_{SC} = 1$ and $F_{CDW} = 0$. In the superconducting state, this
translates to a recombination rate which is identical to that of incoherent electrons. In the
charge density wave state, the relaxation time of gap-edge quasiparticles goes to infinity. Near
$T_c$, the cuprates display coexistence of SC and CDW order parameters [38, 17], requiring
that we consider the nature of quasiparticle coherence in mixed states. Figure 3.11(b)-(c)
illustrate the nature of the electronic pairing in different ground states. The mixed-state
condensate is made up of linear combinations of electron and hole like CDW quasiparticles,
which yield coherence factors which are calculated in detail in Appendix A. In the limit of
low quasiparticle energy, the phonon-mediated recombination coherence factor relevant to
our experiment can be written

$$F = 1 - \frac{\Phi \Phi'}{\epsilon \epsilon'}$$

(3.11)

This is different by only a factor of two from CDW coherence factor, with the caveat that
the energy is $\epsilon^2 = |\Psi|^2 + \xi^2$, where the full gap is given by $\Psi^2 = |\Delta|^2 + |\Phi|^2$. In the mixed
state, electrons at the gap edge have an energy higher than the bare CDW gap. This has
the effect of making the coherence factor non-zero, with a value proportional to $|\Delta|^2$.

This coherence factor is valid for static SC and CDW order. However, the charge ordering
observed in the cuprates is far from static. We can incorporate the effect of phase fluctuations
by writing the coherence factor as a function of the initial and final CDW order parameter
phases.

$$F(\phi', \phi) = 1 - e^{i\phi} |\Phi| e^{i\phi'} |\Phi| \epsilon \epsilon'$$

(3.12)

The phase distribution $P(\phi)$ of the thermal population of quasiparticles can be written as
a gaussian with variance proportional to the square root of $\tau_0 / \tau_c$, where $\tau_0$ is the quasipar-
ticle lifetime and $\tau_c$ is the coherence time of the fluctuating CDW. This describes a process
whereby thermally excited quasiparticles experience random dephasing after excitation. The
expectation value of the coherence factor for recombination between photo-excited and ther-
mal quasiparticles can then be calculated, yielding

$$\langle F \rangle = \int P(\theta) \left( 1 - \frac{\epsilon e^{i\theta} |\Phi|^2}{\epsilon \epsilon'} \right) d\theta$$

$$= 1 - e^{-\tau_0 / \tau_c} \frac{|\Phi|^2}{\epsilon \epsilon'}$$

(3.13)

From this expression we see that $F$ is unity when the CDW phase is fluctuating rapidly, giving
a short coherence time $\tau_c$ compared to $\tau_0$. $F$ then decreases as $\tau_c$ becomes comparable to $\tau_0$.  


This explains the resemblance between our observed cusp in $\tau_d$ and the cusp of the CDW X-ray scattering amplitude, providing a direct link between the quasiparticle decay rate and the CDW coherence time. Additionally, the appearance of a peak on top of a smoothly evolving background follows from a scenario where $F \to 1$ for temperatures well above and below $T_c$. It is clear from Equation 3.11 that as $\Delta$ grows much larger than $\Phi$, $F$ returns to unity irrespective of fluctuations of the CDW order parameter, so the increase in $\tau_c$ near $T_c$ is compensated by the opening of the superconducting gap below $T_c$. In Figure 3.11(a) we plot the doping dependence of the peak in $1 - F$ extracted from the peak in $\tau_d$. This factor corresponds to the timescale of CDW fluctuations at $T_c$, and shows structure indicative of multiple charge ordering instabilities in the underdoped part of the phase diagram.

We turn now to the dependence of $\tau_d$ on magnetic field. It is likely that dependence has little to do with the suppression of superconductivity by the magnetic field, most obviously because the field associated with the vanishing of the peak (2.5 T) is quite low compared to $H_{c2}$ [44]. While low magnetic fields can produce a vortex liquid near $T_c$, the phase of the superconducting gap does not enter into the expression for the coherence factor. A more likely scenario for the strong field dependence of $\tau_d$ at $T_c$ lies in the effect of the magnetic field on individual quasiparticles. As electrons move in a magnetic field, they acquire additional phase via the Aharanov-Bohm effect, effectively washing out the quasiparticle phase coherence at a relatively low field. The small field dependence of $\tau_d$ away from $T_c$ indicates that the rate of fluctuations of the CDW away from the peak minimize the effect of the field on quasiparticle coherence.

3.7 Conclusions and Future Directions

To conclude, we have performed a thorough study of the optical dynamics at 1.5 eV in Hg-1201. The finely stepped temperature dependent measurements have allowed us to construct a detailed phase diagram. We observe a transition at $T^*$ due to the onset of pseudogap order, and another transition at $T^{**}$, which we associate with the onset of a quasiparticle excitation. The value of $T^*$ we observe in lightly underdoped samples is consistent with transport measurements, but these probes disagree at near-optimal and overdoping. While the $T^*$ line terminates near optimal doping according to transport measurements, our TRR
measurements indicate that it runs tangent to the superconducting dome.

Studying the phase of the PG component of $\Delta R/R$ using phase-resolved TGS indicates that the photo-induced change in optical self energy changes abruptly at $\sim 11\%$, which resolves the discrepancy between these two probes. Analysis of the TGS signal in underdoped, optimally doped, and overdoped samples reveals that PG and SC components of $\Delta R/R$ co-exist and compete across the entire phase diagram, with the repulsive interaction between the two becoming weak on the overdoped side. We observe that the abrupt transition in the sign of the SC signal at light overdoping is entirely attributable to the emergence of a strong interband transition at $\sim 1.3$ eV, and speculate that this transition plays an important role in the crossover from underdoped to overdoped behavior.

Finally, we have studied the relaxation dynamics of both the PG and QP responses as a function of doping and temperature. The temperature dependence of the PG relaxation time becomes considerably stronger with increasing doping, and is inconsistent with a purely thermal excitation. The QP relaxation time $\tau_d$ displays a cusp at $T_c$ which is washed out by a magnetic field of $< 6T$. We propose that this peak is evidence of the slowing down of fluctuating CDW order, which couples to the QP recombination time via coherence factors. The doping dependence of this peak suggests that there may be multiple charge ordering instabilities at different points in the phase diagram.

As a final note, we discuss how these observations might fit into a larger picture of fluctuating order above $T_c$ in the cuprates. It has been proposed that the multitude of exotic behaviors observed in the cuprates, including superconductivity, can be explained as resulting from multi-component order stemming from anti-ferromagnetic correlations [46]. Our data indicates a rapid increase in CDW coherence near $T_c$, accompanied by an increase in the PG relaxation time and the onset of long range superconductivity. Within the framework of a multi-component order model, these seemingly different phenomena are manifestations of a single underlying order parameter fluctuating in multiple dimensions. This leads naturally to coupling between the dynamics observed in different $\Delta R$ channels. Further exploration of the relationship between these observations and emerging theories of multi-component order are necessary, and may prove fruitful.
Chapter 4

Charge Density Wave Amplitude Modes in YBa$_2$Cu$_3$O$_{6+x}$

The concept of spontaneous symmetry breaking (SSB) constitutes a paradigm in many branches of physics, most especially high-energy particle phenomenology, and yet has its roots in the study of condensed matter [77, 41, 4]. In metals characterized by strongly-interacting electrons, breaking of U(1) gauge symmetry leads to superconductivity (SC), and breaking of translation and time-reversal symmetry correspond to the formation of charge and spin-density waves. New phenomena may be anticipated in metals in which charge-density waves (CDWs) and SC coexist and interact strongly, such as the coupling of their respective collective modes and possible detection of the SC amplitude mode [88, 65, 16], the condensed matter analog of the Higgs boson.

Recently, great interest has been generated by the observation, using resonant [38, 2, 14] and hard [17, 13] X-ray scattering, of a CDW coexisting with SC in underdoped crystals of the prototypical high-$T_c$ cuprate superconductor, YBa$_2$Cu$_3$O$_{6+x}$ (YBCO). Particularly relevant is the finding that the CDW amplitude increases initially as the temperature ($T$) is lowered, but then decreases as $T$ crosses $T_c$, indicating a repulsive interaction between SC and CDW phases. These discoveries raise key questions concerning the relation of the newly-found CDW in YBCO to the coupled charge and spin (stripe) order in La$_{2-x}$(Sr, Ba)$_x$CuO$_4$ and related systems [94, 1], other phenomena that onset in a similar range of $T > T_c$, such as fluctuating SC [18, 103], anomalies in transient reflectivity, Hall, and Kerr
effects [47, 59, 102], and to the opening of the pseudogap itself.

4.1 Methods

Time-resolved measurements of the photoinduced change in optical reflectivity, $\Delta R$, were performed using a mode-locked Ti:Sapphire oscillator generating pulses of 800 nm wavelength light of duration of 60 fs and repetition rate 80 MHz. Measurements were carried out using both the conventional two-beam pump/probe approach and a four-beam transient grating (TGS) configuration [42, 69]. All measurements reported in this Letter were performed using a pump fluence of $1.5 \mu J/cm^2$. Single crystals of YBCO ortho-VIII, with $x = 0.67$, hole doping $p = 0.12$, and $T_c = 67$ K, and ortho-III, with $x = 0.75$, $p = 0.13$, and $T_c = 75$ K, were studied. By comparing measurements under photoexcitation with thermodynamic and transport measurements, we estimate average laser heating of 5 K in the vicinity of $T_c$.

