Probing emergent behaviour in epitaxial nanocomposites using ultrafast optical spectroscopy

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Abstract

In this thesis, after explaining the experimental setup and data analysis procedure, the main experimental results are presented. Optical pump-optical probe technique has been used to study the photoinduced quasiparticle dynamics of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) single crystals of different hole-doping levels, uranium intermetallic compounds UX_3 ($\text{X} = \text{Al}, \text{Ga}, \text{Sn}$), and finally $\text{BiFeO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (BFO/YBCO) bilayer thin film heterostructure grown on STO substrate. The temperature dependence of the quasiparticle dynamics is closely studied in all of the above materials. Though Bi-2212 and UX_3 samples are not thin films, the results of pump-probe studies on these samples supported the applicability of this technique in studying the relaxation dynamics in epitaxial thin film heterostructures.

Photoexcited quasiparticle relaxation dynamics in overdoped Bi-2212 ($T_c = 65$ K, hole doping $p = 0.22$) single crystal is investigated as a function of temperature. We provide evidence of a ≈ 22 meV pseudogap ($T^* = 100$ K) at this doping level. Moreover, this pseudogap vanishes at T^* . Our data support the scenario where both the superconducting gap and pseudogap coexist in the superconducting state. Our results also suggest an increased scattering rate between electrons and spin fluctuations as the sample enters the pseudogap phase.

The first investigation of probe polarization dependence of pump-probe response of overdoped, optimally doped and underdoped Bi-2212 crystals is also reported. We observed a polarization dependence similar to that reported in orthorhombic YBCO.

The temperature dependence of relaxation dynamics of UX_3 ($\text{X} = \text{Al}, \text{Ga}, \text{Sn}$) compounds is studied using the time resolved pump-probe technique in reflectance geometry. UGa_3 is an itinerant antiferromagnet, while UAl_3 and USn_3 are spin fluctuation systems. For UGa_3 , our data are consistent with the formation of a spin density wave gap as evidenced from the quasidivergence of the relaxation time τ near the Néel temperature T_N . For UAl_3 and USn_3 , the relaxation dynamics shows a change from single-exponential to two-exponential behavior below a particular temperature, suggestive of coherence formation of the $5f$ electrons with

the conduction band electrons. This particular temperature can be attributed to the spin fluctuation temperature T_{sf} , a measure of the strength of Kondo coherence. Our T_{sf} is consistent with other data such as resistivity and susceptibility measurements. The temperature dependence of the relaxation amplitude and time of UAl_3 and USn_3 were also fitted by the Rothwarf-Taylor model. Our results show ultrafast optical spectroscopy is sensitive to the c- f Kondo hybridization in the f -electron systems.

The temperature dependence of relaxation dynamics in bilayer thin film heterostructure composed of multiferroic BFO and superconducting YBCO grown on (001) SrTiO_3 substrate is studied by pump probe technique. The relaxation dynamics is compared with YBCO and BFO thin films of same growth conditions. The superconductivity of YBCO is found to be retained in the heterostructure. We observe the speeding up of YBCO dynamics in the superconducting state in the heterostructure. Also, BFO dynamics is seen to be affected by the YBCO underlayer in the superconducting state in the heterostructure.

We performed terahertz time-domain spectroscopy measurements on YBCO films grown on MgO and LSAT substrates. Our data agrees with literature on optical conductivity measurements of YBCO in the THz regime. This will be used as a starting point to detailed study on terahertz dynamics of heterostructures such as BFO/YBCO bilayer.

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Chapter 1

Introduction

The chapter begins with the motivation for undertaking this thesis work. The scope and main objectives of this thesis will be discussed. The chapter concludes with an overview of the whole thesis.

1.1 Motivation

1.1.1 Why Ultrafast Optical Spectroscopy?

Ultrafast optical spectroscopy is a powerful characterization technique made possible by the advent of reliable ultrafast laser systems. This broad, interdisciplinary research area enables the study of photoinduced ultrafast processes in material systems with sub-picosecond temporal resolution and spectral selectivity. Ultrafast optical spectroscopy is especially useful for spectroscopy of multi-component systems and complex materials since it can distinguish between different excitations by their different relaxation dynamics, or by their different photoexcitation-intensity or temperature dependence. This helps to unravel competing degrees of freedom in multi-component systems or complex materials that ultimately determine their mechanism and functionality. This technique is hence very useful in material science where electronic, spin, and lattice dynamics, and more importantly, the coupling between these degrees of freedom are major concerns. The above mentioned advantages make the ultrafast pump-probe technique the experimental alternative to conventional frequency-domain spectroscopies, giving information on the nature of low-energy electronic structure of material systems.

1.1.2 Interesting physics at interface between complex oxides

Bringing together complex oxides at an interface, it is possible to generate materials with unusual properties and the possibilities are nearly limitless [1]. The physics at the interface between complex oxides is becoming an interesting field of research because understanding the new science at the interface would enhance the potential device applications of such materials. In this context, our research is mainly aimed at studying the photoinduced dynamics in systems with competing/coexisting orders such as overdoped $\text{Bi}_{1.4}\text{Pb}_{0.7}\text{Sr}_{1.9}\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) and multiferroic/superconductor bilayer thin film heterostructure $\text{BiFeO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (BFO/YBCO).

Fundamental Perspective

In strongly correlated systems, strong interactions between electrons produce phenomena that cannot be predicted by studying the behavior of individual non-interacting electrons. The complex interaction between different degrees of freedom (charge, spin, lattice and orbitals) of strongly correlated electron materials provides complex mechanisms for phase transitions and interface properties. Transition metal oxides are examples of strongly correlated electrons systems, where the correlated electrons lead to interesting phenomena such as superconductivity with high transition temperatures in cuprates and colossal magnetoresistance in manganites.

The interaction of the magnetic field from the orbital motion of electron with the magnetic moment from its spin is called the spin-orbit coupling. The spin-orbit coupling increases rapidly with atomic number as its magnitude is proportional to Z^4 (Z is the atomic number) [2]. Transition metal oxides show significant spin-orbit coupling owing to the high atomic number of the transition elements and, as a consequence, unconventional magnetism. Non-saturated internal electronic shells of transition elements in the $3d$ and $4f$ groups can remain unfilled and

retain their magnetism when atoms of these type are incorporated into a multi-atomic system. Also, coupling between orbitals and lattice giving rise to crystalline electric field is possible which leads to anisotropy in the orbital magnetic moment. The anisotropy of the total magnetic moment is thus brought about by spin-orbit coupling. In general, spin-orbit coupling is weak relative to crystal field splitting in d -electron systems; and as a consequence, magnetic anisotropy tends to be small. The opposite limit is found in f -electrons: crystal field splitting is small compared to spin-orbit coupling. The strong correlation between electrons, crystalline electric field, spin-orbit coupling *etc.* in the transition metal oxides, as they occur on different energy scales, lift the degeneracy of electron energy levels [3].

Figure 1.1: “(a) Schematic of the interplay between the different degrees of freedom (charge, orbital, spin and lattice) at heteroepitaxially grown interfaces between different oxide materials. (b) Some examples of interfacial reconstruction and the new emergent interfacial phenomenon that occur in these systems.” Reproduced from Ref. [4].

Oxides with complementary functionalities can be integrated into multilayer films via growth techniques like pulsed laser deposition (PLD) method. Transition metal oxide heterostructures are interesting as the interaction of the different order parameters at the interface together with the symmetry breaking resulting

from abrupt termination of the lattice or composition at the interface may lead to *emergent* behavior, or modified electronic, magnetic and/or structural properties. Here, *emergent* behavior refers to the properties of the composite system that are not found in individual constituents. Some examples of emergent behavior are given in Figure 1.1. The integration of dissimilar transition metal oxides in heterostructures is widely expected in future device applications because of the vast variety of phenomena that they show such as high temperature superconductivity, ferroelectricity, ferromagnetism, semiconducting properties etc. Ultrafast optical spectroscopy is a useful tool to distinguish any *emergent* or modified property in the heterostructure compared to its constituents.

1.1.3 Why study $\text{BiFeO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (BFO/YBCO) bilayer?

Figure 1.2: “(a) Ferromagnet: A spatial inversion produces no change, but time reversal switches the orbit and thus $\mathbf{m}$. (b) Ferroelectrics: There is no net time dependence, but spatial inversion reverses $\mathbf{p}$. (c) Multiferroics that are both ferromagnetic and ferroelectric possess neither symmetry.” Reproduced from Ref. [5].

Multiferroics are materials that demonstrate coexistence of several ferroic orders (e. g. magnetic and electric), with some coupling between them (the magnetoelectric (ME) effect). Multiferroic material lacks both spatial-inversion symmetry and time-reversal symmetry as shown in Figure 1.2. These materials are interesting from the point of view of fundamental physics as well as novel device applications.

Cuprate high-temperature superconductors are also complex materials with different and often competing order parameters. The physics at the interface between such complex materials, as in an epitaxial multilayer or nanocomposite, is a largely unexplored area. The main objective of our research in this context is: with different order parameters in close proximity to one another, such as ferroelectricity, ferromagnetism, antiferromagnetism, and superconductivity, how do they interact with one another, or how is one order *avored* over the others. An emergent phenomenon, where the properties of the composite system are not found in the individual constituents, may arise as a consequence of the interactions at the interface. In this research, we intend to use ultrafast optical spectroscopy to study the interface physics in epitaxial nanocomposites.

1.2 Scope of the thesis

Metal-oxide materials are expected to find wide use in future device applications due to the wide variety of phenomena that they exhibit. At interfaces, the properties of oxides are very much sensitive to the defects and strain which may result in modification of properties [6]. The multifunctionality of heterostructures of multiferroic and superconducting materials is gaining increased interest because of the potential applications in novel multifunctional devices. The research work carried out in this thesis is focused on studying how the interplay of various interactions in the constituent materials determines ultimate functionality in these epitaxial nanocomposites. The research is also aimed at examining the emergent behaviour, if any, at the interface by comparing the optical response of the nanocomposite with that of the constituent materials using ultrafast optical spectroscopy. Ultrafast pump-probe spectroscopy techniques, a useful tool in studying the nonequilibrium carrier dynamics in strongly correlated electron materials, employed in this thesis work can differentiate between different quasiparticle excitations by their different relaxation time scales and thus distinguish the different phases.

Ultrafast optical spectroscopy has been shown to be a useful tool to distinguish the competing phases in a superconductor. For example, in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (Tl-2223) [7], a competing antiferromagnetic order has been found below 40 K that (a) opens up a gap in the density of states (DOS), and (b) competes with superconducting order by depressing the superconducting gap. This is manifested as a two-component probe reflectivity (of opposite signs) below 40 K. This work shows that ultrafast optical spectroscopy is very useful for probing dynamics in an epitaxial nanocomposite because we can discern via the time-domain, competing order parameters which are in very close proximity with each other. Since the interface effects may dominate device performance as the systems become smaller, understanding interface properties would help in finding possible ways of controlling interfaces for better device performance.

In this context, the main objectives of this thesis are listed as follows:

- (a) To use Optical Pump - Optical Probe (OPOP) technique to study the ultrafast dynamics of the high-temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) in the overdoped regime to determine whether the pseudogap phase exists in this sample. If it exists, does it compete/coexist with superconducting phase? Also, we aim to study the polarization dependence of relaxation dynamics of underdoped, optimally doped and overdoped samples of Bi-2212.
- (b) To use OPOP techniques to study the ultrafast dynamics in heavy fermion compounds UX_3 and thereby study the hybridization between conduction electrons and f -electrons (c - f Kondo hybridization) in the f -electron systems.
- (c) After establishing the applicability of OPOP techniques in studying the ultrafast dynamics of the above-mentioned strongly correlated systems, to use this technique to study the ultrafast dynamics of BiFeO_3 (BFO), $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) and a BFO/YBCO bilayer heterostructure to look for any interesting interface effects in the heterostructure.
- (d) To perform Terahertz time-domain spectroscopy (THz-TDS) measurements

on YBCO thin films grown on different substrates (MgO and LSAT) as a preliminary test for future experiments on BFO/YBCO bilayer heterostructures.

1.3 Thesis overview

In this thesis, the OPOP data on a number of strongly correlated electron materials, namely the high-temperature superconductor Bi-2212, the heavy fermion compounds UX₃ (X=Al, Ga, Sn) and the multiferroic-superconductor thin film heterostructure BFO/YBCO, are presented. Though Bi-2212 and UX₃ are not thin film samples, the OPOP results on these samples supported the applicability of this technique in studying the relaxation dynamics in BFO/YBCO heterostructure. Also, THz-TDS data on YBCO thin films on two different substrates, MgO and LSAT, are presented. The structure of the thesis is illustrated in Figure 1.3. The thesis is outlined as follows:

Figure 1.3: Structure of thesis

Chapter 2 gives an overview of the experimental techniques that have been

used in this thesis. This chapter describes the OPOP technique that allows the measurement of photoinduced relaxation dynamics in material systems. This is followed by a section on THz-TDS measurement that has the unique ability to directly and easily measure the complex optical conductivity.

The three chapters that follow, Chapter 3-5, deal with pump-probe measurements on different material systems.

Chapter 3 describes ultrafast time-resolved photoinduced reflectivity measurements on overdoped Bi-2212 single-crystal sample. Our data are consistent with the formation of a pseudogap phase at the pseudogap temperature $T^*=100$ K, which coexists with the superconducting phase below the superconducting transition temperature T_c , *i.e.*, the “two-gap” scenario. We also see an increased scattering rate between electrons and spin fluctuations as the sample enters the pseudogap phase.