4.2 Optical Excitation of the Collective Mode

In this work, we report the observation by time-domain reflectometry of a new collective mode in YBCO crystals in which the CDW order was previously detected. On the basis of the approximate coincidence of the onset $T$ of the transient reflectivity signal and X-ray scattering, we associate the new mode with the presence of CDW amplitude. From analysis of the time-domain data, we obtain the $T$ dependence of the amplitude, frequency, phase, and damping parameter of the mode. We observe clear anomalies in these parameters as $T$ is lowered in the SC state, providing information concerning the nature of the coupling between the two coexisting forms of order.

The three panels of 4.1 present results for $\Delta R(t)$ normalized by the equilibrium reflectance $R$ in a crystal of YBCO ortho-VIII, measured using the two-beam configuration. 4.1a illustrates the pronounced anisotropy of the response in the crystallographic $a$-$b$ plane, with $\Delta R$ changing sign as the probe polarization is rotated from the $a$ to the $b$ axis, while the pump polarization is held parallel to the $a$ axis (the crystallographic axes were oriented by X-ray Laue diffraction to within 5°). An oscillating reflectivity modulation is clearly present in both polarization channels and is highlighted using the expanded scale of 4.1b.
4.2. OPTICAL EXCITATION OF THE COLLECTIVE MODE

Figure 4.1: (a) $\Delta R(t)/R$ for $x = 0.67$ at 15 K with probe beam polarized parallel to the crystallographic $a$ (red) and $b$ (blue) axes. Oscillations are present in both polarization channels. (b) $a$-axis $\Delta R(t)/R$ at 5 K (blue) with the fit to the non-oscillating background (grey dash) and the subtracted oscillating component $\Delta R_\Omega$ (red). (c) $T$ dependence of $\Delta R_\Omega$, shown in 5 K steps between 5 and 120 K. The first maxima are marked by the grey dash, and the curve nearest $T_c$ is plotted in black.

In order to quantify the parameters of the oscillation, we subtract a background function of the form $Ae^{t/\tau_1} + Be^{-t/\tau_2} + C$ from each $\Delta R(t)/R$ curve to obtain the oscillating component $\Delta R_\Omega$. The resulting difference transient is shown for $T = 5$ K in 4.1b and for a series of temperatures between 5 and 120 K in 4.1c.

4.2a shows the $T$ dependence of the oscillation amplitude, $A_\Omega(T)$ as extracted from the data shown in 4.1c. To obtain $A_\Omega(T)$ we first Fourier transform $\Delta R_\Omega(t)$ to obtain the spectral density function $|\Delta R_\Omega(\nu)|^2$ and fit it to a damped harmonic oscillator response function. The spectrum at 5 K and the best fit are shown in the inset to 4.2a. We observe that the temperature dependence of $A_\Omega(T)$ extrapolates to zero at an onset temperature...
4.2. OPTICAL EXCITATION OF THE COLLECTIVE MODE

$T \approx 105$ K, with oscillations clearly observable above the noise level at $T \approx 105$. $A_\Omega(T)$ then begins to increase much more rapidly upon cooling below $T_c$.

Next, we compare $A_\Omega(T)$ with the temperature dependence of the non-oscillatory component of $\Delta R$. The pump-probe reflectivity dynamics of YBCO are similar to those in other cuprate superconductors [23, 54, 34, 36, 87, 19, 48]; a rapidly decaying transient is observed in the normal state, which persists into the superconducting (SC) state, and a larger and longer-lived response appears below $T_c$. The existence of multiple components below $T_c$ is especially clear in the $a$-axis transient shown in 4.1a, where the two components of $\Delta R$ have opposite signs. The component of $\Delta R$ that appears at or near $T_c$ is associated with the ultra-fast photoinduced evaporation of a fraction of the superfluid condensate and its subsequent reformation [84, 55, 53]. The transient that is observed in the normal state is more complicated, consisting typically of at least two components: a nearly $T$ independent bolometric signal associated with photoinduced heating of the electron gas and another component that appears at or below the pseudogap temperature $T^*$ [47, 48].

We have found that performing time-domain reflectivity in the four-beam TGS mode is very useful in helping to distinguish the several contributions to $\Delta R$ (smooth background and oscillatory) on the basis of their optical phase. When applied to YBCO, TGS reveals that, despite the appearance of $\Delta R$ in Fig. 1a, the non-oscillatory components of the transient reflectivity $\delta \tilde{r}_a$ and $\delta \tilde{r}_b$ are identical, with the apparent anisotropy coming entirely from a phase difference between $\tilde{r}_a$ and $\tilde{r}_b$. However, analysis of the TGS data indicates that the oscillatory components do display some anisotropy; the ratio of the oscillatory to background components of $\delta \tilde{r}$ is $35 \pm 18\%$ larger along $a$ than along $b$. Finally, TGS shows that the oscillations are not a modulation of the background $\delta \tilde{r}$, since the two components of the signal have distinct optical phases, by $0.3\pi$.

In 4.2b and 4.2c we plot the amplitude and optical phase (relative to $\tilde{r}_a$), respectively, of $\delta \tilde{r}_a$ as a function of $T$, for two representative time delays. The amplitude, $|\delta \tilde{r}|$, increases sharply at $T_c$ for both delays, in a manner that appears to be correlated with the amplitude of the oscillation. Above $T_c$, $|\delta \tilde{r}|$ displays a weak and featureless $T$ dependence, persisting above 200 K. Despite the smooth $T$-dependence of the $\delta \tilde{r}$ amplitude, the phase (4.2c) shows structure upon cooling below 105 K, the same $T$ at which the reflectivity oscillations become observable. It is likely that this feature in the phase of $\delta \tilde{r}$ reflects the onset of a QP excitation...
4.2. OPTICAL EXCITATION OF THE COLLECTIVE MODE

Figure 4.2: (a) The $T$ dependence of the oscillation amplitude extracted from the Fourier transforms of the $x = 0.67$ data in 4.1c. $\Delta R_Q(\nu)$ at 5 K is inset, with the fit in gray dash. The $T$ dependence of (b) the amplitude and (c) phase of the a-axis TGS signal at probe delays of 0.6 ps and 5 ps, marked on a representative $\Delta R(t)/R$ curve in the inset to (b). The amplitude increases sharply at $T_c$ for all time delays, indicating the onset of the SC response. A phase rotation at 0.6 ps onsets at 105 K, while remaining constant in the normal state at 5 ps. Note the vertical dashed lines indicating the onset of oscillations at 105 K and the enhancement at $T_c$, corresponding to the two onset temperatures observed in the TGS dynamics.
due to CDW order, as this temperature is higher than observed onsets of SC fluctuations.

The most striking aspect of data plotted in 4.2 is the enhancement \( A_{\Omega}(T) \) correlated with the onset of superconductivity. The result is surprising given the direct observation by X-ray scattering of the reduction of the CDW amplitude with the appearance of superconductivity in the same material [17]. Since we associate \( \Delta R_{\Omega} \) with the onset of CDW order, it would be natural to expect a suppression of the collective mode due to competition with superconductivity. Below we show how this seemingly anomalous behavior can emerge as a consequence of SC-CDW coupling.

A simple description of coupled order parameters is given by the Ginzburg-Landau free energy [17],

\[
F(\Phi, \Psi) = -a |\Phi|^2 + \frac{b}{2} |\Phi|^4 - \alpha |\Psi|^2 + \frac{\beta}{2} |\Psi|^4 + \lambda |\Phi|^2 |\Psi|^2
\]  

(4.1)

where \( \Phi \) and \( \Psi \) are the CDW and SC order parameters, respectively, and \( \lambda \) is a constant representing the strength of coupling between the two. For the case of coexisting orders with a repulsive interaction, the parameters \( a \), \( \alpha \), and \( \lambda \) are all positive. Minimizing the free energy with respect to \( |\Phi| \) yields for the equilibrium value of the CDW order parameter,

\[
|\Phi_{eq}|^2 = \frac{a - \lambda |\Psi|^2}{b},
\]

(4.2)

showing that for a repulsive interaction between the two orders, the CDW amplitude is suppressed in the presence of SC order.

4.3a shows how the repulsive interaction between the two order parameters provides a mechanism for photoexcitation of the CDW-related mode in the SC state. The lower part of this figure \( (T < T_c) \) is a plot of the free energy as a function of the CDW order parameter for two values of the SC amplitude. The curve with the lowest free energy corresponds to the equilibrium value of \( \Psi \) while the curve above it is calculated using a smaller value of \( \Psi \). As expected from the repulsive interaction between the two orders, the CDW amplitude is larger in the state with weaker SC. As illustrated in 4.3a by the directed laser pulse, the effect of photoexcitation is to impulsively reduce the SC order, inducing a transition from the lower to upper free energy curves. The sudden shift in the value of \( |\Phi| \) that minimizes the free energy drives the oscillation of the CDW amplitude.

The initial amplitude of the ensuing oscillation is the shift in the minimum of \( \Phi \) that
accompanies photoexcitation, which to first order in \( \lambda \) is equal to,

\[
\delta |\Phi| = |\Phi_0| \frac{\lambda}{2a} \delta |\Psi|^2 \propto |\Psi|^2,
\]

where \( \Phi_0 \) is the equilibrium value CDW order in the absence of coupling to SC. The proportionality to \( |\Psi|^2 \) on the right-hand side of Eq. 3 follows from the previous demonstration [54] that, for all temperatures below \( T_c \), the photoinduced decrease in SC order for a fixed laser fluence is proportional to \( |\Psi|^2 \) itself. This simple calculation reproduces the counter-intuitive result that the amplitude of the CDW oscillations is proportional to \( |\Psi|^2 \), and therefore is enhanced by superconductivity, even as \( |\Phi_{eq}| \) is suppressed.

Figure 4.3: (a) Schematic representation of displacive excitation mechanism described in the text. Below \( T_c \), pump excitation raises the free energy via partial evaporation of the SC condensate, decreasing the SC order parameter \( |\Psi| \). This leads to an increase in the quasi-equilibrium value of the CDW order parameter \( |\Phi| \), as represented schematically in the lower half of (a). Above \( T_c \), the free energy increases via direct photo-suppression of CDW order, leading to a reversal in the initial displacement of the free energy minimum. (b) and (c) give the \( T \) dependence of the frequency and phase of the CDW oscillations, respectively. The grey dash in (b) gives the fit to \( \nu_\Omega(T) \) obtained from coupled Ginzburg-Landau model.
The $T$ dependence of the oscillation frequency $\nu_\Omega$ obtained from the fits to $\Delta R_\Omega(\nu)$ is plotted in 4.3b. The frequency in the normal state, 1.87 THz (62 cm$^{-1}$) is well below that of the lowest optic phonon in the YBCO system, which is a Ba-O mode whose frequency is $\approx$120 cm$^{-1}$, as measured both by both Raman [33] and time-domain reflection spectroscopies [3, 68, 72]. As 4.3b shows, $\nu_\Omega$ begins to decrease with the appearance of SC order, accompanied by a decrease in the damping time from $1.9 \pm 0.5$ ps averaged over $T > T_c$ to $1.3 \pm 0.2$ ps for $T < T_c$, further evidence for a picture of coupled order parameters. Softening of the restoring force of the oscillation is expected from the curvature of $F$ evaluated at equilibrium value of CDW order,

$$\frac{\partial^2 F}{\partial |\Phi|^2} \Big|_{eq} = 4(a - \lambda |\Psi|^2). \tag{4.4}$$

The dashed curve through the data points in 4.3b is a fit to Eq. 4 assuming an approximately BCS-like temperature dependent SC order parameter $|\Psi|^2(T) \propto (1 - T^2/T_c^2)^{1/2}$.

Another clear, and yet unexpected, feature of the $T$ dependence of the collective mode parameters is the shift in the phase $\phi_\Omega$ of the oscillations upon entering the SC state, as shown in 4.3c (note that this phase is different from the optical phase of the reflectivity amplitude discussed above). The phase shift is apparent from the time-domain oscillations plotted in 4.1c, where the dotted vertical line traces out the delay time of the first crest of the oscillation as a function of $T$. As indicated in 4.3c, total phase difference from $T > T_c$ to low temperature is quite close to $\pi$. To explain this effect, we consider the excitation mechanism of the CDW oscillation in the normal state. In the absence of a competing SC state, pumping is expected to weaken the CDW order [93, 89, 24]. This corresponds to a decrease in the quasi-equilibrium value of $|\Phi|$, as shown in the upper part of 4.3a, where we plot $F$ as a function of $|\Phi|$ in equilibrium (lower curve) and after photoexcitation (upper curve). As the horizontal arrows indicate, the sign of the initial displacement above $T_c$ is opposite to that predicted in the SC state, in agreement with our observation of a $\pi$ phase shift.

In addition to the measurements reported above, we have observed and characterized the collective mode oscillations in YBCO ortho-III, in which CDW ordering has also been observed. In 4.4 we compare the amplitude of the oscillations in the two compounds that we have studied thus far. Overall, the behavior of $A_\Omega(T)$ is qualitatively the same - onset
in the normal state and rapid increase for $T < T_c$ - although in YBCO ortho-III the onset of the oscillations extrapolates to a higher $T \approx 130$ K. In addition, in the ortho-III compound we have found the same shift in phase and reduction in frequency upon entering the superconducting state as shown for the ortho-VIII sample in 4.3.

Figure 4.4: The $T$ dependence of the CDW oscillations for (a) $x = 0.67$ (ortho-VIII) and (b) $x = 0.75$ (ortho-III). The black dashed lines are guides to the eye. Oscillations initially onset at approximately 105 K in ortho-VIII and 130 K in ortho-III, with both dopings displaying a pronounced enhancement in oscillation amplitude at $T_c$. 
4.3 Conclusions and Future Directions

By way of conclusion, we address some of the questions raised by our observations and their implications for future research. The first such question is whether the mode we have observed is, in fact, the amplitude mode of the CDW. On the basis of the measured frequency of 60 cm$^{-1}$, we can rule out phonon modes of the structure above the CDW ordering temperature, $T_{CDW}$. The fact that the new mode appears only at $T < T_{CDW}$ strongly suggests that it is correlated with symmetry-breaking in a low $T$ phase. However, the parameters of the oscillation do not show some of the signatures expected for an amplitude mode. At the level of mean-field theory, the frequency of the amplitude mode should go to zero as $T$ approaches the CDW ordering temperature, $T_{CDW}$. Although in real CDW systems the frequency does not shift all the way to zero, the mode is found to soften considerably and become overdamped as $T \rightarrow T_{CDW}$ [25, 95]. By contrast, the frequency and damping parameters that we observe remain constant even as the amplitude of the mode vanishes with increasing $T$. This behavior is in agreement with the observation of a Kohn anomaly in inelastic X-ray scattering, which broadens and suppresses the acoustic phonon at the CDW wavevector [58]. The dynamics of the CDW amplitude mode are then tied to the acoustic phonon, which is effectively zone-folded by the charge modulation [56].

A second question is the nature of the coupling between the CDW amplitude mode and the reflectivity. As discussed in Chapter 3, modulation of the CDW gap and the SC gap would presumably have the same optical signature. However, we have demonstrated that the optical phase of $\Delta R_\Omega$ is distinct from that of $\Delta R_{SC}$. This implies that the CDW is strongly coupled to a specific component of the optical conductivity. Possible scenarios include direct coupling of the CDW to the Drude peak, or most intriguingly, to an interband transition corresponding to the Cu-O bonds which participate most strongly in the charge ordering. Investigation of the dependence of the amplitude mode on photon energy is therefore of vital importance to understanding the nature of the CDW in YBCO.

A third and final question is the relation of the new mode in YBCO to low-frequency collective modes observed in the La$_{2-x}$(Sr$_x$Ba$_x$)CuO$_4$ family of cuprates. In particular, the mode frequency ($\nu \approx 2.0$ THz) and $T$-dependent amplitude recently reported [93] in thin films of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) are strikingly similar to what we observe in the YBCO
crystals, although the damping time is roughly five times shorter. The similarity is surprising in that scattering probes suggest very different CDW structures in the two compounds: stripe-like coupled spin and charge fluctuations in LSCO [94, 1], as opposed to charge density waves uncorrelated with spin fluctuations, perhaps with a 2D checkerboard structure, in YBCO [38]. However, the similarity might be explained by the fact that the energy of the collective mode is tied to the acoustic phonons, which have comparable dispersion in both systems. We believe that, regardless of what ultimately proves to be their origin, the careful study of these new collective modes as a function of temperature, doping, and photon energy will contribute greatly to our understanding of the role of CDW and SC coupling in the cuprate family of superconductors.
Chapter 5

Competition Between Pseudogap and Superconductivity in the Electron Doped Cuprate \( \text{Nd}_2-x\text{Ce}_x\text{CuO}_{4+\delta} \)

Historically, research on high-transition temperature superconductors has pursued two goals: uncovering their diverse properties, while at the same time identifying those that are essential to superconductivity. The latter path leads naturally to searching for those features that are common to the electron and hole-doped cuprates, as well as iron-pnictide superconductors. Certainly the most discussed of these features, aside from superconductivity itself, are the pseudogap (PG) phenomena. However, in contrast with their prominence in hole-doped systems, PG phenomena in the electron-doped cuprates [7] and iron-based superconductors are less well explored. As demonstrated in Chapter 3, time resolved optical spectroscopy has proven to be a powerful method for tracking the onsets of both PG and superconducting (SC) order with a single technique. In this work, we study the temperature and doping dependence of \( \Delta R/R \) in four NCCO samples ranging from \( x = 0.106 \) to \( x = 0.156 \). This range extends from deep in the anti-ferromagnetic phase to the lightly overdoped superconductor.
5.1 Methods

Crystals of NCCO were grown in a traveling-solvent floating-zone furnace in an oxygen atmosphere of 5 bar. To remove the excess oxygen and achieve superconductivity, the crystals were annealed for 10 hours in flowing argon at 970°C, followed by 20 hours in flowing oxygen at 500°C [66]. The Ce concentration was measured by atomic emission spectrometry. Samples were prepared for optical measurements by cleaving along the a-b plane. Our measurements were performed using a mode-locked Ti:Sapphire oscillator generating pulses of 800 nm wavelength light of duration of 150 fs and repetition rate 80 MHz. A pulse picker was employed in order to lower the repetition rate and control average laser heating effects. This was especially important in these experiments due to the necessity of separating average heating out of the superconducting phase from photo-evaporation of the SC condensate.