In **Chapter 4**, we discuss the polarization dependence of the photoinduced relaxation dynamics of underdoped, optimally doped and overdoped samples of Bi-2212 single crystals. We see a polarization dependence similar to orthorhombic YBCO. We have shown that polarization dependent pump-probe spectroscopy is very sensitive in the superconducting state to even a very small difference in the a- and b-axes of the crystal.

In **Chapter 5**, the temperature dependence of relaxation dynamics of UX_3 ($X = \text{Al, Ga, Sn}$) compounds is studied using time-resolved degenerate pump-probe techniques in the reflectance geometry. We have shown the pump probe technique to be sensitive to c- f hybridization.

Chapter 6 describes the pump-probe data on multiferroic-superconductor heterostructure BFO/YBCO. This study enables us to probe into the effect of the BFO overlayer on the superconducting properties of YBCO. We show some preliminary results which show recovery of the superconducting state is faster in the presence of a BFO overlayer.

Chapter 7 elaborates on the THz-TDS data on YBCO thin films on different substrates. Though previous works are reported on THz-TDS measurements of

YBCO thin films, this work forms the basis of our future experiments where we grow BFO on top of the YBCO. The work of chapters 4, 6 and 7 is still on-going.

Finally **Chapter 8** summarizes the results and suggests future work.

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Chapter 2

Experimental Techniques

This chapter is devoted to a description of the experimental techniques employed in this thesis. Following a brief introduction to the ultrafast optical spectroscopy technique, the chapter is organized into two parts - Optical pump - optical probe technique and Terahertz time domain spectroscopy.

2.1 Ultrafast Optical Spectroscopy

Through investigating fast processes, it is possible to study the dynamic properties of excited atoms and molecules which is of key importance in many branches of science. Experimental study of these processes requires the minimum time resolution to be shorter than the time scale of the process. The advent of reliable femtosecond lasers enables the experimental study of the fast processes. Ultrafast optical spectroscopy which temporally resolves phenomena at femtosecond (fs) and picosecond (ps) time scales is very useful in studying ultrafast processes taking place in a medium.

In pump-probe experiments (Figure 2.1), the sample is excited with a pump pulse which changes the sample's optical properties. These changes are subsequently probed with a probe pulse. The temporal evolution of the recovery dynamics is obtained by varying the relative time delay of the pump and probe pulses. The recovery dynamics of the sample is obtained either by measuring the photoninduced changes in optical properties of the sample such as differential reflectivity ($\Delta R/R$) or differential transmission ($\Delta T/T$).

In this thesis, we are focusing on the Optical Pump - Optical Probe (OPOP) technique and Terahertz-Time Domain Spectroscopy (THz-TDS). The following two sections detail these experimental techniques.

Figure 2.1: The sample is excited with a pump pulse with center frequency ω_1 and subsequently probed with a pulse with center frequency ω_2 for the pump-induced changes. Reproduced from Ref. [1].

2.2 Optical Pump - Optical Probe Technique

The OPOP technique is the simplest and most utilized ultrafast optical technique (Figure 2.2). Here the pump-induced reflectivity/transmission changes of the probe pulse are measured in the visible or near-infrared as a function of time delay between the pump and probe pulses. The small beam spots allow use of small pump fluence thereby minimizing sample heating without sacrificing signal to noise ratio, thus enabling data to be taken at low temperature. The probe intensity is usually much weaker than the pump. The diameter of the probe on the sample is made smaller than that of pump so that the probe beam sees a region of uniform photoexcited carrier density. For the degenerate pump-probe technique, one uses a mechanical chopper or an acousto-optic modulator to modulate the pump beam and the component of reflected/transmitted probe beam at a frequency that is detected using a lock-in amplifier. This technique can detect changes in reflectivity $\Delta R/R$ or transmissivity $\Delta T/T$ of $\sim 10^{-6}$..

For the reflection pump-probe technique (Figure 2.2), the data is normally expressed in the form of the differential reflectivity $\frac{\Delta R}{R_0}(t) = \frac{(R(t) - R_0)}{R_0}$, where $\Delta R(t) = R(t) - R_0$ is the change in reflectivity induced by the pump, t is the time delay between the pump and probe pulses, $R(t)$ and R_0 are the reflectivity of the

Figure 2.2: Time-resolved transmission/ reflection pump-probe spectroscopy. Reproduced from Ref. [2].

probe in the presence and absence of the pump, respectively. The experimental setup will be detailed in Section 2.2.1.

All optical pump-probe spectroscopy is the one simple technique to get insight into the carrier dynamics of a material. These studies help in gaining information on the nature of low-energy electronic structure of correlated electron systems like high-temperature superconductors where the dynamics are sensitive to presence of a gap in the density of states (DOS) near the Fermi level. Also this technique can differentiate between different quasiparticle excitations by their different relaxation timescales and thus distinguish the different phases, for example, the pseudogap phase in cuprate and pnictide high-temperature superconductors [3–6]. The sensitivity of this technique to the presence of a gap is detailed in Section 2.2.3.

2.2.1 Experimental Setup

Figure 2.3 shows a schematic diagram of our experimental setup. Figure 2.4 is a photograph of the set up. Sub-50 fs-wide, 800 nm-wavelength (1.55 eV) optical pulses are generated at a repetition rate of ~ 80 MHz using a commercial Ti:Sapphire laser [Micra-18 (Coherent Inc., USA) or Griffin-5 (Kapteyn-Murnane Laboratories, Inc., USA)]. These pulses get broader during their propagation to the sample because of group velocity dispersion (GVD) and relatively wide spec-

Figure 2.3: Schematic of 800 nm degenerate optical pump - optical probe set up.

Figure 2.4: Photograph of 800 nm degenerate optical pump - optical probe set up.

trum of ultra short pulses. As a result, the longer wavelength part of the pulse propagates faster than the shorter wavelength part. This pulse broadening can be compensated using a prism compressor.

Figure 2.5: Schematic of prism compressor. Red represent longer wavelengths and blue represent shorter wavelengths. This setup has a negative dispersion. M is a mirror, and P1 and P2 are prisms. Reproduced from Ref. [7].

A schematic of the prism compressor is shown in Figure 2.5. A prism compressor is installed to compensate for any GVD acquired along the optical path from oscillator to the sample, such as air, mirrors and lenses. The prisms are arranged such that the incoming p-polarized beam enters and exits the prisms under Brewster angle, thus minimizing the reflection losses. The first prism disperses the beam whereas the second prism collimates it. The beam is reflected back by the mirror M so that it again passes through both prisms. The prisms are made of SF10 material which provide, in the double-pass configuration, a negative GVD. This scheme can be adjusted to compensate for positive GVD due to propagation through optics. The negative GVD of the scheme can be explained as follows [8,9].

The optical path length contributing to dispersion is given by,

$$P = 2l \cos \beta \quad (2.1)$$

where l is the distance between the apex of the prisms and β is the angle of the dispersed beam after the first prism.

The group velocity dispersion coefficient is given by,

$$D = \frac{\lambda}{cl} \frac{d^2 P(\lambda)}{d\lambda^2}. \quad (2.2)$$

We obtain, using the chain rule for derivatives,

$$\frac{d^2 P(\lambda)}{d\lambda^2} = \left[\frac{d^2 n}{d\lambda^2} \frac{d\beta}{dn} + \left(\frac{dn}{d\lambda} \right)^2 \frac{d^2 \beta}{dn^2} \right] \frac{dP}{d\beta} + \left(\frac{dn}{d\lambda} \right)^2 \left(\frac{d\beta}{dn} \right)^2 \frac{d^2 P}{d\beta^2}. \quad (2.3)$$

From Equation (2.1),

$$\frac{dP}{d\beta} = -2l \sin \beta, \quad (2.4)$$

and

$$\frac{d^2 P}{d\beta^2} = -2l \cos \beta. \quad (2.5)$$

For minimum deviation and Brewster angle incidence, we obtain

$$\frac{d\beta}{dn} = -2, \quad (2.6)$$

and

$$\frac{d^2 \beta}{dn^2} = -4 + \frac{2}{n^3}. \quad (2.7)$$

Inserting the relations (2.4)-(2.7) into Equation (2.3), we obtain

$$\frac{d^2 P(\lambda)}{d\lambda^2} = 4l \left\{ \left[\frac{d^2 n}{d\lambda^2} + \left(2n - \frac{1}{n^3} \right) \left(\frac{dn}{d\lambda} \right)^2 \right] \sin \beta - 2 \left(\frac{dn}{d\lambda} \right)^2 \cos \beta \right\}. \quad (2.8)$$

In general, β is relatively small, so $\sin \beta \ll \cos \beta$. So this arrangement of prisms has a negative dispersion for sufficiently large values of l , provided $\frac{d^2 n}{d\lambda^2}$ is not excessively large compared with $\left(\frac{dn}{d\lambda} \right)^2$.

The pulse train coming out of the prism compensator is then split into the pump and probe beams using a beam splitter (BS1-800-20-1012-45P, CVI Melles Griot, USA), where 20% of the beam is reflected and 80% is transmitted. The intense beam is the pump beam and the weak beam is the probe beam. Before focussing onto the sample, the pump beam is intensity modulated using an acousto-optic modulator (AOM) (Model No: 15210 with driver 21210-1DS, Neos Technologies, USA) at a reference frequency of 100 kHz or 1 MHz to enable lock-in detection. The lock-in detection greatly increases the sensitivity in pump-probe experiments as it

uses phase-sensitive detection to pick out the component of the probe beam at the modulation frequency and phase, and reject noise signals at frequencies other than the modulation frequency [10]. A function generator (DS335 Function Generator, Stanford Research Systems, Inc., USA) provides the modulation (reference) signal for AOM and the trigger for the lock-in amplifier (SR844 RF Lock-In Amplifier, Stanford Research Systems, Inc., USA). The time-delayed probe beam is focused on the sample, overlapping with the pump beam. The delay between pump and probe pulses is realized by a retro-reflector mounted on top of a 250 mm travel linear stage (M-ILS250CC DC Servo Linear Stage, Newport Corporation, USA). The stage can be moved stepwise using a motion controller (ESP300 Controller/Driver, Newport Corporation, USA). The resolution of the delay stage is $1\text{ }\mu\text{m}$, corresponding to a time delay of 6.6 fs considering the round trip. The reflected probe signal is collected by an Avalanche Photodiode (APD) module (C5460, Hamamatsu Photonics K. K., Japan). The pump and probe beams are cross-polarized to eliminate a coherence artifact. A polarizer is placed in front of the APD module to reject the light scattered from the pump beam. A pump-beam fluence as low as $0.5\text{ }\mu\text{J}/\text{cm}^2$ (average power 1 mW) is typically used to minimize the pump induced heating effects. The probe-beam intensity is kept at least ten times lower. The overlap of the pump and probe beams on the sample is monitored with a reading telescope (1.2x, Linos, Germany) and Infrared Viewer (FIND-R-SCOPE, FJW Optical Systems, Inc., USA).

Before the sample is mounted, the pump and probe beams are focused in a beta barium borate (BBO) crystal, that produces second harmonic generation (SHG) in transmission which is detected by Si Amplified Detector, PDA100A-EC (Thorlabs, USA). The collected autocorrelation data is fitted with a gaussian and the full width at half maxima (FWHM) is measured. The pulse width of the laser pulse can be calculated using the known ratio between FWHM and pulsewidth. The width of a gaussian pulse is 0.707 times the FWHM of the gaussian autocorrelation function. The width of the pulse in the experiments mentioned in this thesis has been set to

sub-50-fs.

The sample is housed in a cryostat [ST-500 (Janis Research Company, USA) or CFM-1738-102 (Cryo Industries of America Inc., USA)]. The ultrafast time-resolved optical pump - optical probe experiments are performed at temperatures ranging from 5 K to 300 K. The temperature is controlled using a temperature controller (Model 331 Cryogenic Temperature Controller, Lake Shore Cryotronics, Inc., USA). A computer with a LabVIEW program is used to control the experiment and collect the data.

Figure 2.6: Ultrafast dynamics of electrons in conventional metals. Reproduced from Ref. [1].

Figure 2.6 shows what happens when we send a very short pump pulse to a sample [1]. This pump pulse creates a nonthermal electronic distribution that quickly thermalizes to become a Fermi-Dirac Distribution within tens of femtoseconds because of the very strong electron-electron coupling resulting in the electronic temperature being greater than the lattice temperature. Thereafter the electrons will start to cool via coupling to other degrees of freedom such as electron-phonon

coupling, electron-spin fluctuation coupling, *etc.* In materials, energy relaxation mainly occurs via an electron-phonon interaction that determines the electrical conductivity. The electron-phonon interaction is important in formation of ordered electronic states such as a conventional superconducting state, charge density wave state, *etc.* The strength of the electron-phonon interaction is defined as the second moment $\lambda\langle\omega^2\rangle$ of the Eliashberg spectral function $\alpha^2F(\omega)$. Since the primary way in which electron relaxation occurs is via scattering from phonons, $\lambda\langle\omega^2\rangle$ can be obtained from the electron-phonon relaxation time τ_{e-ph} . The pump-probe experiments are usually analyzed in the framework of two-temperature model which provides a theoretical expression relating τ_{e-ph} and $\lambda\langle\omega^2\rangle$ given by [11, 12],

$$\lambda\langle\omega^2\rangle = \frac{\pi}{3} \frac{k_B T_e}{\hbar \tau_{e-ph}} \quad (2.9)$$

2.2.2 Data Collection & Analysis

In our pump-probe experiments, a Ti:Sapphire laser of 80 MHz repetition rate was used as the source of both pump and probe pulses. The laser provided sub-50 fs pulses at ≈ 800 nm (1.55 eV). The pump and probe beams were polarized orthogonal to each other. The pump spot diameter was 60 μm and that of probe was 30 μm . The reflected probe beam was focused onto an avalanche photodiode detector. The photoinduced change in reflectivity $\Delta R/R$ was measured using lock-in detection. In order to minimize noise, the pump beam was modulated at 100 kHz with an acousto-optical modulator. The probe intensity was kept approximately ten times lower than the pump intensity. The temperature rise of the pump illuminated region has been considered in all the data.