5.2 Doping Dependence of the PG Signal

The range of dopings which possess a superconducting ground state is much smaller in n-type cuprates than in p-type. This is related to the fact that the antiferromagnetic parent state extends to much higher larger doping, directly giving way to superconductivity at 13% carrier concentration (Figure 5.1(b)). It is thought that antiferromagnetic correlations may play a more significant role in the electron-doped cuprates than in their hole-doped counterparts [7]. It is interesting, then, that the ultrafast-optical phenomenology of the pseudogap phase is somewhat similar between these two systems. Figure 5.1(a) shows the temperature dependence of the $\Delta R/R$ response in the sample with 12.1% electron concentration. This sample is antiferromagnetic and non-superconducting, and the temperature dependence of large negative signal is somewhat similar to the temperature dependence of the PG signal in lightly underdoped Hg-1201 (see Chapter 3). The amplitude 5.1(c) and relaxation time (d) change in a similar manner upon cooling, with $\tau$ increasing with $\Delta R_{peak}$. These parameters also show a smooth, pronounced doping dependence. The onset temperature $T^*$ decreases and the transition becomes much sharper as doping is increased. Moreover, the temperature dependence of both parameters becomes much stronger at higher dopings. We now describe a detailed investigation of the behavior of the overdoped sample, where the PG signal shows
the strongest temperature dependence and coexists with superconductivity.

Figure 5.1: (a) Temperature dependence of $\Delta R/R$ in the underdoped sample with $x = 0.121$. (b) Temperature dependence of the peak amplitude of $\Delta R/R$ for all dopings. (c) The value of $T^*$ extracted from transient reflectivity (red circles) is compared with optical that determined by optical conductivity in NCCO single crystals (black squares) [78] and PCCO thin films (grey triangles) [107]. (d) The temperature dependence of the exponential decay time constant vs. temperature for all four dopings.

5.3 Detailed Study Near Optimal Doping

In this section we investigate the lightly overdoped sample with $x = 0.156$ in detail. 5.2a shows the transient reflectivity as a function of probe delay and temperature as a false color image, and 5.2b shows the the maximum amplitude of the transient reflectivity, $\Delta R/R$, induced at low fluence (0.6 $\mu$J/cm$^2$). We observe two distinct signals of opposite sign,
similar to observations described in Chapter 3. We associate the positive signal that appears at \( T_c \) with superconductivity and the negative signal with the PG, as its onset at 75 K lies on an extrapolation of the pseudogap temperature \( T^*(x) \) determined from the appearance of gaps in optical conductivity \([78, 107]\) and photoemission spectra \([67]\) as shown in 5.1(b).

\[
\frac{\Delta R}{R} \quad \text{measured at a pump fluence of 0.6 \( \mu \)J/cm}^2 \text{ over a range of temperatures.}
\]

(a) Dependence on temperature and time delay displayed as a false color image. (b) Temperature dependence of the peak value of \( \Delta R(t)/R \). Note the onset of the negative PG signal at \( T^* \approx 75 \) K and the onset of the positive SC signal at \( T_c = 23 \) K.

While the amplitude of the TRR signal shows features reminiscent of hole-doped cuprates, the decay of \( \Delta R \) with time, \( t \), is very different. \( \Delta R(t) \) decays much more slowly and, in the normal state displays scaling behavior indicative of approach to \( T = 0 \) order. In further contrast to hole-doped cuprates, we observe that very low fluence (\( \approx 2 \) \( \mu \)J/cm\(^2\)) per laser
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pulse, is sufficient to vaporize the SC condensate in NCCO. We use this effect to measure the temperature dependence of the PG signal below $T_c$ as the strength of SC order is tuned by photoexcitation, revealing a repulsive interaction between SC and PG order.

We focus first on the temperature dependence of the PG signal in the normal state. In 5.3a we plot $\Delta R(t)$ for several temperatures in the range $T_c < T < T^*$. The time-resolved data show that the increase in amplitude of the transient reflectivity with decreasing $T$ is accompanied by a slowing of response time. We find that $\Delta R(t; T)$ scales such that its rise and decay time are described with a single parameter, $\tau_{PG}$. 5.3b shows that the data in 5.3a collapse to a single curve of the form, $\Delta R(t; T) = A(T)te^{-t/\tau_{PG}}$. $A(T)$ increases rapidly with decreasing temperature near $T^*$ and levels off below 50 K. 5.3c shows that $\tau_{PG}$ grows approximately in proportion to $1/T$ in the normal state, providing strong evidence that TRR is probing critical fluctuations of $T = 0$ PG order.

We next address the question of how the critical fluctuations shown in 5.3, which are a property of the equilibrium state, arise in a pump-probe measurement. When considering the physical origin of the TRR signal, it is useful to divide photoexcitation by the pump beam into two classes. In one, photoexcitation generates a non-equilibrium population of single-particle excitations, which eventually decay as the system returns to equilibrium. In the cuprates, the SC signal is of this type; pump photons break Cooper pairs into superconducting quasiparticles which ultimately recombine pairwise to produce phonons, a process that can be described by the phenomenological Rothwarf-Taylor equations [82, 84, 35, 53]. For such processes the excitation and recombination steps are decoupled, and the rise and fall of the amplitude is not expected to obey the one parameter scaling that we observe.

The other class of photoexcitation involves coupling to a collective mode through the Raman interaction, described by a Hamiltonian of the form [70],

$$H_R = \frac{1}{2} \frac{\partial \epsilon_{ij}}{\partial \hat{Q}} \delta \hat{Q} E_i E_j,$$

where $\epsilon$ is the dielectric tensor, $E_i$ are components of the electric field of the light, and for simplicity of notation we take $\hat{Q}$ to be a scalar collective mode coordinate such as electron density, a component of spin density, or local Néel order $S_m \cdot S_n$. A linearly polarized pump
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Figure 5.3: (a) $\Delta R(t)/R$ shown for normal state temperatures between 25 K and 65 K. (b) Same data collapsed onto a single curve according to the scaling relation described in the text. (c) $\tau_{PG}$ extracted from this collapse plotted vs. temperature. The grey dashed line is proportional to $1/T$, and the solid line is a fit to $T^{-\alpha}$, with $\alpha = 1.18$. (d) Spontaneous Raman intensity obtained by Fourier transforming the PG data as described in the text.

Electric field $E_i(t) = f(t) \cos(\omega t)$ exerts a force on $\hat{Q}$ given by,

$$F(t) = \frac{1}{4} \frac{\partial \epsilon_{ii}}{\partial \hat{Q}} f^2(t)[1 + \cos(2\omega t)],$$  \hspace{1cm} (5.2)

where $\omega$ is the radiation frequency and $f(t)$ is the pulse profile. The response of the mode coordinate to this force is

$$\langle \delta \hat{Q}(t) \rangle = \int \chi_Q(t - t') F(t') dt',$$  \hspace{1cm} (5.3)

where $\chi_Q(t)$ is the impulse response function. In the limit that the pulse is short compared
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to the typical response time, Eq. (3) simplifies to \( \langle \delta \hat{Q}(t) \rangle = I \chi_Q(t) \), where

\[
I = \frac{1}{4} \frac{\partial \epsilon_{ii}}{\partial \hat{Q}} \int f^2(t) dt.
\]  \hspace{1cm} (5.4)

The same Raman interaction causes the mode displacement driven by the pump beam to modulate the reflectivity of a time-delayed probe, a process known as impulsive stimulated Raman scattering (ISRS) [104]. The mode displacement induces a change in \( \epsilon \) given by

\[
\langle \delta \epsilon_{ij}(t) \rangle = \frac{\partial \epsilon_{ij}}{\partial \hat{Q}} I \chi_Q(t),
\]  \hspace{1cm} (5.5)

which, in turn, generates a corresponding change in the reflection amplitude, that is \( \Delta r \propto \langle \delta \epsilon_{ii}(t) \rangle \). Thus ISRS provides a mechanism by which the equilibrium time-domain response function, \( \chi_Q(t) \), can be observed in TRR measurements.

For a collective mode \( \hat{Q} \) that obeys damped oscillator dynamics, the impulse response function in the overdamped regime is given by,

\[
\chi_Q(t) \propto e^{-\gamma_+ t} - e^{-\gamma_- t},
\]  \hspace{1cm} (5.6)

where \( \omega_0 \) and \( \gamma \) are the resonant frequency and damping parameter of the mode, respectively, and \( \gamma_\pm = \gamma \pm (\gamma^2 - 4\omega_0^2)^{1/2} \). At critical damping, \( \gamma = 2\omega_0 \), the impulse response function is proportional to \( te^{-\gamma t} \), which is the scaling form for TRR that we measure.

Based on the analysis presented above we conclude that fluctuations of a collective mode first become visible to our probe at \( T^* \) and with further decrease of \( T \) these fluctuations slow in a manner that is characteristic of the approach to \( T = 0 \) PG order. It is possible that the same scenario is responsible for the TRR signal that onsets near \( T^* \) in the hole-doped cuprates. However, the characteristic relaxation times of TRR in the normal state of the hole-doped cuprates are at least a factor of ten shorter than what we have observed in NCCO and therefore the the simple time-temperature scaling may be obscured by insufficient temporal resolution.

If the interpretation in terms of ISRS given above is correct, there should be a direct relationship between TRR signal and spontaneous Raman scattering in the normal state. The connection between the two measurements is through the fluctuation-dissipation theorem, which gives for the scattered intensity,

\[
S(\omega) \propto \frac{2k_B T}{\omega} \text{Im}[\chi_Q(\omega)],
\]  \hspace{1cm} (5.7)
where \( \chi_Q(\omega) \) is the Fourier transform of \( \chi_Q(t) \). In 5.3d we plot the spontaneous Raman spectra corresponding to the TRR transients shown in 5.3a. To compare with frequency-domain Raman data, we note that TRR performed with linear polarized light corresponds to the \( xx \) or \( yy \) scattering geometries, which selects modes of \( A_{1g} \) symmetry. Previously measured Raman spectra of electron-doped cuprates are consistent with our results, in that they show increased intensity with decreasing frequency in the \( A_{1g} \) channel [81], down to the low-frequency limit of the measurement, \( \approx 20 \text{ cm}^{-1} \). Measuring \( \chi_Q \) in the time rather than frequency domain enables us to follow the quantum critical scaling of the dynamics to significantly lower frequency.

Possessing an understanding of the response in the normal state allows us to examine the interplay of the PG and SC signals below \( T_c \) as a function the laser fluence, \( \Phi \). 5.4(a-c) show plots of \( \Delta R(t)/R \) at several temperatures spanning \( T_c \) for pulse fluencies of 2, 4, and 8 \( \mu \text{J/cm}^2 \), respectively. In recording these data the pulse repetition rate was varied in inverse proportion to the energy per pulse, such that the average optical power delivered to the sample remained the same. Thus the average temperature rise, estimated at less than 1 K based on the observed shifts in \( T_c \), is the same for all the data shown in 5.4. Below \( T_c \), and at the lowest fluence, the positive SC signal dominates the response and the PG signal is not clearly discernible. As \( \Phi \) is increased, the relative strength of the two signals reverses, with \( \Delta R/R \) approaching a single component PG response at high fluence.

To determine the relationship between PG and SC responses, we resolve \( \Delta R/R \) into its components, \( \Delta R(t) = \Delta R_{PG}(t) + \Delta R_{SC}(t) \). In performing this decomposition, we assume that \( \Delta R_{PG}(t, T) \) obeys the same scaling form as in the normal state. A further assumption is that the rise and decay of \( \Delta R_{SC}(t) \) can be described by exponential functions, that is, \( \Delta R_{SC}(t) = A_{SC}(1 - e^{-t/\tau_r})e^{-t/\tau_d} \). Given these forms for the PG and SC components, we then vary the parameters \( \tau_d \), \( \tau_{PG} \), and \( A_{SC} \) to achieve the best fit to \( \Delta R(t, T) \). The dashed lines in 5.4 illustrate the high quality of the fits obtained by the superposition of PG and SC responses described above (an example of the decomposition is shown in the 5.4a inset). In 5.5a and b we plot the peak values \( \Delta R_{PG}(T, \Phi) \) and \( \Delta R_{SC}(T, \Phi) \) as determined by the fitting procedure described above. 5.5a shows \( \Delta R_{PG} \) and \( \Delta R_{SC} \) as functions of \( \Phi \), for a representative temperature above \( T_c \) (26 K) and one below \( T_c \) (5 K). While above \( T_c \), \( \Delta R_{PG} \) is linear in laser fluence, both components of \( \Delta R \) are nonlinear functions of \( \Phi \).
in the superconducting state. The SC signal plateaus at a rather low saturation fluence, \( \Phi \approx 1.5 \mu J/cm^2 \), a value that is much smaller than found in the higher-\( T_c \) materials BSCCO and \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) (YBCO), but is consistent with the scaling \( \Phi_S \propto T_c^2 \) recently reported in hole-doped cuprates and pnictide superconductors [89]. This saturation phenomenon is generally associated with photoinduced vaporization of the SC condensate. In contrast, \( \Delta R_{PG} \) at 5 K grows superlinearly in the same fluence regime where \( \Delta R_{SC} \) is sublinear. The clear implication is that with increasing fluence the PG correlations strengthen as SC order weakens, suggestive of a repulsive interaction between two order parameters.

Evidence for repulsive interaction is seen as well in 5.5b, which is a plot of the fluence-normalized components, \( \Delta R_{PG}/(R\Phi) \) and \( \Delta R_{SC}/(R\Phi) \), as functions of \( T \), for the same three values of \( \Phi \) as in 5.4. Above \( T_c \), \( \Delta R_{PG}/(R\Phi) \) is independent of fluence, indicating
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Figure 5.5: (a) The PG (red squares) and SC (blue circles) components of the transient reflectivity as a function of laser fluence at 5 K, compared with the normal state signal (red triangles) as measured at 23 K. In the normal state the transient reflectivity is linear in fluence. Below $T_c$ the SC component saturates while the PG component exhibits a superlinear dependence on fluence. (b) The fluence-normalized SC (upper circles) and PG (lower squares) components as a function of temperature. At the lowest fluence, 2 $\mu$J/cm$^2$, the PG component is suppressed at the onset of superconductivity. The extent of this suppression becomes smaller as increased laser fluence causes a weakening of superconducting order.

that $\Delta R_{PG}/R$ is linear in $\Phi$ throughout the normal state. However, at 23 K the normalized amplitudes for PG and SC diverge, demonstrating that nonlinearity appears abruptly at $T_c$. Specifically, at low fluence the pump pulse does not appreciably weaken superconductivity, and the PG signal is maximally suppressed. At high fluences the SC signal saturates, indicating evaporation of the superconducting condensate, and the suppression of the PG signal is lifted. Based our hypothesis relating $\Delta R_{PG}$ to the impulsive response of a Raman active collective mode, we would tend to associate the suppression of the PG signal that begins at $T_c$ with a decrease in the correlation time of PG fluctuations in the presence of superconductivity.
5.4. CONCLUSIONS AND FUTURE DIRECTIONS

While our TRR measurements reveal a critically fluctuating order which competes with superconductivity, we emphasize that we cannot directly distinguish between charge order, spin order, or a combination of the two. Previous work on NCCO has linked the formation of the pseudogap to the onset of fluctuating antiferromagnetic order [78, 6, 57, 7]. Probing incipient antiferromagnetic order through ISRS is a plausible scenario for describing our data, and is consistent with theoretical calculations showing a repulsive interaction between superconductivity and antiferromagnetism [74]. However, this scenario is notably inconsistent with inelastic neutron scattering results [75] which reveal that the magnetic correlation length is roughly constant over the doping and temperature range where our TRR measurements indicate diverging correlations. On the other hand, the suppression of the PG response below $T_c$ bears a striking resemblance to the behavior of the PG signal in hole doped cuprates, as well as $T$-dependence of recently reported fluctuating charge density wave (CDW) order in YBCO measured using resonant soft [38] and hard [17] X-ray scattering. It is possible that our TRR measurement in NCCO probes as yet undiscovered charge fluctuations that onset near $T^*$ in the electron doped cuprates. Yet another candidate for the fluctuating order are orbital currents [96] whose existence in hole doped cuprates is inferred from spin-flip neutron scattering measurements [62].

5.4 Conclusions and Future Directions

To conclude, we have measured the photoinduced reflectivity $\Delta R$ as a function of time delay, temperature, and laser fluence in Nd$_{2-x}$Ce$_x$CuO$_{4+\delta}$. We observed the onset of a $\Delta R$ in the normal state near 75 K, with a response time that grows as approximately $T^{-1}$ with decreasing temperature. We proposed that $\Delta R(t)$ directly measures the Raman susceptibility in the time-domain, exhibiting a form of time-temperature scaling consistent with critical fluctuations. At $T_c$ we observed the onset of a second component of $\Delta R$ that is clearly associated with superconductivity. The SC and PG components of the transient reflectivity were found to be strongly coupled below $T_c$, indicating a repulsive interaction between superconductivity and some other order; further study is needed to reveal the nature of the competing order.