The energy relaxation of the photoexcited carrier distribution created by the pump is monitored by a time-delayed probe pulse through changes in the transient optical properties of the sample. The raw data in our OPOP experiments is differential reflectivity $\Delta R/R$ versus the time delay between pump and probe pulses, which is proportional to the photoexcited quasiparticle density. The $\Delta R/R$ signal

Figure 2.7: Typical shape of pump-probe signal. Solid line shows exponential decay fit.

is measured with an APD module using the lock-in amplifier phase locked to the acousto-optical modulator. A typical pump-probe signal is shown in Figure 2.7. The relaxation dynamics is usually fitted using an exponential decay function.

2.2.3 Rothwarf-Taylor model: Sensitivity to the presence of gap

Figure 2.8: Schematic of the superconductor photoexcitation and relaxation processes. Adapted from Ref. [13].

The Rothwarf-Taylor Model is a phenomenological model that was used to describe the relaxation of photoexcited superconductors [14, 15], itinerant antifer-

romagnets [16, 17], and heavy-fermion metals [18], where the presence of a gap in the electronic DOS gives rise to a relaxation bottleneck for carrier relaxation. Figure 2.8 shows the superconductor photoexcitation and relaxation processes schematically. Following photoexcitation, each photon with energy $\geq 2\Delta$ breaks one Cooper pair into two quasiparticles. Whereas in heavy fermions, photoexcitation creates electron-hole pairs (EHPs). The measured differential reflectivity in OPOP experiments corresponds to the number of photoexcited carriers. These nonequilibrium quasiparticles thermalize to states near the gap edge via electron-electron ($e-e$) and electron-phonon ($e-ph$) interactions. When two quasiparticles (or an EHP in heavy fermions) with energies $\geq \Delta$ (Δ is the gap magnitude for superconductors or hybridization gap for heavy fermions) recombine, one high frequency phonon with $\omega \geq 2\Delta$ is emitted. These high frequency phonons are trapped within the excited volume and can further rebreak Cooper pairs (or re-excite EHPs in heavy fermions), or anharmonically decay to low frequency phonons that have an energy lower than 2Δ . These low frequency phonons will not be able to break any more Cooper pairs. The effective recombination of the quasiparticles (or EHPs) thus slows down as it is decided by decay rate of high frequency phonons [18]. This effect is often called the phonon bottleneck.

Figure 2.9: Gap size for a superconductor in the BCS (Bardeen-Cooper-Schrieffer) model as a function of temperature.

The probability of decay of high frequency phonons to low frequency phonons, $I_{ph}(\Delta)$ is proportional to Δ^n ($n > 1$) [19]. Consider two temperatures T_1 and

T_2 as shown Figure 2.9. For $T_1 < T_2$, $\Delta_1 > \Delta_2$. The probability of decay of high frequency phonons to low frequency phonons is higher at temperature T_1 , i.e. $I_{ph}(\Delta_1) > I_{ph}(\Delta_2)$. As a result, there is higher number of high frequency phonons at temperature T_2 compared to T_1 , and hence a higher number of quasiparticles is created at T_2 by the phonons rebreaking the Cooper pairs. The quasiparticle relaxation process thus slows down because of the presence of a large number of high frequency phonons, resulting in a quasi-divergence of the quasiparticle lifetime as the temperature approaches T_c from below. An example of quasi-divergence of recombination time is shown in Figure 2.10 for superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films [20].

Figure 2.10: Temperature dependence of quasiparticle recombination time for superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film. Reproduced from Ref. [20].

The pump pulse of energy 1.55 eV (far exceeding the gap magnitude of cuprate superconductors) can excite the quasiparticles to energy levels well above the gap edge. In existing model, we assume the photoexcited quasiparticles to relax to the gap edge in around a few tens of femtoseconds, but we do not exactly know how this cascading takes place. In other words, in the above assumption, we are not considering any intermediate process that may occur. Also further recombination processes are evaluated under the assumption that the quasiparticles reside at the gap edge and that all have the same energy. Hence we do not know the exact energy distribution of the quasiparticles and the high frequency phonons. The existing theory is suitable for pump-probe experiments with low excitation fluence, where

superconducting condensate is merely perturbed but not destroyed. A recent article by J. Tao *et. al.* [21] discusses a theory aimed to address directly the situation where the superconducting condensate can be destroyed by pump pulse.

2.3 Terahertz time-domain spectroscopy

THz-TDS is a far-infrared spectroscopic method in which the properties of a material are probed using terahertz (THz) pulses generated by femtosecond laser pulses. These THz transients are nearly single-cycle electromagnetic transients of typically sub-1 ps duration.

2.3.1 THz generation and detection techniques

The generation and detection of THz pulses is mainly by two methods:

(1) Photoconductive generation and detection

Figure 2.11: THz generation using photoconductive antenna. Reproduced from Ref. [22].

A photoconductive antenna is most commonly used for THz generation as well as detection. The photoconductive antenna consists of two metal electrodes on a semiconductor substrate like GaAs. Femtosecond laser pulses focussed onto the gap between electrodes creates electron-hole pairs. These photoexcited carriers driven by the voltage applied across the electrodes produce a photocurrent.

The photocurrent that varies in time generates the THz pulse. Photoconductive detection operates reverse to photoconductive generation. When a photoconductive antenna is used as the detector, the two electrodes are connected to a current sensor.

(2) Optical rectification and electro-optical sampling

Figure 2.12: THz generation using optical rectification. Reproduced from Ref. [23].

Optical rectification, a second-order nonlinear optical process, refers to generation of a quasi-DC polarization and thus difference-frequency mixing when intense laser beams propagate through an electro-optic (EO) crystal. As the femtosecond pulse has a large bandwidth, the frequency components get differenced with each other to generate THz with broad spectral bandwidth. For THz detection, a reciprocal process called electro-optical sampling is used which refers to the change of polarization of an EO crystal from the THz electric field.

2.3.2 Experimental setup

An example of a THz-TDS setup is shown in Figure 2.13 which uses optical rectification and electro-optical sampling for THz generation and detection. The second off-axis paraboloidal mirror in the beam path focuses the THz pulse onto the sample and the fourth off-axis paraboloidal mirror focuses the transmitted THz pulse onto the detector. The time-domain profile of a THz pulse transmitted through a sample is compared to that of a reference pulse where the reference pulse is a THz

pulse transmitted through vacuum or a medium with known properties. The optical properties of the sample can be obtained from analysis of the frequency spectra obtained by Fourier transformation of the time domain signal. The brightness of THz transients far exceeds that of thermal sources owing to coherent detection. The optical gating leads to much better signal-to-noise ratio ($\sim 10^5$) compared to bolometric detection. Also ultrafast time resolution is possible because of the short temporal resolution of the terahertz time-domain sources. THz-TDS, most important of all, measures *both amplitude and phase* of the electric field of the THz pulse with high linearity.

Figure 2.13: “THz-TDS and OPTP set-up. BS2 allows for the incorporation of a pump beam (red line) for OPTP experiments.” Reproduced from Ref. [1].

Most of the work in THz-TDS is being done in the frequency range 0.3 THz to 3 THz ($10 \text{ cm}^{-1} - 100 \text{ cm}^{-1}$). THz-TDS provides direct access to the real and imaginary parts of the complex optical conductivity of the sample over the measured frequency range without the need for Kramers-Kronig analysis. The THz response can also be expressed in terms of real and imaginary parts of dielectric

permittivity or in terms of the absorption and refractive index. The conductivity of a many body system describes the response of current to an electric field which is very useful in studying conducting systems. THz-TDS has been evolved as a useful contactless tool to study the light-matter interactions in material systems such as correlated electron materials, nanomaterials, etc. In these materials, many elementary excitations take place at low energies. The THz frequency range is very rich in fundamental resonances. THz-TDS can provide detailed insight into the nonequilibrium dynamics, quasiparticle dynamics, or phase transitions in materials. For example, the real part $\sigma_1(\omega)$ of optical conductivity measured in the superconducting state of a superconductor describes the quasiparticle response whereas the imaginary part $\sigma_2(\omega)$ describes the response of the superconducting condensate.

Optical Pump - Terahertz Probe Spectroscopy (OPTP)

Figure 2.14: OPTP spectroscopy of MgB_2 . (a) Frequency dependent imaginary (σ_i) and real (σ_r) conductivities at various time delays after photoexcitation at 7 K. Insets: Transmitted electric field at 7 K and 35 K. (b) The photoinduced change in conductivity ($\Delta\sigma \propto \Delta E_{sam}$) at different temperatures. The superconductivity state recovery time τ_R as a function of temperature is shown in the insets. Reproduced from Ref. [15].

THz-TDS combined with a synchronized optical pump pulse provides OPTP as shown in Figure 2.13. Here the transmitted THz electric field is measured at a certain time delay after photoexcitation (the pump delay is fixed at a certain time delay) from which the photoinduced changes in complex optical conductivity

can be determined with picosecond resolution using appropriate Fresnel equations. This method also does not require Kramers-Kronig analysis. The ability to directly measure photoinduced changes in optical conductivity is the distinct advantage of OPTP over all-optical techniques. An example of an OPTP experimental result is shown in Figure 2.14 for MgB_2 [15]. In the first case shown in Figure 2.14(a), the pump delay line is fixed at a certain time delay and the transmitted THz electric field is measured as the detector-delay line is scanned. Analysis using Fourier transforms and appropriate Fresnel equations yields the optical conductivity at several time delays after photoexcitation. In Figure 2.14(b), the detector-delay line associated with the THz probe is fixed at the position t_0 where the THz electric field is maximum $[\Delta E_{sam}(t = t_0)]$. By measuring ΔE_{sam} as the pump delay line is scanned, the photoinduced conductivity dynamics $\Delta\sigma(t)(\propto \Delta E_{sam})$ of the sample can be extracted with high temporal precision. Figure 2.14 shows the photoinduced conductivity dynamics as a function of temperature. The relaxation time obtained by fitting the data shows a quasidivergence as T_c ($T_c \sim 34$ K) is approached as shown in the inset to Figure 2.14. The reason for this quasidivergence is explained previously in Section 2.2.3.

2.3.3 Data Collection

Figure 2.15: TPS spectra 3000 from TeraView Ltd., UK., with a schematic showing coherent detection mechanism [24].

We use a TPS spectra 3000, shown in Figure 2.15, for terahertz time-domain spectroscopy measurements. TPS Spectra 3000 is a terahertz spectrometer from Teraview Ltd, UK. This system uses photoconductive antennas for generation and detection of THz radiation. It is expected to have optimized measurement performance from 0.06 THz to 3 THz, and the signal-to-noise ratio is very good due to high transmission throughput coupled with time-gated signal detection [25]. The sample compartment can be purged to avoid spectra interference from absorption of terahertz radiation by water vapour.

Figure 2.16: Photograph of ST-100 FTIR (Janis Research Company, USA) cryostat with attached motorized vertical stage MN10-0050-M02-21 BiSlide (Velmex Inc., USA).

The TPS Spectra 3000 is used with a ST-100 FTIR (Janis Research Company, USA) Cryostat shown in Figure 2.16 so that THz spectroscopy measurements can be performed on superconducting and semiconducting materials and other sample types within a range of temperatures from ~ 2.5 K to 325 K. Custom made sample holders have been used in place of the sample holder that comes with the cryostat.

The THz-TDS experiment is carried out in the transmission configuration. The substrate and sample are mounted on a sample holder in the cryostat, see Figure 2.17. The cryostat is connected to a motorized vertical stage with $2.5 \mu\text{m}$ reso-

Figure 2.17: Schematic of sample holder for THz-TDS.

lution (MN10-0050-M02-21 BiSlide, Velmex Inc., USA) that can move the cryostat up and down. The vertical stage is controlled by a VXM Stepping Motor Controller (Velmex Inc., USA) operated with the graphical user interface COSMOS (Computer Optimized Stepper Motor Operating System) software. The travel distance for the vertical stage is 5 inches.

Figure 2.18: Sample (YBCO film on MgO substrate) and reference (MgO substrate) time-domain signals in a THz-TDS measurement at room temperature.

In a THz-TDS measurement, the raw data is the transmitted THz electric field in time-domain. When the cryostat is moved down, the THz pulse transmits through the substrate and the reference THz signal is obtained. Subsequently the cryostat is moved up to let the THz transmit through the sample to obtain the

sample THz signal. The sample (YBCO thin film on MgO substrate) and reference (MgO substrate) signals in a THz-TDS measurement at room temperature are shown in Figure 2.18.

Both pulses are of very short duration. Usually, the sample signal has a lower amplitude and will be delayed. The modifications to the shape of the sample signal compared to the reference signal are associated with the optical properties of the sample.

2.3.4 Data Analysis

Figure 2.19: (a) Amplitude and (b) phase of sample (YBCO film on MgO substrate) and reference (MgO substrate) signals at room temperature.