The scaling behavior of the pseudogap, which is readily apparent in the $x = 0.156$ sample,
can also be observed in the superconducting $x = 0.141$ sample. It is then intriguing that this behavior is completely absent in the non-superconducting samples with $x = 0.106$ and $x = 0.121$. This change in dynamics is captured in Figure 5.6(a), which displays the $\Delta R/R$ response at 30 K for each doping. The signal in the underdoped samples is characterized by a sharp rise followed by a much slower decay. These dynamics of an incoherent excitation process, and are inconsistent with the critically damped oscillator model which describes the data in the overdoped sample. Figure 5.6(b) displays the exponential rise and decay times of these signals. The decay time evolves quite smoothly with doping, while the rise time changes abruptly. This may suggest that the underlying dynamics are evolving smoothly, while the nature of the photo-excitation process changes discontinuously. This abrupt change in dynamics may also be related to behavior described in Chapter 3 in Hg-1201, which displays a discontinuous change in the nature of the pseudogap excitation at light underdoping. There is also a qualitative similarity between evolution of the PG relaxation time with doping and temperature in the electron and hole-doped compounds. Further study of the doping dependence of the PG signal in NCCO is warranted, with a finer doping dependence and phase sensitive measurements being especially relevant to performing a direct comparison to the PG signal in Hg-1201.

![Figure 5.6](image)

*Figure 5.6:* (a) Normalized $\Delta R/R$ response at 30 K for all four dopings studied. Note the sharp transition in dynamics between $x = 0.121$ and $x = 0.141$. (b) The doping dependence of the exponential rise and decay time constants of the curves in (a).
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Appendix A

Calculation of Mixed-State Coherence Factors

A.1 Mixed CDW-SC State

We show the coherence factors for a mixed charge density wave and superconducting state in mean field theory. The Hamiltonian for superconducting and density wave states can be written in a similar form:

\[
H_{SC} = \sum_k (a^\dagger_k \sigma a^\dagger_{-k}) \begin{pmatrix} \xi_k & \Delta^* & 0 & 0 \\ \Delta & \xi_k & 0 & -\Phi^* \\ 0 & \Delta^* & -\xi_{-k} & \Phi \\ 0 & 0 & \Phi^* & -\xi_{-(k+Q)} \end{pmatrix} \begin{pmatrix} a_k \sigma \\ a^\dagger_{-k} \sigma \end{pmatrix}
\]

\[
H_{DW} = \sum_k (a^\dagger_{k\sigma} a^\dagger_{(k+Q)\pm\sigma}) \begin{pmatrix} \xi_k & \Phi^* & 0 & 0 \\ \Phi & \xi_k & 0 & -\Phi^* \\ 0 & \Phi^* & -\xi_{-k} & \Phi \\ 0 & 0 & \Phi & -\xi_{-(k+Q)} \end{pmatrix} \begin{pmatrix} a_k \sigma \\ a^\dagger_{-k} \sigma \end{pmatrix}
\]

The plus and minus spins in the second Hamiltonian correspond to CDW and SDW, respectively. In order to piece these together into a single \(4 \times 4\) matrix, we note that both Hamiltonians are Hermitian. Therefore, when \(a^\dagger \rightarrow a\), \(\Phi \rightarrow -\Phi^*\). Suppressing the summation, we write the model Hamiltonian as

\[
H_{SC+DW} = v_a M v_a^\dagger = \begin{pmatrix} \xi_k & \Phi^* & 0 & 0 \\ \Phi & \xi_k & 0 & -\Phi^* \\ 0 & \Phi^* & -\xi_{-k} & \Phi \\ 0 & 0 & \Phi & -\xi_{-(k+Q)} \end{pmatrix} \begin{pmatrix} a_k \sigma \\ a^\dagger_{(k+Q)\sigma} \\ a^\dagger_{-k} \sigma \\ a^\dagger_{-(k+Q)\sigma} \end{pmatrix}
\]

where \(\Delta\) is the SC gap, \(\Phi\) is the CDW gap, and \(\xi\) is the single electron energy. The plus and minus signs in the momentum indices refer to the case of \(k > 0\) and \(k < 0\), respectively. In the case that either order parameter vanishes, this simplifies to two copies of the single-order Hamiltonian. For the purposes of this calculation, we consider only electrons near the
Fermi surface, expanding the single electron dispersion linearly about the Fermi energy such
that \( \xi_k = k v_k \). This assumption is valid in general for CDW electrons, and allows us to set
\( \xi_{k+Q} = -\xi_k \). For arbitrary phases of \( \Delta \) and \( \Phi \), this Hamiltonian diagonalizes to give the
following Eigenvalues:

\[
\epsilon_k^2 = \pm [\xi_k^2 + |\Delta|^2 + |\Phi|^2 \pm \sqrt{3|\Phi|^2|\Delta|^2}]
\]  
(A.3)

For simplicity, we’ll assume \( \Delta \) and \( \Phi \) are real, though the complex case warrants further
investigation. We introduce the normal CDW quasiparticle operators

\[
\eta_{\alpha k 1} = s_k a_{\sigma} + t_k a_{(k \pm Q)\sigma} \quad (A.4)
\]

\[
\eta_{\alpha k 2} = -t_k a_{\sigma} + s_k a_{(k \pm Q)\sigma} \quad (A.5)
\]

\[
\eta_{\beta k 1} = s_k a_{-\sigma} + t_k a_{-(k \pm Q)\sigma} \quad (A.6)
\]

\[
\eta_{\beta k 2} = -t_k a_{-\sigma} + s_k a_{-(k \pm Q)\sigma} \quad (A.7)
\]

\[
|s_k|^2 = 1 - |t_k|^2 = \frac{1}{2} (1 + \frac{\xi_k}{E_k}) \quad (A.8)
\]

\[
E_k^2 = \xi_k^2 + \Phi^2 \quad (A.9)
\]

\( s \) and \( t \) are real, so it is clear that \( s_{k+Q} = t_k = t_{-k} \). The indices \( \alpha \) and \( \beta \) contain information
about the sign of \( k \) and the spin, i.e. \( \alpha \to \beta \) takes \( k \), \( (k \pm Q) \), \( \sigma \) to \( -k \), \( -(k \pm Q) \), \( -\sigma \). Applying
this transformation to our Hamiltonian gives

\[
\mathbf{v}_{\eta} = \mathbf{v}_{\eta} B_{\eta}^{-1} = \begin{pmatrix} \eta_{\alpha k 1} & \eta_{\alpha k 2} & \eta_{\beta k 1} & \eta_{\beta k 2} \end{pmatrix} \quad (A.10)
\]

\[
B_{\eta} = \begin{pmatrix} s_k & t_k & 0 & 0 \\
-t_k & s_k & 0 & 0 \\
0 & 0 & s_k & t_k \\
0 & 0 & -t_k & s_k \end{pmatrix} \quad (A.11)
\]

\[
M_{\eta} = B_{\eta} M B_{\eta}^{-1} = \begin{pmatrix} E_k & 0 & \Delta & 0 \\
0 & -E_k & 0 & \Delta \\
\Delta & 0 & -E_k & 0 \\
0 & \Delta & 0 & E_k \end{pmatrix} \quad (A.12)
\]

We now introduce four mixed-state quasiparticle operators, given by

\[
\gamma_{\alpha k 1} = u_k \eta_{\alpha k 1} + v_k \eta_{\beta k 1}^\dagger \quad (A.13)
\]

\[
\gamma_{\beta k 2} = u_k \eta_{\beta k 2} + v_k \eta_{\alpha k 2}^\dagger \quad (A.14)
\]

\[
\gamma_{\beta k 1}^\dagger = -v_k \eta_{\alpha k 1} + u_k \eta_{\beta k 1}^\dagger \quad (A.15)
\]

\[
\gamma_{\alpha k 2}^\dagger = -u_k \eta_{\alpha k 2} + v_k \eta_{\beta k 2} \quad (A.16)
\]

\[
u_k^2 = 1 - v_k^2 = \frac{1}{2} (1 + \frac{E_k}{\epsilon_k}) \quad (A.17)
\]

\[
\epsilon_k^2 = E_k^2 + \Delta^2 = \xi_k^2 + \Phi^2 + \Delta^2 \quad (A.18)
\]
This transformation diagonalizes the Hamiltonian.

\[
\mathbf{v}_\gamma = \mathbf{v}_\eta B_\gamma^{-1} = \begin{pmatrix} \gamma_{\alpha k_1}^\dagger & \gamma_{\beta k_2}^\dagger \\ \gamma_{\beta k_1} & \gamma_{\alpha k_2} \end{pmatrix}
\]  
(A.19)

\[
B_\gamma = \begin{pmatrix} u_k - v_k & 0 \\ 0 & u_k \end{pmatrix}
\]  
(A.20)

\[
M_\gamma = B_\gamma \mathbf{M} B_\gamma^{-1} = \begin{pmatrix} 0 & 0 \\ 0 & -\epsilon_k \end{pmatrix}
\]  
(A.21)

We now consider an interaction Hamiltonian of the form

\[
H_{\text{int}} = B_{k'\sigma'k\sigma} a_{k'\sigma'}^\dagger a_{k\sigma}
\]  
(A.22)

We can now write the single electron operators in terms of the mixed state quasiparticle operators. The single electron operators can be written in terms of the quasiparticle operators as follows

\[
\begin{pmatrix}
    a_{k\uparrow}^\dagger \\
a_{(k\pm Q)^\dagger} \\
a_{-k\downarrow} \\
a_{-(k\pm Q)^\dagger}
\end{pmatrix} = \begin{pmatrix}
    su - tv - sv & tu \\
tu & sv - tu - tv \\
tv & su \\
su - tv - sv - tv
\end{pmatrix} \begin{pmatrix}
    \gamma_{\alpha k_1}^\dagger \\
\gamma_{\beta k_2}^\dagger \\
\gamma_{\beta k_1}^\dagger \\
\gamma_{\alpha k_2}^\dagger
\end{pmatrix} 
\]  
(A.23)

The single electron transitions which connect the same quasiparticle states are

\[
a_{k'\uparrow} a_{k\uparrow} = (s' u' \gamma_{\alpha k_1}' - t' v' \gamma_{\beta k_2}' - s' u' \gamma_{\beta k_1}' + t' u' \gamma_{\alpha k_2}')
\]
\[
\times (su\gamma_{\alpha k_1} - tv\gamma_{\beta k_2} - sv\gamma_{\beta k_1} + tu\gamma_{\alpha k_2})
\]

\[
a_{k'\pm Q\uparrow} a_{k\pm Q\downarrow} = (t' u' \gamma_{\alpha k_1}' + s' u' \gamma_{\beta k_2}' - t' v' \gamma_{\beta k_1}' - s' u' \gamma_{\alpha k_2}')
\]
\[
\times (tu\gamma_{\alpha k_1} + sv\gamma_{\beta k_2} - tv\gamma_{\beta k_1} - su\gamma_{\alpha k_2})
\]

\[
a_{-k\downarrow} a_{-k'\downarrow} = -(s' u' \gamma_{\alpha k_1}' - t' u' \gamma_{\beta k_2}' + s' u' \gamma_{\beta k_1}' - t' v' \gamma_{\alpha k_2}')
\]
\[
\times (sv\gamma_{\alpha k_1} - tu\gamma_{\beta k_2} + su\gamma_{\beta k_1} - tv\gamma_{\alpha k_2})
\]

\[
a_{-(k\pm Q)\downarrow} a_{-(k'\pm Q)\downarrow} = -(t' v' \gamma_{\alpha k_1}' + s' u' \gamma_{\beta k_2}' + t' u' \gamma_{\beta k_1}' + s' v' \gamma_{\alpha k_2}')
\]
\[
\times (tv\gamma_{\alpha k_1} + su\gamma_{\beta k_2} + tu\gamma_{\beta k_1} + sv\gamma_{\alpha k_2})
\]

(A.24)

We assume that the interaction depends only on the momentum transfer, and is either odd or even with respect to inversion. This gives

\[
B_{k'\gamma k\gamma} = \pm B_{(k'\pm Q)\gamma(k\pm Q)} = \pm B_{-k\gamma-k\gamma} = B_{-(k\pm Q)\gamma-(k'\pm Q)}
\]  
(A.25)

In order to obtain coherence factors for quasiparticle recombination, we sum the terms
A.1. MIXED CDW-SC STATE

with two quasiparticle annihilation operators. This gives the following expression

\[ B_{k'k\uparrow}[-\sqrt{F_1}(\gamma_{\beta k'1}\gamma_{\alpha k1} + \gamma_{\alpha k'2}\gamma_{\beta k2}) + \sqrt{F_2}(\gamma_{\beta k'1}\gamma_{\beta k2} - \gamma_{\alpha k'2}\gamma_{\beta k1})] \]

\[ F_1 = (s'v'su \pm s'u'sv \pm t'v'tu + t'u'tv)^2 \]

\[ F_2 = (s'v'tv \pm s'u'tu \mp t'v'sv - t'u'su)^2 \]

These two coherence factors are associated with terms that affect the total spin differently. 

\( F_1 \) multiplies processes which conserve spin, and \( F_2 \) multiplies processes which change spin.

In order to check the validity of this expression, we compare the limiting single-order cases to the established results. In the case that \( \Delta \to 0, v \to 0 \) and \( F_1 \) vanishes. \( F_2 \) reduces to

\[ F_2 = (t's \mp s't)^2 = \frac{1}{2} \left( 1 - \frac{\xi\xi'}{EE'} \mp \frac{|\Phi|^2}{EE'} \right) \]

\[ = \frac{1}{2} \left( 1 \pm \frac{|\Phi|^2}{EE'} \right) \]

The final equality comes from an implicit summation over \( \xi \) and \( \xi' \), leading to a cancellation of terms linear in \( \xi \).

The case of vanishing CDW order is more subtle, as the limiting behavior of the Bogoliubov coefficients depends on the sign of \( \xi \). For example, if \( \xi \) and \( \xi' \) are both less than zero, then we have \( s,s' \to 0 \). \( F_2 \) then vanishes and we obtain

\[ F_1 = (u'v \pm v'u)^2 = \frac{1}{2} \left( 1 - \frac{|\xi||\xi'|}{\epsilon\epsilon'} \pm \frac{|\Delta|^2}{\epsilon\epsilon'} \right) \]

which would give the expected answer if the second term could be made to vanish. However, this term is not odd in \( \xi \) or \( \xi' \), so it cannot be summed away. Consider then \( \xi \to -\xi > 0 \), in which case \( t \to 0 \). In this case, \( F_1 \) vanishes, leaving

\[ F_2 = (u'u \pm v'v)^2 = \frac{1}{2} \left( 1 + \frac{|\xi||\xi'|}{\epsilon\epsilon'} \pm \frac{|\Delta|^2}{\epsilon\epsilon'} \right) \]

Adding this factor to the one in Equation A.28 cancels the unwanted term, leaving the anticipated SC recombination coherence factor.

\[ F = \frac{1}{2} \left( 1 \pm \frac{|\Delta|^2}{\epsilon\epsilon'} \right) \]
This holds for all of the SC coherence factors, indicating that the correct limiting cases are obtained from this calculation.

For the case of quasiparticle recombination after photo-excitation, we consider phonon mediated recombination. The interaction matrix-element is then even in momentum, so we choose the upper sign in the coherence factor. Under the assumption that the quasiparticle population is small and that photo-injected quasiparticles rapidly thermalize to the bottom of the gap, we set $\xi = 0$. This gives $s^2 = t^2 = 1/2$, $u^2 = (1 + \Phi/\epsilon)/2$, and $v^2 = (1 - \Phi/\epsilon)/2$. $F_2$ vanishes, and we obtain

$$F_1 = \frac{\Delta^2}{\Delta^2 + \Phi^2} \quad (A.31)$$

For case II coherence factors, the situation is reversed. The first coherence factor vanishes and the second can be written.

$$F_2 = \frac{\Phi^2}{\Delta^2 + \Phi^2} \quad (A.32)$$

### A.2 Mixed SDW-SC State

We employ the same prescription for the SDW-SC mixed state, with some differences. Note that, in the SC Hamiltonian $\sigma \rightarrow -\sigma$ requires that $\Delta \rightarrow -\Delta$. The Hamiltonian is

$$H = v_a M v_a^\dagger = \begin{pmatrix} a_{k\uparrow}^\dagger & a_{(k\pm Q)\downarrow}^\dagger & a_{-k\downarrow} & a_{-(k\pm Q)\uparrow} \end{pmatrix} \begin{pmatrix} \xi_k & \Phi & \Delta & 0 \\ \Phi^* & \xi_{k+Q} & 0 & -\Delta^* \\ \Delta^* & 0 & -\xi_{-k} & -\Phi^* \\ 0 & -\Delta & -\Phi & -\xi_{-(k\pm Q)} \end{pmatrix} \begin{pmatrix} a_{k\uparrow} \\ a_{(k\pm Q)\uparrow} \\ a_{-k\downarrow} \\ a_{-(k\pm Q)\uparrow} \end{pmatrix} \quad (A.33)$$

The Eigenvalues of this system are

$$\epsilon_k^2 = \pm [\xi_k^2 + |\Delta|^2 + |\Phi|^2 \pm \sqrt{\Re\{\Phi\}^2|\Delta|^2}] \quad (A.34)$$
In this case, the total gap is the quadrature sum of the individual gap if $\Delta$ and $\Phi$ are out of phase. We therefore choose $\Delta$ real and $\Phi$ imaginary. The SDW quasiparticle operators are

\begin{align*}
\eta_{\alpha k1} &= s_k a_{k\uparrow} + t_k a_{(k\pm Q)\downarrow} \\
\eta_{\alpha k2}^\dagger &= -t_k^* a_{k\uparrow} + s_k a_{(k\pm Q)\downarrow} \\
\eta_{\beta k1}^\dagger &= s_k a_{-k\downarrow} - t_k a_{-(k\pm Q)\uparrow} \\
\eta_{\beta k2} &= t_k^* a_{-k\downarrow} + s_k a_{-(k\pm Q)\uparrow} \\
|s_k^2| &= 1 - |t_k|^2 = \frac{1}{2} (1 + \frac{\xi_k}{E_k}) \\
E_k^2 &= \xi_k^2 + \Phi^2
\end{align*}

where $t$ is imaginary so $t^* = -t$. The transformed Hamiltonian is

\begin{align*}
\mathbf{v}_\eta &= \mathbf{v}_a B_\eta^{-1} = (\eta_{\alpha k1} \eta_{\alpha k2}^\dagger \eta_{\beta k1} \eta_{\beta k2}^\dagger) \\
B_\eta &= \begin{pmatrix}
s_k & t_k & 0 & 0 \\
-t_k^* & s_k & 0 & 0 \\
0 & 0 & s_k & -t_k \\
0 & 0 & t_k & s_k
\end{pmatrix} \\
M_\eta &= B_\eta M_\eta B_\eta^{-1} = \begin{pmatrix}
E_k & 0 & \Delta & 0 \\
0 & -E_k & 0 & -\Delta \\
\Delta & 0 & -E_k & 0 \\
0 & -\Delta & 0 & E_k
\end{pmatrix}
\end{align*}