The data analysis involves, firstly, Fourier transformation of the sample and reference signals to obtain the respective amplitude and phase as function of frequency. The result is shown in Figure 2.19.

After Fourier transformation, the complex transmission function of the sample is calculated by taking the ratio of the amplitudes and the difference in phases of the sample and reference signals. The calculation of complex transmission function for two different sample configurations is discussed below.

2.3.4.1 Sample on substrate–Substrate configuration

Considering the simplest case, let us assume the sample to have two flat and parallel sides. In the *Sample on substrate–substrate* configuration, the sample (Medium

2) of thickness d can be assumed to be placed between two media 1 and 3 (see Figure 2.20). Medium 1 is vacuum and Medium 3 is a substrate of thickness $L2$.

Figure 2.20: Sample on substrate–Substrate configuration: Optical path of the terahertz beam with insertion of substrate only and with insertion of sample on substrate.

In the first case in Figure 2.20 where there is no sample, the THz beam is transmitted only through a substrate of thickness $L1$. The spectral component of the electric field of the terahertz wave transmitted without the sample $E_{ref}(\omega)$ is then given by,

$$E_{ref}(\omega) \propto T_{13}(\omega) \cdot P_1(\omega, d) \cdot T_{31}(\omega) \cdot P_3(\omega, L1) \cdot E(\omega) \quad (2.10)$$

where $E(\omega)$ is the electric field of the incident terahertz wave. Here we consider no multiple reflection to be taking place inside the substrate.

The THz electric field at angular frequency ω , $E_{sam}(\omega)$, transmitted through the sample is given by,

$$E_{sam}(\omega) \propto T_{12}(\omega) \cdot P_2(\omega, d) \cdot T_{23}(\omega) \cdot P_3(\omega, L2) \cdot T_{31}(\omega) \cdot P_1(\omega, \Delta L) \cdot FP(\omega) \cdot E(\omega) \quad (2.11)$$

In the above two cases,

$$T_{13}(\omega) = \frac{2\tilde{n}_1}{\tilde{n}_1 + \tilde{n}_3} \quad (\text{transmission coefficient from vacuum to substrate})$$

$$T_{31}(\omega) = \frac{2\tilde{n}_3}{\tilde{n}_3 + \tilde{n}_1} \quad (\text{transmission coefficient from substrate to vacuum})$$

$$T_{12}(\omega) = \frac{2\tilde{n}_1}{\tilde{n}_1 + \tilde{n}_2} \text{ (transmission coefficient from vacuum to sample)}$$

$$T_{23}(\omega) = \frac{2\tilde{n}_2}{\tilde{n}_2 + \tilde{n}_3} \text{ (transmission coefficient from sample to substrate)}$$

$$P_1(\omega, d) = \exp \left[i \frac{\tilde{n}_1 \omega d}{c} \right] \text{ (propagation coefficient in vacuum over a distance } d \text{)}$$

$$P_1(\omega, \Delta L) = \exp \left[i \frac{\tilde{n}_1 \omega d}{c} \right] \text{ (propagation coefficient in vacuum over a distance } \Delta L \text{)}$$

$$P_2(\omega, d) = \exp \left[i \frac{\tilde{n}_1 \omega d}{c} \right] \text{ (propagation coefficient in sample over a distance } d \text{)}$$

$$P_3(\omega, L1) = \exp \left[i \frac{\tilde{n}_1 \omega d}{c} \right] \text{ (propagation coefficient in substrate over a distance } L1 \text{)}$$

$$P_3(\omega, L2) = \exp \left[i \frac{\tilde{n}_1 \omega d}{c} \right] \text{ (propagation coefficient in substrate over a distance } L2 \text{)}$$

where $\tilde{n}_a = n_a + i\kappa_a$ is the complex refractive index of medium a ($a = 1$ is vacuum, $a = 2$ is sample, and $a = 3$ is substrate) which depends on the angular frequency ω . The multiple reflections (backward and forward reflections) in the sample (Fabry-Pérot effect) are represented by the summation $FP(\omega)$. Any difference in thickness of substrates is taken care of by the ΔL term where $\Delta L = L1 - L2$.

The complex transmission coefficient $T(\omega)$ is then obtained by dividing the signal with the sample $E_{sam}(\omega)$ by the signal without the sample $E_{ref}(\omega)$

$$\begin{aligned} T(\omega) = \frac{E_{sam}(\omega)}{E_{ref}(\omega)} &= \frac{T_{12}(\omega).T_{23}(\omega)}{T_{13}(\omega)} \cdot \frac{P_2(\omega, d).P_1(\omega, \Delta L).P_3(\omega, L2)}{P_1(\omega, d).P_3(\omega, L1)} \cdot FP(\omega) \\ &= \frac{T_{12}(\omega).T_{23}(\omega)}{T_{13}(\omega)} \cdot \frac{P_2(\omega, d).P_1(\omega, \Delta L)}{P_1(\omega, d).P_3(\omega, \Delta L)} \cdot FP(\omega) \end{aligned} \quad (2.12)$$

Substituting the expressions for the transmission coefficients and the propagation coefficients, we get the complex transmission coefficient for the “sample on

substrate–substrate” configuration as

$$T(\omega) = \frac{2\tilde{n}_2(\tilde{n}_1 + \tilde{n}_3)}{(\tilde{n}_1 + \tilde{n}_2)(\tilde{n}_2 + \tilde{n}_3)} \cdot \exp\left[\frac{i(\tilde{n}_2 - \tilde{n}_1)\omega d}{c}\right] \cdot \exp\left[\frac{i(\tilde{n}_1 - \tilde{n}_3)\omega \Delta L}{c}\right] \cdot FP(\omega) \quad (2.13)$$

with

$$FP(\omega) = \frac{1}{1 + \left(\frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2}\right) \cdot \left(\frac{\tilde{n}_2 - \tilde{n}_3}{\tilde{n}_2 + \tilde{n}_3}\right) \cdot \exp\left[2i\tilde{n}_2 \frac{\omega d}{c}\right]} \quad (2.14)$$

for infinite reflections.

2.3.4.2 Sample–Vacuum configuration

Figure 2.21: Sample–Vacuum configuration: Optical path of the terahertz beam before and after sample insertion.

For the “sample–vacuum” configuration shown in Figure 2.21, we get the following expression for the complex transmission coefficient by substituting $L1 = 0$, $L2 = 0$ and $\tilde{n}_3 = \tilde{n}_1$ in Equation 2.13,

$$T(\omega) = \frac{4\tilde{n}_2\tilde{n}_1}{(\tilde{n}_1 + \tilde{n}_2)^2} \cdot \exp\left[\frac{i(\tilde{n}_2 - \tilde{n}_1)\omega d}{c}\right] \cdot FP(\omega) \quad (2.15)$$

with

$$FP(\omega) = \frac{1}{1 - \left(\frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2}\right)^2 \cdot \exp\left[2i\tilde{n}_2 \frac{\omega d}{c}\right]} \quad (2.16)$$

for infinite reflections. Here, the obtained transmission function for YBCO at room

temperature is given in Figure 2.22.

Figure 2.22: (a) Transmission amplitude and (b) transmission phase of the YBCO thin film at room temperature.

Figure 2.23: (a) n and (b) k of the YBCO thin film at room temperature.

Mostly, the optical properties of the sample are represented in terms of the absorption coefficient (related to the imaginary part of refractive index) and the real part of refractive index. If the thickness of sample is known, the complex index of refraction $\tilde{n}(\omega)$ can be obtained from the complex transmission function. The transmission amplitude is related to the imaginary part of the complex index of refraction and the transmission phase is related to the real part of complex index of refraction. Figure 2.23 shows the real part n and imaginary part k of the complex index of refraction of the YBCO thin film at room temperature. Optical properties are also represented in terms of the dielectric function and optical conductivity. One of the above representations is chosen depending on the properties of the sample. Complex index of refraction can be changed to complex optical conductivity or complex dielectric function depending on the properties of the sample.

The complex refractive index is given by,

$$\tilde{n}(\omega) = n(\omega) + ik(\omega). \quad (2.17)$$

The real part of refractive index n_{real} and the imaginary part of refractive index n_{imag} are obtained by solving for $T(\omega)$.

The complex dielectric function in terms of the complex refractive index is given by,

$$\tilde{\epsilon}(\omega) = \tilde{n}(\omega)^2 \quad (2.18)$$

The real and the imaginary parts of the dielectric function are obtained using the following equations:

$$\epsilon_1(\omega) = n(\omega)^2 - k(\omega)^2 = n(\omega)^2 - \left[\frac{c\alpha(\omega)}{2\omega} \right]^2 \quad (2.19)$$

and

$$\epsilon_2(\omega) = 2n(\omega)k(\omega) = cn(\omega)\alpha(\omega)/\omega. \quad (2.20)$$

The complex optical conductivity $\tilde{\sigma}(\omega)$ is related to the complex dielectric function through the relation:

$$\tilde{\epsilon}(\omega) = 1 + \frac{i}{\epsilon_0\omega} \tilde{\sigma}(\omega) \quad (2.21)$$

Hence, the real and the imaginary parts of complex optical conductivity are given by,

$$\sigma_1(\omega) = \epsilon_0\omega\epsilon_2(\omega) = 2\epsilon_0\omega n(\omega)k(\omega) \quad (2.22)$$

and

$$\sigma_2(\omega) = -\epsilon_0\omega [\epsilon_1(\omega) - \epsilon_\infty] = -\epsilon_0\omega [n(\omega)^2 - k(\omega)^2 - \epsilon_\infty]. \quad (2.23)$$

Figure 2.24 shows the real part σ_1 and imaginary part σ_2 of the complex optical conductivity of the YBCO thin film at room temperature.

Thus THz-TDS is a very useful tool for the extraction of material parameters in the terahertz frequency regime.

Figure 2.24: (a) σ_1 and (b) σ_2 of the YBCO thin film at room temperature.

2.3.4.3 Conductivity models

The extracted complex optical conductivity or complex dielectric function can be fitted with theoretical models (*e.g.* Drude model, Lorentz model, Drude-Lorentz model, *etc.*) depending on the properties of the sample.

Drude Model

The Drude model is generally used to describe optical properties of conducting

Figure 2.25: Frequency dependence of real and imaginary parts of the complex conductivity $\tilde{\sigma}(\omega)$ calculated using the Drude model for plasma frequency $\omega_p = 5$ THz and the scattering rate $\Gamma = 1$ THz.

materials. The expression for complex optical conductivity and complex dielectric

function in the Drude model is given by:

$$\begin{aligned}\tilde{\sigma}_D &= \sigma_1 + i\sigma_2 = \left(\omega_p^2 \varepsilon_0 \frac{\Gamma}{\omega^2 + \Gamma^2} \right) + i \left(\omega_p^2 \varepsilon_0 \frac{\omega}{\omega^2 + \Gamma^2} \right) \\ \tilde{\varepsilon}_D &= \varepsilon_1 + i\varepsilon_2 = \left(1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} \right) + i \left(\frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)} \right)\end{aligned}\quad (2.24)$$

where $\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m^*}$ is the plasma frequency, and $\Gamma = \tau^{-1}$ is the scattering rate.

Figure 2.25 shows σ_1 and σ_2 as a function of frequency calculated using the Drude model for plasma frequency $\omega_p = 5$ THz and the scattering rate $\Gamma = 1$ THz.

Lorentz Model

The Lorentz model is generally used to describe optical properties of insulating

Figure 2.26: Frequency dependence of real and imaginary parts of the complex conductivity $\tilde{\sigma}(\omega)$ calculated using the Lorentz model for center frequency $\omega_0 = 2$ THz, width $\Gamma = 1$ THz, and the plasma frequency $\omega_p = 5$ THz.

materials. The expressions for complex optical conductivity and complex dielectric function in single-oscillator Lorentz model are given by:

$$\begin{aligned}\tilde{\sigma}_L &= \sigma_1 + i\sigma_2 = \left(\omega_p^2 \varepsilon_0 \frac{\omega^2 \Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2} \right) + i \left(-\omega_p^2 \varepsilon_0 \frac{\omega(\omega_0^2 - \omega^2)^2}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2} \right) \\ \tilde{\varepsilon}_L &= \varepsilon_1 + i\varepsilon_2 = \left(1 + \frac{\omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2} \right) + i \left(\frac{\omega_p^2 \omega \Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2} \right)\end{aligned}\quad (2.25)$$

where $\omega_p^2 = \frac{Ne^2}{\epsilon_0 m^*}$ is the plasma frequency describing the oscillator strength, ω_0 is the center frequency and $\Gamma = \tau^{-1}$ is the scattering rate. Figure 2.26 shows σ_1 and σ_2 as a function of frequency calculated using the Lorentz model for center frequency $\omega_0 = 2$ THz, width $\Gamma = 1$ THz, and the plasma frequency $\omega_p = 5$ THz.

Drude-Lorentz Model

The Drude-Lorentz model combines the Drude model and Lorentz model into a single model which takes account of both free electron effects and bound electron effects. The complex optical conductivity and complex dielectric function in this model are given by the sum of the Drude and Lorentz terms.

$$\begin{aligned}\tilde{\sigma}_{DL} &= \tilde{\sigma}_D + \tilde{\sigma}_L \\ \tilde{\epsilon}_{DL} &= \tilde{\epsilon}_D + \tilde{\epsilon}_L\end{aligned}\tag{2.26}$$

In this thesis, we are studying THz conductivity of superconducting thin films aiming at future THz studies on heterostructures based on superconducting thin films. The complex optical conductivity of a superconductor is explained using the two-fluid model which is explained in the following section.

2.3.5 Optical conductivity of superconductor

For a superconductor, σ_1/σ_n and σ_2/σ_n as function of frequency and temperature evaluated theoretically are shown in Figure 2.27 and Figure 2.28 respectively [26] where σ_n is the conductivity in the normal state. The electrons which form the condensate and the electrons thermally excited across the superconducting gap — both respond to the applied electromagnetic field. First consider Figure 2.27(a). At $T = 0$, the real part of conductivity denotes the response of normal carriers. It accounts for the contribution of thermally-excited and photo-excited quasiparticles. For temperature well below T_c (see $T = 0$ line), absorption has a well defined threshold which defines the superconducting gap. Thereafter, i.e. for $\omega > 2\Delta/\hbar$,

the conductivity increases with increasing frequencies. No absorption is observed at $T = 0$ for frequencies $\omega < 2\Delta/\hbar$ because the energy of the electromagnetic field is very low for pair breaking to happen. But at higher temperatures $0 < T < T_c$, we can see a low frequency response from normal carriers excited across the gap. At $T = 0$ and $\omega < 2\Delta/\hbar$, the imaginary part of conductivity shown in Figure 2.27(b) denotes the response of the Cooper pair condensate. We can see that the imaginary part of conductivity scales like $1/\omega$.

Figure 2.27: (a) $\sigma_1(\omega)/\sigma_n$ and (b) $\sigma_2(\omega)/\sigma_n$ of a superconductor at different temperatures. Reproduced from Ref. [26].

The real part of temperature dependent optical conductivity shown in Figure 2.28(a) has a peak just below T_c which disappears for $\hbar\omega \geq \Delta/2$. The peak disappears well before the gap opens up. The imaginary part of temperature dependent optical conductivity, see Figure 2.28(b), saturates at low temperatures and the saturation value is equal to $\pi\Delta(0)/\hbar\omega$.

Figure 2.29 discusses a terahertz time-domain experiment performed on a niobium thin film on a quartz substrate [26]. Figure 2.29(a) shows the time-domain THz signal at two temperatures, above and below T_c . Both the real and imaginary parts of conductivity shown in Figure 2.29(b) have been obtained from the THz signals without the use of Kramers-Kronig relations. On transition of the material from normal to superconducting states, the THz signal shows an increase in am-

Figure 2.28: (a) $\sigma_1(T)/\sigma_n$ and (b) $\sigma_2(T)/\sigma_n$ of a superconductor at different frequencies. Reproduced from Ref. [26].

Figure 2.29: THz-TDS data of Niobium film ($T_c \approx 7$ K). (a) Time-resolved THz fields at $T = 4.7$ K (solid line) and 7 K (dashed line). (b) Real and imaginary parts of complex optical conductivity at $T = 4.7$ K normalized to the normal state conductivity (solid lines) are evaluated from the THz-TDS data shown in (a). Theoretical calculations are shown as dashed lines. Reproduced from Ref. [26].

plitude and also shift in phase. This change in the signal results from changes to the complex optical conductivity $\tilde{\sigma}(\omega)$ [27]. We can arrive at the real and imaginary part of the optical conductivity by doing a Fourier transformation of the time-domain THz signals and by subsequent calculations using standard thin film formulas. This is discussed in detail in Section 2.3.3. The frequency dependence of real and imaginary parts of the complex optical conductivity for $T = 4.7$ K normalized to the normal state value are shown in Figure 2.29(b). As discussed previously, the real part of the conductivity, proportional to the photoexcited quasi-

particle population, shows a strong depletion on opening of the superconducting gap and the imaginary part of conductivity reveals a $1/\omega$ -like response.

2.3.5.1 Two-Fluid Model

The two-fluid model [28] is used to explain the complex optical conductivity of superconductors. According to this model, the conductivity of a superconductor comprises of one part due to normal carriers described by the Drude equation and a second part due to superconducting carriers described by the London equation. The two critical assumptions in the two-fluid model are: “(1) the carrier response to an applied field is local; and (2) each type of carriers has its own frequency-dependent conductivity and the total conductivity is the sum of conductivities due to normal and superconducting carriers.”

The complex optical conductivity in the two-fluid model is given by [28]:

$$\tilde{\sigma}(\omega, T) = \frac{ne^2}{m^*} \left\{ \frac{x_n(T)}{\Gamma(\omega, T) - i\omega} + x_s(T) \left(\frac{i}{\omega} + \pi\delta(\omega) \right) \right\} \quad (2.27)$$

where n is the total carrier concentration, m^* is the effective mass, $x_n(T) = \frac{n_n(T)}{n}$ and $x_s(T) = \frac{n_s(T)}{n}$ are the relative normal and superconducting carrier fractions ($x_n + x_s = 1$ at all temperatures) respectively, $\Gamma = \tau^{-1}$ is the scattering rate where τ is the collision time for the normal carriers, and T is the temperature. The angular frequency ω is given by $\omega = 2\pi\nu$ where ν is the ordinary frequency. The temperature dependence of the conductivity results from the temperature dependence of x_n , x_s , and Γ . The first term in Equation (2.27) with a Drude response corresponds to a contribution from normal carriers. The second term corresponds to the contribution from the superconducting carriers. The delta function in the superconducting term exists to satisfy the Kramers-Kronig relations.

The complex conductivity of the superconductor away from $\omega = 0$ can be written as

$$\tilde{\sigma}(\omega, T) = \frac{ne^2}{m^*} \left\{ \frac{x_n(T)}{\Gamma(\omega, T) - i\omega} + i\frac{x_s(T)}{\omega} \right\} \quad (2.28)$$

since $\delta(\omega \neq 0) = 0$.

The factor $\frac{ne^2}{m^*}$ can be written in terms of the plasma frequency ω_p , since $\omega_p^2 = \frac{ne^2}{\varepsilon_0 m^*}$. Hence the above equation can be rewritten in terms of plasma frequency ω_p as:

$$\begin{aligned}\tilde{\sigma}(\omega, T) &= \varepsilon_0 \omega_p^2 \left\{ \frac{x_n(T)}{\Gamma(\omega, T) - i\omega} + i \frac{x_s(T)}{\omega} \right\} \\ &= \varepsilon_0 \omega_p^2 \left\{ \frac{x_n(T)\Gamma(\omega, T)}{\Gamma^2(\omega, T) + \omega^2} + i \left(\frac{x_n(T)\omega}{\Gamma^2(\omega, T) + \omega^2} + \frac{x_s(T)}{\omega} \right) \right\}. \quad (2.29)\end{aligned}$$

where the real part of the conductivity σ_1 is given by,

$$\sigma_1(\omega, T) = \varepsilon_0 \omega_p^2 \left[\frac{x_n(T) \cdot \Gamma}{\Gamma^2(\omega, T) + \omega^2} \right] \quad (2.30)$$

and the imaginary part of the conductivity σ_2 is given by,

$$\sigma_2(\omega, T) = \varepsilon_0 \omega_p^2 \left[\frac{x_n(T) \cdot \omega}{\Gamma^2(\omega, T) + \omega^2} + \frac{x_s(T)}{\omega} \right] \quad (2.31)$$

Below T_c , the imaginary component $\sigma_2(\omega, T < T_c)$ is dominated by a $1/\omega$ dependence of the superconducting condensate population $x_s(T)$, whereas the real part of the conductivity $\sigma_1(\omega, T < T_c)$ is proportional to the quasiparticle fraction $x_n(T)$.

The plasma frequency, the temperature dependence of normal and superconducting fractions and the temperature dependence of the quasiparticle scattering rate can be obtained by fitting the experimentally obtained complex conductivity with the two-fluid model.

The remaining quantities of interest can be derived from the complex optical conductivity by using the following procedure [28]:

At every temperature $T < T_c$, penetration depth $\lambda_L(T)$ is obtained from the imaginary conductivity $\sigma_2(\omega, T)$ using the relation

$$\sigma_2(\omega, T) = \frac{1}{\mu_0 \omega \lambda_L^2(T)} \quad (2.32)$$

over the frequency range with $\omega\tau \ll 1$. Equation (2.32) results from Equation (2.31) since $x_s(T) = \left(\frac{\lambda_L(0)}{\lambda_L(T)}\right)^2$ and $\omega_p = \frac{c}{\lambda_L(0)}$. $\lambda_L(0)$ is obtained by extrapolating the obtained values of $\lambda_L(T)$ down to $T = 0$ via quadratic regression.

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Chapter 3

Quasiparticle dynamics in overdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

Photoexcited quasiparticle relaxation dynamics in overdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ($T_c = 65$ K, hole doping $p = 0.22$) single crystal is investigated as a function of temperature. We provide evidence of a ~ 22 meV pseudogap ($T^ \simeq 100$ K) at this doping level. Moreover, this pseudogap vanishes at T^* . Our data support the scenario where both the superconducting gap and pseudogap coexist in the superconducting state. Our results also suggest an increased scattering rate between electrons and spin fluctuations as the sample enters the pseudogap phase.*

3.1 Introduction

All hole-doped cuprate high-temperature superconductors exhibit an unusual normal state characterized by the opening of a gap, called the pseudogap, in the electronic spectrum at a temperature T^* above the superconducting transition temperature T_c . Much theoretical and experimental effort has been spent in ascertaining the origin of this pseudogap [1], for the answer may prove crucial in the understanding of high- T_c superconductivity. A fundamental issue regarding the pseudogap phase is [2]: does it compete with, is unrelated to, or is a precursor of, superconductivity? Related to this is the number of energy gaps below T_c : a single energy gap would imply that the pseudogap is a precursor state, while two gaps would suggest that the pseudogap is a competing or coexisting phase [3]. Another issue is the understanding of the high-temperature superconductor phase diagram: does the T^* line merge with the T_c line on the overdoped side, or does it cross the superconducting dome around optimal-doping and fall to zero at a quantum critical point? In the former case, does the pseudogap phase coexist with the super-

conducting phase below T_c , or is it a precursor to superconductivity by smoothly evolving into the superconducting phase below T_c ? These scenarios related to the high-temperature superconductor phase diagram are depicted in Figure 3.1.

Figure 3.1: Different possibilities for the temperature-doping phase diagram of the high-temperature superconducting cuprates [4, 5] reproduced from Ref. [5]. In (a) T^* line merge with T_c on the overdoped side, in (b) T^* line crosses the superconducting dome around optimal-doping and falls to zero at a quantum critical point, and in (c) T^* line touches the superconducting dome around the optimal-doping. $T^* > T_c$ at all dopings in (a), $T^* < T_c$ beyond optimal doping in (b), and T^* does not exist above optimal doping in (c).

A variety of experimental techniques have sought to answer some of these questions. The existence of the pseudogap in underdoped hole-doped high-temperature superconductors is now not in doubt but the issue is not so clear in the overdoped regime. Angle-resolved photoemission spectroscopy (ARPES) data in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) [Ref. [6]] revealed a “peak-dip-hump” feature in the superconducting phase which persists above T_c in the pseudogap phase. Two energy scales were associated with the pseudogap — a low-energy one given by the location of the leading-edge midpoint (before the “peak”) and a high-energy one given by the position of a broad peak (hump) near the $(\pi, 0)$ point [see Figure 3.2]. The low-energy pseudogap smoothly evolves into the superconducting gap upon going from the underdoped to the overdoped regime and disappears in overdoped samples, while the high-energy pseudogap persists in overdoped samples up to a hole doping $p \approx 0.22$. On the other hand, tunneling spectroscopy data [7], whose pseudogap energies correspond to the high-energy scale in ARPES, showed that the pseudogap exists in a highly overdoped sample ($T_c=56$ K). Other measurements like c-axis transport [8]

also observed a pseudogap for an overdoped sample with $p = 0.22$, though it is not clear whether it is measuring the low-energy or high-energy pseudogap.

Figure 3.2: Pseudogap determined by position of leading-edge midpoint (circles) and high-energy feature (diamonds) in the $(\pi,0)$ ARPES spectra from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) as function of doping, reproduced from Ref. [6]. The dome represents the d-wave mean-field approximation $\Delta(x) = 4.3k_B T_c(x)/2$ with scale on the left axis.

Ultrafast time-domain pump-probe spectroscopy has been shown to be a useful tool to study the nonequilibrium carrier dynamics in high-temperature cuprate superconductors. This technique can differentiate between different quasiparticle excitations by their different relaxation timescales and thus distinguish the different phases, for example, the pseudogap phase in cuprate high-temperature superconductors [9–12]. In these experiments, a pump pulse first breaks Cooper pairs into quasiparticles which rapidly relax to states close to the Fermi energy (E_F) by electron-electron and electron-phonon scattering. The presence of a gap near E_F causes a relaxation bottleneck, so that carriers accumulate in states near the gap edge, and the subsequent relaxation and recombination dynamics give rise to a transient change in optical transmission or reflection of a time-delayed probe pulse which can be measured. These studies help in gaining information on the nature of the low-energy electronic structure of correlated electron systems like high-temperature superconductors where the dynamics are sensitive to the presence of a gap.