The mixed-state quasiparticle operators are

\begin{align*}
\gamma_{\alpha k1} &= u_k \eta_{\alpha k1} + v_k \eta_{\beta k1}^\dagger \\
\gamma_{\alpha k2}^\dagger &= u_k \eta_{\alpha k2}^\dagger + v_k \eta_{\beta k2} \\
\gamma_{\beta k1}^\dagger &= -v_k \eta_{\alpha k1} + u_k \eta_{\beta k1}^\dagger \\
\gamma_{\beta k2} &= -v_k \eta_{\alpha k2} + u_k \eta_{\beta k2} \\
u_k^2 &= 1 - v_k^2 = \frac{1}{2} (1 + \frac{\epsilon_k}{E_k}) \\
\epsilon_k^2 &= E_k^2 + \Delta^2 = \epsilon_k^2 + \Phi^2 + \Delta^2
\end{align*}

The diagonalized Hamiltonian is written in terms of the following matrices.

\begin{align*}
\mathbf{v}_\gamma &= \mathbf{v}_\eta B_\gamma^{-1} = (\gamma_{\alpha k1}^\dagger \gamma_{\alpha k2} \gamma_{\beta k1} \gamma_{\beta k2}^\dagger) \\
B_\gamma &= \begin{pmatrix}
u_k & 0 & v_k & 0 \\
0 & u_k & 0 & v_k \\
-v_k & 0 & u_k & 0 \\
0 & -v_k & 0 & u_k
\end{pmatrix} \\
M_\gamma &= B_\gamma M_\eta B_\gamma^{-1} = \begin{pmatrix}
\epsilon_k & 0 & 0 & 0 \\
0 & -\epsilon_k & 0 & 0 \\
0 & 0 & -\epsilon_k & 0 \\
0 & 0 & 0 & \epsilon_k
\end{pmatrix}
\end{align*}
The single electron operators can be written in terms of the quasiparticle operators as follows

\[
\begin{pmatrix}
a_{k \uparrow} \\
a_{(k+Q) \uparrow} \\
\gamma_{ak} \\
a_{-k \downarrow} \\
a_{-(k+Q) \downarrow}
\end{pmatrix} =
\begin{pmatrix}
su & -tu & -sv & tv \\
t^*u & su - t^*v - sv & tu \\
su & tv & su & tu \\
t^*v & sv & su & t^*u \\
t^*u & su & sv & t^*v
\end{pmatrix} 
\begin{pmatrix}
\gamma_{ak1} \\
\gamma_{ak2} \\
\gamma_{bk1} \\
\gamma_{bk2}
\end{pmatrix}
\]  

(A.53)

Figure A.1: The coherence factor for mixed SC-SDW (left) and SC-CDW (right). In each case, we plot vs. \( \Delta^2 \), assuming that \( \Delta^2 + \Phi^2 = \Psi^2 \) is fixed.

The single electron transitions which connect the same quasiparticle states are

\[
a_{k' \uparrow} a_{k \uparrow} = (s'u' \gamma_{ak'1} - t^*u' \gamma_{ak'2} - s'u' \gamma_{bk'1} + t^*v' \gamma_{bk'2}) \\
\times (su \gamma_{ak1} - tu \gamma_{ak2} - sv \gamma_{bk1} + tv \gamma_{bk2}) \\
a_{k' + Q \uparrow} a_{k + Q \uparrow} = (t'u' \gamma_{ak'1} + s'u' \gamma_{ak'2} - t^*v' \gamma_{bk'1} - s'u' \gamma_{bk'2}) \\
\times (t^*u \gamma_{ak1} + su \gamma_{ak2} - t^*v \gamma_{bk1} - sv \gamma_{bk2}) \\
a_{-k' \downarrow} a_{-k \downarrow} = -(s'u' \gamma_{ak'1} + t^*v' \gamma_{ak'2} + s'u' \gamma_{bk'1} + t^*u' \gamma_{bk'2}) \\
\times (sv \gamma_{ak1} + tv \gamma_{ak2} + su \gamma_{bk1} + t^*u \gamma_{bk2}) \\
a_{-(k+Q) \uparrow} a_{-(k'+Q) \downarrow} = -(t'u' \gamma_{ak'1} + s'u' \gamma_{ak'2} - t^*u' \gamma_{bk'1} + s'u' \gamma_{bk'2}) \\
\times (-t^*v \gamma_{ak1} + sv \gamma_{ak2} - t^*u \gamma_{bk1} + su \gamma_{bk2})
\]

(A.54)

We then obtain for the recombination coherence factors

\[
B_{k' \uparrow k \uparrow} = \sqrt{F_1(\gamma_{ak'2} \gamma_{bk2} + \gamma_{bk'1} \gamma_{ak1})} \\
+ \sqrt{F_2(\gamma_{ak'2} \gamma_{ak1} - \gamma_{bk'1} \gamma_{bk2})}
\]

\[
F_1 = |t'u'tv \pm s'u'sv \pm t^*u'tu + s'u'su|^2 \\
F_2 = |t'u'su \pm s'u'tu \pm t^*v'sv - s'u'tv|^2
\]

(A.55)
These expressions are identical to those in the mixed SC-CDW case, even though the quasiparticle operators are different. The dependence of $F_1$ is identical in the SC-CDW and SC-SDW cases. However, because $t$ is imaginary, the behavior of $F_2$ is significantly different, as can be seen in Figure A.1. The presence of any SDW order completely suppresses type I coherence factors for gap-energy quasiparticles, even as the $\Phi$ goes to zero. However, as $\Delta/\Phi F$ recovers more quickly for nonzero $\xi$. 
Appendix B

Example of TGS Phase Analysis

Obtaining the magnitude and absolute phase of $\Delta R$ requires that the time dependence of the reflectivity in both probe beams must be recorded simultaneously for a series of coverslip angles. Figure B.1 shows an example of a single TGS measurement. At a single time delay, we plot $\Delta R/R$ as a function of the coverslip angle $\theta$ in Figure B.2. We fit these points with a function of the form $A + B \sin(a\theta + b)$. This fitting is repeated for every time delay. The parameter $a$ should be fixed for all time delays, as this is the conversion factor between coverslip angle and optical phase. The results of these fits are plotted in the top row of Figure B.3.

In order to extract the absolute phase, we follow the prescription given in Reference [37]. The spatially uniform part of the signal is given by $\Delta R/R = (A_{\text{upper}} + A_{\text{lower}})/2$, and the amplitude of the transient grating signal is $TG/R = (B_{\text{upper}} + B_{\text{lower}})/2$. The absolute phase of the sample $\phi_s = \phi_r - \phi_{\delta r}$ is equal to $(b_{\text{upper}} - b_{\text{lower}})/2$. In order to get the correct sign for $\phi_s$, we assume that the upper beam is the one whose phase is directly modulated by the coverslip. There is a $\pi$ ambiguity in $\phi_s$ resulting from the $2\pi$ ambiguity in $b$ for each of the beams. However, the correct branch for each beam can be determined by the requirement that the real part of the transient grating signal correspond to the spatially uniform reflectivity transient, that is, $TG/R \cos(\phi) \sim \Delta R/R$.

This procedure yields a complex number at every time delay, $(TG(t)/R) \exp(i\phi_s(t))$, which completely characterizes the photo-induced change in reflectivity.
Figure B.1: The dependence of $\Delta R/R$ on coverslip angle and time delay for $T_C = 91$ K underdoped Hg-1201 for both probe beams. The lower plot corresponds to the "upper" beam, whose phase is directly controlled by the coverslip angle.
Figure B.2: The dependence of $\Delta R/R$ on the coverslip phase is shown at a time delay of 1 ps for the data corresponding to the lower plot in Figure B.1. The fitting function is as given in the text.

Figure B.3: The top row shows the time dependence of the fit parameters as given in the fitting function given in the text for the upper (purple) and lower (blue) probe beams. The bottom row shows the full physical TG parameters obtained from the fit parameters.
Figure B.4: The real (blue) and imaginary (purple) parts of the transient grating data, corresponding to the component of $\delta r$ in and out of phase with $r$, respectively.