Bi-2212 is one of the most studied high-temperature superconductors because

of its extremely large anisotropy and cleavability, containing only CuO_2 planes and not chains, and the possibility of growing samples with a larger range of T_c s. The interpretation of the femtosecond (fs) quasiparticle dynamics in Bi-2212 with regards to the pseudogap phase has only been reported for underdoped [9] and optimally doped [10] samples. Liu *et al.* [9] reported the coexistence of the pseudogap and superconducting quasiparticles in the superconducting state of an underdoped sample by simultaneously detecting two distinct components via tuning the probe beam polarization and energy. Cao *et al.* [10] interpreted the dynamics of an optimally doped sample using the Rothwarf-Taylor (RT) model and showed the coexistence of a BCS-like temperature-dependent superconducting gap and a temperature-independent pseudogap. We analyze pump-probe data of an overdoped Bi-2212 single-crystal sample. In fitting the temperature dependence of the relaxation amplitude in the superconducting state, we require the presence of two temperature-dependent gaps to fit the data. Our data are consistent with the scenario where the superconducting gap and the pseudogap coexist below T_c , i.e., the “two-gap” scenario. The results of this chapter have been published in *Physical Review B*, **82**(21), 212503 (2010).

3.2 Experimental Setup

The experiments were performed on single crystals of Bi-2212 grown using the traveling-solvent-floating-zone method [13]. The samples were provided by Prof. S. Uchida (The University of Tokyo, Japan). The overdoped sample has been doped with Pb to obtain a T_c of 65 K ($p=0.22$). The value of T_c obtained from magnetization data collected using a magnetic property measurement system corresponds to the midpoint of the superconducting transition. The onset of superconductivity occurs at 68 K. The hole-doping value (p) was obtained from the T_c values using the parabolic law [14] $T_c = T_c^{max}[1 - 82.6(p - 0.16)^2]$, where $T_c^{max} = 95$ K. The sample was cleaved before data were taken.

The details of the experimental setup has been given in Section 2.2.2. The experiments were performed with an average pump power of $500 \mu\text{W}$, giving a pump fluence of $\sim 0.3 \mu\text{J}/\text{cm}^2$ and a photoexcited quasiparticle density of $\sim 1 \times 10^{-3}/\text{unit cell}$, showing that the system is in the weak perturbation limit.

3.3 Analysis of Temperature-rise

The temperature-rise, T_{rise} , can be analyzed in the following way:

1. Experimental data are taken at different temperatures for the pump power for which T_{rise} is to be calculated and also for a lower pump power. For this example, data were taken at 0.5 mW and 0.3 mW pump powers. Figure 3.3 plots relaxation time τ versus Temperature T for the two different pump powers. Given $\tau_1(0.5 \text{ mW}, T_1)$, we use a spline function to calculate $T'_1(0.3 \text{ mW}, \tau_1)$

Figure 3.3: Relaxation time vs cryostat temperature at different pump powers. The solid lines are cubic spline fit to the data.

2. Therefore, $T_{rise}(\tau_1) = T'_1 - T_1$
3. Plot T_{rise} versus $T(0.5 \text{ mW})$. Fit to exponential decay,

$$T_{rise} = y_0 + A \exp\left(\frac{-T(0.5 \text{ mW})}{t}\right)$$

4. Use parameters obtained from exponential decay fitting to calculate T_{rise} for each $T(0.5 \text{ mW})$. Make sure that the difference between the calculated and actual T_{rise} is small (say $< 2 \text{ K}$).
5. Obtain the relation between $T(0.5 \text{ mW})$ and $T(0.3 \text{ mW})$ by plotting $T(0.3 \text{ mW})$ versus corresponding $T(0.5 \text{ mW})$ and fitting the curve with exponential decay function.
6. Calculate “Actual” $T = T(0.5 \text{ mW}) + T_{rise}$. This is still not the “Real” temperature because of heating even at 0.3 mW .
7. Now, plot the relaxation time τ versus pump power at different temperatures. Figure 3.4 shows an example. Fit exponential decay function to each temperature curve. From this, calculate the relaxation time for zero pump power, $\tau(T, 0 \text{ mW})$ at each temperature.

Figure 3.4: Relaxation time vs pump power at different temperatures. Solid lines are exponential fit to the data.

8. We now have $\tau(T, 0 \text{ mW})$. Use spline function to calculate equivalent $T(0.3 \text{ mW})$ that gives the same τ as in Step 1.
9. Calculate $T'_{rise} = T(0 \text{ mW}) - T(0.3 \text{ mW})$ for same τ . Plot T'_{rise} as function of $T(0.5 \text{ mW})$. The relation obtained in Step 5 is used to convert $T(0.3 \text{ mW})$ to $T(0.5 \text{ mW})$. Fit T'_{rise} to exponential decay function, but force $y_0=0$.
10. Finally,

$$\text{Real } T = T(0.5 \text{ mW}) + T_{\text{rise}} + T'_{\text{rise}}$$

where T_{rise} is exponential function obtained in Step 3 and T'_{rise} is the exponential function obtained in Step 9.

3.4 Results & Discussions

Figure 3.5: Waterfall plots of transient reflection $\Delta R/R$ versus pump-probe time delay at different temperatures. Solid lines at 32 and 100 K are two-exponential fits.

In Figure 3.5 we show $\Delta R/R$ as a function of pump-probe time delay, at various temperatures above and below T_c . At low temperatures, a fast positive ~ 100 fs decay (A_{fast}) and a slow picosecond negative decay (A_{slow}) were observed, with the negative signal disappearing above T_c . We therefore ascribe A_{slow} to the reformation of superconducting order following photoexcitation. Above T_c , a two-exponential positive decay was seen up to 300 K.

Using a two-exponential decay function, we extract the temperature dependence of the relaxation amplitudes and relaxation times, as shown in Figure 3.6(a) and Figure 3.7. Notice that A_{slow} (1) crosses zero at ~ 65 K, and (2) exhibits a dip at ~ 100 K. The slow relaxation time τ_{slow} , on the other hand, exhibits an upturn near two temperatures: (1) 65 K (T_c) and (2) 100 K, the latter which we denote

Figure 3.6: (a) Temperature dependence of A_{slow} (solid circles), with fit of data above T_c with $\beta P(T)$ (dashed line), and fit of data from 28 K to T^* with $\beta G_{\text{PG}}(T) - \gamma G_{\text{SC}}(T)$ (solid line). The fitted values of T_c and T^* are 71 K and 104 K, respectively. (b) “Doping dependence of the pseudogap as determined by the position of leading-edge midpoint ($\circ$, left axis) and high-energy feature ($\diamond$, right axis) in the $(\pi,0)$ ARPES spectra from Bi-2212.” The solid circle corresponds to the pseudogap energy scale (22 meV) deduced from our data. The dome represents the d-wave mean-field approximation $\Delta(x) = 4.3k_B T_c(x)/2$. Dashed line is a guide to the eyes. Adapted from Ref. [6].

Figure 3.7: (a) Solid circles: $\tau_{\text{slow}}(T)$ data. Solid line: Fit to Equation (3.3) for $T < T_c$. Dotted line: fit to Equation (3.3) for $T_c < T < T^*$. Dashed line: fit to Equation (3.4) for $T < T_c$. (b) $\tau_{\text{fast}}(T)$ data (solid circles), with fit to $1/T^n$ (solid line) where $n = 1.3$.

as T^* , the pseudogap temperature. Both the dip in A_{slow} at 100 K and the upturn in τ_{slow} at 65 K and 100 K were reproducible upon releasing the same sample. In order to quantitatively analyze the temperature dependence of A_{slow} , we use the model proposed by Kabanov *et al.* [15] The temperature dependence of the relaxation amplitude in the superconducting state for an isotropic *temperature-*

dependent gap¹ $\Delta_c(T)$ is given by,

$$G(T) = \frac{\epsilon_I / (\Delta_c(T) + k_B T / 2)}{1 + \zeta \sqrt{2k_B T / \pi \Delta_c(T)} \exp[-\Delta_c(T) / k_B T]}. \quad (3.1)$$

where ϵ_I the pump laser intensity per unit cell and ζ is a constant. The above expression for $G(T)$ describes a reduction in the photoexcited quasiparticle density with increase in temperature, due to the decrease in gap energy and corresponding enhanced phonon emission during the initial relaxation. On the other hand, the temperature dependence of the relaxation amplitude for a temperature-independent gap Δ_p is given by,

$$P(T) = \frac{\epsilon_I / \Delta_p}{1 + \zeta \exp(-\Delta_p / k_B T)}. \quad (3.2)$$

We first fit $A_{slow}(T > T_c)$ with $\beta P(T)$, shown by the dashed line in Figure 3.6(a)– the fit obviously does not reproduce the dip in A_{slow} at 100 K. Next, we proceeded to fit $A_{slow}(T)$ with the difference $\beta G_{PG}(T) - \gamma G_{SC}(T)$. Here β and γ are positive fitting prefactors, $G_{SC}(T)$ is a function of the temperature-dependent superconducting gap $\Delta_{SC}(T)$ which closes at T_c , and $G_{PG}(T)$ is a function of the *temperature-dependent* pseudogap $\Delta_{PG}(T)$ which closes at T^* . Both $\Delta_{SC}(T)$ and $\Delta_{PG}(T)$ are assumed to obey the BCS temperature dependence in this overdoped regime. The results are shown as solid lines in Figure 3.6(a). The dip in A_{slow} at 100 K is reproduced. The fitted values of T_c and T^* are 71 K and 104 K, respectively, and the fitted $\zeta = 11$. We attribute the discrepancy between the data and fitted lines near T_c to fluctuation effects. These discrepancies may also result from the inadequate nature of Equation (3.1) to describe the region $T \approx T_c$ — the derivation of Equation (3.1) itself involves the approximation $k_B T \ll \Delta_{SC}$ [15]. Nevertheless the quality of the fits to $\tau_{slow}(T)$ later are not affected. The fitted values of the zero-temperature gaps are $\Delta_{SC}(0) = (3.0 \pm 0.2)k_B T_c$ and $\Delta_{PG}(0) = (4.1 \pm 1.5)k_B T_c$.

¹The gap, of course, is not isotropic in the momentum space. Pump-probe technique does not give any momentum dependent information. The gap that pump-probe technique sees is the average across the Fermi surface.

The fitted value of the zero-temperature superconducting gap $\Delta_{SC}(0)$ agrees well with tunneling data [$2\Delta_{SC}(0)/k_B T_c = 5.3$] [5]. Note that our treatment of the pseudogap to be temperature-dependent was motivated by the dip of A_{slow} , and the concurrent upturn of τ_{slow} , at 100 K ($\approx T^*$). Compare this with pump-probe data of other cuprates, such as $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [11], $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ [16], and optimally doped Bi-2212 [10], where no dip in the relaxation amplitude, nor upturn in the relaxation time, was seen at T^* — hence the pseudogaps there were treated as temperature independent. We attribute this difference to the large amount of overdoping of our sample. In tunneling data on an overdoped ($T_c = 74.3$ K) Bi-2212 sample, the pseudogap has a smaller magnitude than the underdoped pseudogap, and has already almost vanished at 89 K [2, 7]. The attribution of a temperature dependence to our overdoped pseudogap is also consistent with the behavior of τ_{slow} near T^* — the rapid appearance of a (pseudo)gap at T^* presents a relaxation bottleneck, which causes an upturn in τ_{slow} at T^* . If the pseudogap were to be temperature independent, there would not be a relaxation bottleneck, and we would not have seen the upturn in τ_{slow} at T^* . Our analysis suggests that, even in the overdoped regime, there is a coexistence of the superconducting and pseudogap phase below T_c . Our results are thus consistent with the two-gap scenario. Our conclusions are also consistent with recent tunneling data on an overdoped Bi-2201 sample [17], where two gaps were observed below T_c . Note that our value of $\Delta_p(0) \approx 22$ meV, is consistent with the trend in the positions of the leading-edge midpoint of ARPES data at lower dopings [see Figure 3.6(b)]. It is interesting to see that our pump-probe technique yields values of the pseudogap energy scale that coincide with the low-energy pseudogap scale from ARPES.

Next we analyze the temperature dependence of the slow relaxation time $\tau_{slow}(T)$ by using the Rothwarf-Taylor model [18] explained in Section 2.2.3. In the superconducting state ($T < T_c$), the temperature dependence of τ_{slow}^{-1} is determined by

the temperature dependence of the amplitude $A_{slow}(T)$ and is given by [10, 19, 20],

$$\tau_{slow}^{-1}(T) = \Gamma \left\{ \delta G_{SC}(T) + \eta \sqrt{\Delta_{SC}(T)T} \exp[-\Delta_{SC}(T)/T] \right\} \times [\Delta_{SC}(T) + \alpha T \Delta_{SC}(T)^4]. \quad (3.3)$$

while in the pseudogap phase ($T_c < T < T^*$), $G_{SC}(T)$ is replaced by $G_{PG}(T)$ and $\Delta_{SC}(T)$ replaced by $\Delta_{PG}(T)$, with Γ , δ , η and α as fitting parameters. Figure 3.7(a) shows the temperature dependence of τ_{slow} and the fits given by Equation (3.3) that reproduce the upturn of τ_{slow} at both T_c and T^* . The good fits show that the relaxation dynamics in both the superconducting phase and the pseudogap phase can be explained by the presence of a relaxation bottleneck due to a gap in the DOS. The term $[\Delta_{SC}(T) + \alpha T \Delta_{SC}(T)^4]$ in Equation (3.3) accounts for the temperature dependence of phonon decay rate and ensures that the values of $\Delta_{SC}(0)$ and $\Delta_{PG}(0)$ obtained from fits to $A_{slow}(T)$ and $\tau_{slow}(T)$ are the same [20]. Also note that $\Delta_{PG}(0)/k_B T^* = 2.6$ — this ratio is consistent with the value of 2.4 obtained from tunneling data of an overdoped sample with $T_c = 82$ K [2, 21], providing additional justification that the transition to the pseudogap phase really does take place at 100 K.

One might question the wisdom of using just $G_{SC}(T)$ and $\Delta_{SC}(T)$ components in Equation (3.3) for $T < T_c$. After all, in overdoped Bi-2212, the gap distribution on the sample surface is more homogeneous than in underdoped or optimally doped samples [22, 23]. One may suspect therefore that, in the superconducting state, the superconducting gap and pseudogap add in quadrature to yield an effective gap $\Delta_{eff}(T) = \sqrt{\Delta_{SC}(T)^2 + \Delta_{PG}(T)^2}$ [24]. We attempt to fit the data for τ_{slow} below T_c using,

$$\tau_{slow}^{-1}(T) = \Gamma \left\{ \delta [G_{SC}(T) + G_{PG}(T)] + \eta \sqrt{\Delta_{eff}(T)T} \times \exp[-\Delta_{eff}(T)/T] \right\} [\Delta_{eff}(T) + \alpha T \Delta_{eff}(T)^4]. \quad (3.4)$$

The poor fit of Equation (3.4) (dashed line) to data, shown in Figure 3.7(a), shows that this “effective-gap” picture does not work. ARPES data, near the antinodes of an overdoped Bi-2212 sample ($T_c = 86$ K) [25], are also inconsistent with the superconducting gap and pseudogap adding in quadrature.

We now turn to the fast component, which is positive at all temperatures. A two-exponential positive decay was also seen in optimally doped Bi-2212 (Ref. [26]) – there the authors attributed the fast decay to coupling between electrons and “hot” phonons (i.e., phonons that are strongly coupled to the electrons) while the slow decay was due to anharmonic coupling between the hot phonons and the cold lattice bath. Figure 3.7(b) shows the temperature dependence of τ_{fast} — notice its rise with decreasing temperature, before peaking at T^* and decreasing to ~ 100 fs at 30 K. Notice also the slight change in slope of τ_{fast} at T_c . The change in behavior of τ_{fast} at T^* , and to a lesser extent at T_c , is intriguing — they suggest that the fast relaxation may result from an admixture of electron-phonon and electron-spin fluctuation coupling. The peak at T^* , and its subsequent decrease below T^* , may be due to an increased scattering rate between electrons and spin fluctuations as the sample enters the pseudogap phase. This scenario is further confirmed by the T dependence of τ_{fast} above T^* — a fit to $1/T^n$ yields $n = 1.3$, which disagrees with the behavior predicted by Kabanov and Alexandrov [27] for the electron-phonon relaxation time for good ($n = 2$) and poor ($n = 3$) metals.

A further experimental work that we suggest for the overdoped crystals would be to tune the probe beam energy [9] below T_c which may help in simultaneous observation of the superconducting and pseudogap components.

3.5 Conclusion

We have performed ultrafast time-resolved photoinduced reflectivity measurements on overdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ single crystals. Our data are consistent with the formation of a pseudogap phase at $T^* = 100$ K, which coexists with the super-

conducting phase below T_c . We also see an increased scattering rate between electrons and spin fluctuations as the sample enters the pseudogap phase. Experimental studies on other moderate-to-extreme overdoped cuprates are clearly needed to confirm whether the pseudogap exists, is also temperature dependent, and whether τ_{fast} also peaks at T^* , in these materials.

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Chapter 4

Polarization dependence of photoinduced relaxation dynamics of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

The polarization dependence of relaxation dynamics in underdoped, optimally doped and overdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) is studied by time-resolved pump-probe technique in reflectance geometry. We observe that the relaxation amplitude corresponding to temperature-dependent gap show a polarization dependence similar to orthorhombic YBCO and can similarly be fitted with polarization-dependent model which considers the anisotropy of the probe transition matrix elements. Our results show ultrafast optical spectroscopy with variable probe polarization is sensitive to even very small difference in a - and b -axes of single crystals of superconducting materials in the presence of a temperature-dependent gap.

4.1 Introduction

The most important structural element of high-temperature cuprate superconductors is the two-dimensional CuO_2 plane. The mobile charge carriers in the cuprate superconductors are believed to be contained in the CuO_2 planes. The a - b plane anisotropy within the CuO_2 planes is an interesting field of research. There has been Fourier Transform InfraRed (FTIR) spectroscopy studies on the a - b plane anisotropy of Bi-2212 crystals [1] which showed that the a - b plane optical properties are anisotropic in both the normal and the superconducting state even though a and b bond lengths differ only slightly.

Ultrafast pump-probe spectroscopy is a useful tool in studying the nonequilibrium carrier dynamics in high-temperature superconductors. This technique has also been used to study the polarization dependence of photoexcited carrier dynamics in superconducting single crystals [2–8] and thin films [9, 10]. A po-

larization dependence study on detwinned single crystals of YBCO by Gay *et al.* [2] showed that the pump-probe response along the a-axis and b-axis are different (see Figure 4.1). Note that YBCO has an orthorhombic structure ($a \neq b \neq c$).

Dvorsek *et al.* have reported femtosecond pump probe experiments in untwinned

Figure 4.1: (a) Ultrafast dynamics of detwinned YBCO-123 single crystals with light polarized parallel to the a-axis (ΔR^a) and b-axis (ΔR^b). (b) ΔR^a and ΔR^b peak amplitudes as a function of temperature. Adapted from Ref. [2].

Figure 4.2: Differential reflectivity as a function of time delay with probe polarization (a) parallel to a-axis and (b) parallel to b-axis. (c) The polarization dependence of photoinduced amplitudes for Y124 at $T = 45$ K. Reproduced from Ref. [6]. The amplitude $P(\theta)$ is associated with the temperature-dependent superconducting gap and $G(\theta)$ with the temperature-independent pseudogap. Note the anisotropy in the amplitude component corresponding to the temperature-dependent gap.

$\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124) single crystal as a function of temperature (Figure 4.2(a) and (b)) and polarization (Figure 4.2(c)) [5, 6]. The data showed a two-exponential behavior, one component being associated with a temperature-dependent superconducting gap below the superconducting transition temperature T_c and the other

with a temperature-independent pseudogap below the pseudogap temperature T^* . A strong polarization anisotropy of the amplitude component corresponding to the temperature-dependent superconducting gap was observed below T_c which was attributed to the anisotropy of the probe transition matrix elements in Y124. Much of the anisotropy of YBCO has been attributed to the CuO chains. The presence of the CuO chains in YBCO makes it difficult to determine whether the CuO_2 planes themselves have any anisotropy.

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) is one of the most studied high temperature superconductors because of its extremely large anisotropy and cleavability, containing only CuO_2 planes and not chains, and the possibility of growing samples with a larger range of T_c 's. The absence of CuO chains makes Bi-2212 a better material to study the a - b plane anisotropy of CuO_2 planes. Although Bi-2212 has a nearly tetragonal structure, x-ray single crystal diffraction data has shown the true structure of Bi2212 to be orthorhombic resulting from a very small ($\sim 0.5\%$) difference in the a and b axes [11]. We have reported on the femtosecond quasiparticle dynamics in overdoped Bi-2212 in Chapter 3. In this study on probe polarization dependence of relaxation dynamics in Bi-2212 samples with different hole-doping, we see that the amplitude corresponding to the superconducting component shows a polarization anisotropy which could be explained with the model proposed by Dvorsek *et al.* taking into account the anisotropy of the probe transition matrix elements [5, 6].

4.2 Experiment

The experimental setup is detailed in Section 2.2.2. The experiments were performed with an average pump power of 1 mW, giving a pump fluence of $\sim 0.5 \mu\text{J}/\text{cm}^2$.

The experiments were performed on single crystals of Bi-2212 grown using the traveling-solvent-floating-zone method [12]. The samples were provided by Prof. S. Uchida (The University of Tokyo, Japan). We performed polarization dependence

studies of relaxation dynamics in underdoped (UD), optimally doped (OPT) and overdoped (OD) Bi-2212 samples. The T_c of the samples is obtained from magnetization data collected using a magnetic property measurement system. The overdoped sample has been doped with Pb to obtain a T_c of 65 K. The underdoped sample has a T_c of 65 K and the optimally doped sample has a T_c of 95 K. The samples were cleaved before data were taken.

The polarization rotation is achieved using a half-wave plate as it is not possible to rotate the cryostat housing the sample. The Jones vector [13] for the polarized light with incident polarization angle α after passing through the half-wave plate is,

$$M_R(\theta) \begin{pmatrix} \cos \alpha \\ \sin \alpha \end{pmatrix} = \begin{pmatrix} \cos(\alpha - 2\theta) \\ \sin(\alpha - 2\theta) \end{pmatrix} \quad (4.1)$$

where

$$M_R(\theta) = \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix}$$

is Jones matrix for a half wave plate with fast axis at angle θ with respect to the x-axis, and

$$\begin{pmatrix} \cos \alpha \\ \sin \alpha \end{pmatrix}$$

is the Jones vector for light polarized at an angle α to the x-axis. Thus the polarization will be rotated by an angle 2θ with respect to the incident polarization angle α on rotating the half-wave plate by an angle θ . A schematic of the initial sample orientations is shown in Figure 4.3.

The initial polarization direction (0°), shown in Figure 4.3, is the direction of the polarization of the probe beam before polarization rotation. The rest are the polarization angles measured in the direction of polarization rotation. The beam from the laser is horizontally polarized. Hence the probe beam on the sample is vertically polarized as the pump and probe are cross polarized.

Figure 4.3: Schematic of sample orientations of (a) underdoped Bi-2212, (b) optimally-doped Bi-2212 and (c) overdoped Bi-2212. The initial probe polarization direction is shown with the direction of rotation of polarization.

4.3 Results & Discussions

4.3.1 Underdoped Bi-2212

Figure 4.4: Pump-probe data of underdoped Bi-2212 as a function of time delay at different temperatures. Solid lines are exponential fit to the data.

Figure 4.4 shows the differential reflectivity data as a function of pump-probe delay at different temperatures below and above T_c of *underdoped* Bi-2212 together with a single-exponential decay fit to the data. Figure 4.5(a) and Figure 4.5(b) show the temperature dependence of amplitude $\frac{\Delta R}{R}$ and relaxation time τ obtained from the pump-probe data of underdoped Bi-2212, respectively. Note the upturn at 63 K just before T_c . Also, there is a larger drop in the reflectivity amplitude compared to temperatures lower than 58 K. This indicate that there is indeed the superconducting transition taking place above 63 K. A negative peak is observed

in reflectivity signal at temperatures above T_c that persists to higher temperatures and disappears above ~ 210 K. We attribute this negative signal to pseudogap phase.

Figure 4.5: Temperature dependence of (a) amplitude and (b) relaxation time [Inset: Magnified view of the region around T_c in (b)] of underdoped Bi-2212 obtained from single-exponential fit to the experimental data. Note the upturn at 63 K just before the T_c indicative of the superconducting transition. The solid line in (a) is fit using Equation (4.2) and the solid line in (b) is fit using Equation (4.3).

We use the model proposed by Kabanov *et al.* [14] to analyze the temperature dependence of the relaxation amplitude $\frac{\Delta R(T)}{R}$. The temperature dependence of the relaxation amplitude in the superconducting state for an isotropic temperature-dependent gap $\Delta(T)$ is given by¹,

$$\frac{\Delta R(T)}{R} = \frac{\epsilon_I / (\Delta(T) + k_B T / 2)}{1 + \zeta \sqrt{2k_B T / \pi \Delta(T)} \exp[-\Delta(T) / k_B T]} \quad (4.2)$$

where ϵ_I the pump laser intensity per unit cell, ζ is a constant, and $\Delta(T)$ obeys a weak-coupling BCS temperature dependence. The above expression for $\frac{\Delta R(T)}{R}$ describes a reduction in the photoexcited quasiparticle density with increase in temperature, due to the decrease in gap energy and corresponding enhanced phonon emission during the initial relaxation.

The temperature dependence of the relaxation time $\tau(T)$ is quantitatively analyzed using the Rothwarf-Taylor model [15] explained in Section 2.2.3. In the

¹For an anisotropic gap, $\Delta(T)$ in Equation (4.2) will be replaced by the Fermi-surface average $\langle \Delta_k(T) \rangle_{FS}$.

superconducting state ($T < T_c$), the temperature dependence of τ^{-1} is determined by the temperature dependence of $\frac{\Delta R(T)}{R}$ and is given by [16, 17],

$$\tau^{-1}(T) = \Gamma \left\{ \delta A(T) + \eta \sqrt{\Delta(T)T} \exp[-\Delta(T)/T] \right\} \times [\Delta(T) + \alpha T \Delta(T)^4] \quad (4.3)$$

where Γ , δ , η and α are fitting parameters.

We simultaneously fit the experimentally obtained temperature-dependent amplitude using Equation (4.2) and temperature dependent relaxation time using Equation (4.3). The fits are shown as solid lines in Figure 4.5(a) and Figure 4.5(b). The fitted value of the zero-temperature gap is $\Delta(0) = (1.05 \pm 0.07)k_B T_c$. The fitted value of T_c is 69 K.

4.3.2 Optimally-doped Bi-2212

Figure 4.6: Pump-probe data of optimally doped Bi-2212 as a function of time delay at different temperatures. Solid lines are exponential fit to the data.

Figure 4.6 shows the differential reflectivity data as a function of pump-probe delay at different temperatures below and above T_c of *optimally-doped* Bi-2212 together with single-exponential decay fit to the data. Note that the signal has an obvious negative peak at 95 K. This negative peak persists to higher temperatures and disappears above ~ 180 K and is attributed to pseudogap phase. Figure 4.7(a) and Figure 4.7(b), respectively, show the temperature dependence of the amplitude

Figure 4.7: Temperature dependence of (a) amplitude and (b) relaxation time [Inset: Magnified view of the region around T_c in (b)] of optimally-doped Bi-2212 obtained from single-exponential fit to the experimental data. Note the upturn at 90 K just before the T_c indicative of the superconducting transition. The solid line in (a) is fit using Equation (4.2) and the solid line in (b) is fit using Equation (4.3).

$\frac{\Delta R}{R}$ and relaxation time τ obtained from the pump-probe data of optimally doped Bi-2212. Note the upturn at 90 K just before T_c , and also the sudden decrease in the reflectivity amplitude after 90 K. This indicates that there is indeed the superconducting transition taking place around 95 K. We simultaneously fit the experimentally obtained temperature-dependent amplitude using Equation (4.2) and the temperature dependent relaxation time using Equation (4.3). The fits are shown as solid lines in Figure 4.7(a) and Figure 4.7(b). The fitted value of the zero-temperature gap is $\Delta(0) = (0.64 \pm 0.01)k_B T_c$. The fitted value of T_c is 95 K.

We notice the small value of the zero-temperature gap obtained for the underdoped and optimally doped Bi-2212 samples. There are two possible reasons for it: (1) the temperature dependence of $A(T)$ is a combination of the contributions from the SC gap (T -dependent) and the pseudogap (T -independent) [14] (2) we took pump probe data when the pump and probe polarizations are not parallel to the a - and b - crystal axes. It may be that the T -dependence of $A(T)$ depends sensitively on the polarizations of the laser pulses relative to the crystal axis [18]. We then took pump-probe data with the pump and probe polarizations parallel to the crystal axes, and found that the polarization does not affect the temperature dependence of amplitude as can be seen in Figure 4.8 and Figure 4.9. This rules out

reason (2). A future work will be to analyze $A(T)$ considering it as a combination of T -dependent SC gap and T -independent pseudogap below T_c .

Figure 4.8: Temperature dependence of (a) amplitude and (b) relaxation time of underdoped Bi-2212 obtained from single-exponential fit to the experimental data. Black circles: Data in Figure 4.5, Red circles: New data with pump and probe polarizations parallel to the crystal axes.

Figure 4.9: Temperature dependence of (a) amplitude and (b) relaxation time of optimally-doped Bi-2212 obtained from single-exponential fit to the experimental data. Black circles: Data in Figure 4.7, Red circles: New data with pump and probe polarizations parallel to the crystal axes.

4.3.3 Overdoped Bi-2212

Finally, we consider the *overdoped* Bi-2212 sample. Our pump-probe data on overdoped Bi-2212 indicated that the superconducting gap and pseudogap coexist below T_c . Details of the data analysis can be found in Chapter 3. In this polar-

ization dependence study of relaxation dynamics in overdoped Bi-2212, particular attention will be given to the response of the slow amplitude below T_c which contains the photoresponse of the temperature-*dependent* superconducting gap and the temperature-*dependent* pseudogap.

4.3.4 Polarization dependence of relaxation amplitude

Figure 4.10: Relaxation amplitude of differential reflectivity data of underdoped Bi-2212 at temperatures below and above T_c . The solid lines show fit to the data using Equation (4.4). Dotted lines are guide to the eye.

Figure 4.11: Relaxation amplitude of differential reflectivity data of optimally doped Bi-2212 at temperatures below and above T_c . The solid lines show fit to the data using Equation (4.4). Dotted lines are guide to the eye.

Figure 4.12: Relaxation amplitude of differential reflectivity data of overdoped Bi-2212 at temperatures below and above T_c . Polarization anisotropy is observed below $T^* = 100$ K also. The solid lines show fit to the data using Equation (4.4). Dotted lines are guide to the eye.

Now we consider the polarization dependence of the pump-probe response. At two temperatures below and above T_c , the pump-probe data of overdoped, optimally doped and underdoped Bi-2212 samples are taken for different polarization angles. The relaxation amplitudes of the differential reflectivity data corresponding to the superconducting gap, the pseudogap and the normal state are plotted as a function of polarization rotation angle in Figure 4.10–Figure 4.12. For the underdoped Bi-2212 sample, the amplitude shown in Figure 4.10 is a minimum around 60° and maximum around 150° for $T < T_c$. For the optimally doped Bi-2212 sample, the amplitude shown in Figure 4.11 is a minimum around 120° and maximum around 30° for $T < T_c$ (considering the trend of change in amplitude at both temperatures below T_c). If we consider the absolute value of amplitude for the overdoped Bi-2212 sample, 0° and 180° show that the minimum amplitude and the maximum amplitude is around 90° as seen in Figure 4.12 for $T < T^*$. Note that the pseudogap is temperature-*dependent* for the overdoped Bi-2212 sample [see Section 3.4]. Here, a temperature-dependent gap refers to a gap with BCS temperature dependence. We didn't see any observable polarization dependence above T_c for underdoped and optimally-doped Bi-2212 samples, and above T^* for the overdoped Bi-2212 sample. Comparing these observations with the sample

orientations in Figure 4.3, we can see that the amplitudes shown in Figure 4.10–Figure 4.12 change from a minimum to a maximum value on changing the probe polarization from being parallel to one side of the sample to the being perpendicular to it in the presence of a temperature-*dependent* gap. This result agrees with previously reported polarization dependence studies [2, 5, 6]. It should be noted that Bi-2212 does not have any CuO chains when compared to YBCO. Hence we attribute the observed polarization dependence to the a - b plane anisotropy of the CuO_2 planes.

We use the model based on the anisotropy of the probe transition matrix element to quantitatively explain polarization dependence of our pump-probe data of underdoped, optimally doped and overdoped Bi-2212 samples, shown in Figure 4.10, Figure 4.11 and Figure 4.12 respectively. According to Dvorsek *et al.* [5, 6], the dipolar matrix element in the vicinity of the Fermi energy is expressed in the form: $M_{x,y}(\epsilon) = M_0 + \gamma_{x,y}\epsilon$ where $\gamma_{x,y}$ are the derivatives of the dipolar matrix element taken at the Fermi energy. The angular dependence of the probe signal in terms of the probe transition matrix elements is given by [5, 6]:

$$\Delta R \propto \Delta\alpha \propto M_0 [\gamma_x \sin^2(\theta) + \gamma_y \cos^2(\theta)] \Delta n \quad (4.4)$$

where ΔR is the reflectivity amplitude, $\Delta\alpha$ is the photoinduced absorption, θ is the polarization angle, and Δn is the number of photoexcited quasiparticles. We use Equation (4.4) to fit our data where the ratio of γ_x to γ_y is given by the ratio of the maximum to minimum amplitude of polarization dependent pump-probe data for a particular temperature. Δn is proportional to $\frac{\Delta R(T)}{R}$ obtained in Equation (4.2) as described in Ref. [14]. We can obtain $\frac{\Delta R(T)}{R}$ at a particular temperature for each sample from a fit to the corresponding temperature-dependent amplitude using Equation (4.2) for each sample. Using the obtained values of $\frac{\Delta R(T)}{R}$, γ_x and γ_y , we fit the data shown in Figure 4.10–Figure 4.12 taking the orientation of the samples also into consideration. We see that the polarization dependence

given by Equation (4.4) describes the experimental data quite well.

4.4 Conclusion

We performed polarization dependent pump-probe measurements on overdoped, optimally doped and underdoped Bi-2212. We found polarization dependence of the relaxation amplitudes corresponding to the temperature-dependent gap which could be fitted with the model considering the anisotropy of the probe transition matrix elements proposed by Dvorsek *et al.* Our study shows that the polarization dependent ultrafast optical spectroscopy is sensitive to even a very small difference between a- and b-axes of the crystal structure in the presence of a temperature-dependent gap.

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Chapter 5

Coherent energy scale revealed by ultra-fast dynamics of UX_3 ($X=Al, Sn, Ga$) single crystals

The temperature dependence of relaxation dynamics of UX_3 ($X = Al, Ga, Sn$) compounds is studied using the time resolved pump-probe technique in reflectance geometry. UGa_3 is an itinerant antiferromagnet, while UAl_3 and USn_3 are spin fluctuation systems. For UGa_3 , our data are consistent with the formation of a spin density wave gap as evidenced from the quasidivergence of the relaxation time τ near the Néel temperature T_N . For UAl_3 and USn_3 , the relaxation dynamics shows a change from single-exponential to two-exponential behavior below a particular temperature, suggestive of coherence formation of the 5f electrons with the conduction band electrons. This particular temperature can be attributed to the spin fluctuation temperature T_{sf} , a measure of the strength of Kondo coherence. Our T_{sf} is consistent with other data such as resistivity and susceptibility measurements. The temperature dependence of the relaxation amplitude and time of UAl_3 and USn_3 were also fitted by the Rothwarf-Taylor model. Our results show ultra-fast optical spectroscopy is sensitive to c-f Kondo hybridization in the f-electron systems.

5.1 Introduction

The uranium compounds UX_3 , where X is a IIIb (Al, Ga, In, Tl) or IVb (Si, Ge, Sn, Pb) element, crystallize in the cubic $AuCu_3$ -type structure [1] and have U-U distances (d_{U-U}) much larger than the Hill limit ($\sim 3.5 \text{ \AA}$) for uranium compounds [2]. Table 5.1 summarizes the structural data of these compounds. The variation in degree of hybridization of the 5f electron orbitals with the conduction electron orbitals in these compounds leads to a wide range of magnetic behavior

Table 5.1: Lattice data of UX_3 compounds [3]

Compound	Lattice constant (Å)	U-X distance (Å)	U-U distance (Å)
UAl_3	4.287	3.031	4.287
UGa_3	4.248	3.003	4.248
UIn_3	4.601	3.253	4.601
UTl_3	4.674	3.306	4.674
USi_3	4.035	2.853	4.035
UGe_3	4.206	2.974	4.206
USn_3	4.626	3.271	4.626
UPb_3	4.792	3.388	4.792

such as Pauli enhanced paramagnetism (UAl_3 , USi_3 , and UGe_3), antiferromagnetism (UGa_3 , UPb_3 , and UIn_3), and heavy fermion behavior (USn_3) [1, 3, 4]. Due to the the above-mentioned properties and the availability of crystals of high quality, UX_3 compounds are ideal candidates for studying how physical properties are related to the underlying electronic structure.

Spin fluctuations in the narrow $5f$ bands lead to anomalous behavior of the resistivities in UX_3 compounds [5, 6]. A temperature characteristic of the spin fluctuations in the UX_3 compounds is the spin fluctuation temperature T_{sf} , which expresses the strength of hybridization between f and conduction electrons (c - f hybridization). The degree of hybridization is related to the degree of delocalization of the f electrons. A high value of T_{sf} corresponds to more easily hybridized (delocalized) electrons. Above T_{sf} , f electrons are localized; whereas below T_{sf} , there is quasiparticle coherence from the hybridization between f electrons and conduction electrons, i.e., f electrons now become more delocalized (or itinerant). The effective hybridization below T_{sf} leads to changes in measured physical properties. For example, the electrical resistivity changes from a T -linear law above T_{sf} to a T -quadratic law below this temperature [6–9]. Figure 5.1 shows temperature dependence of electrical resistivity of UAl_3 and USn_3 , and UGa_3 . The temperature at which the magnetic susceptibility reaches a Curie-Weiss law is theoretically of the order of T_{sf} [6]. A modified Curie-Weiss law, i.e., $\chi(T) = \chi_0 + C/(T + T^*)$, associates T^* with T_{sf} for relatively strong c - f hybridization [10, 11]. The temper-

ature dependence of the magnetic susceptibility of UAl_3 , UGa_3 , and USn_3 is shown in Figure 5.2, Figure 5.4 and Figure 5.3, respectively.

Figure 5.1: The electrical resistivity versus temperature of UAl_3 , UGa_3 and USn_3 . Reproduced from Ref. [12]

Figure 5.2: The magnetic susceptibility versus temperature of UAl_3 . Reproduced from Ref. [13]

Figure 5.3: The magnetic susceptibility versus temperature of USn_3 . Reproduced from Ref. [10]

Ultrafast time-resolved pump-probe spectroscopy has been recognized as a powerful technique to study the nonequilibrium carrier dynamics in strongly correlated

Figure 5.4: The magnetic susceptibility versus temperature of UGa_3 . Reproduced from Ref. [14]

electron materials. In addition to distinguishing different phases in a material by their different relaxation dynamics, it can discern whether one phase coexists or competes with another phase in close proximity [15–17], giving information on the nature of low energy electronic structure of correlated electron systems, for example, in high-temperature superconductors. Pump-probe experiments have also been performed on actinide compounds, such as the itinerant antiferromagnets $UNiGa_5$ and $UPtGa_5$ [18, 19], and the heavy-fermion superconductor $PuCoGa_5$ [20].

The hybridization between the conduction electrons and the localized f electrons also causes a narrow gap to form in the density of states (DOS) near the Fermi level [21]. This gap, called the hybridization gap, results in a relaxation bottleneck, evidenced by an increase in the relaxation time τ at low temperatures. For example, in heavy fermions such as $YbAgCu_4$ and SmB_6 , τ increases monotonically with decreasing temperature [21]. The temperature dependence of the relaxation amplitude and time was fitted using the Rothwarf-Taylor (RT) model. We investigate the ultrafast dynamics in three isostructural uranium compounds, UAl_3 , UGa_3 and USn_3 , using the ultrafast pump-probe technique. The variation in hybridization strength is responsible for the differences in properties of these three isostructural compounds. UAl_3 and USn_3 are categorized as spin fluctuation systems [7, 12, 22–25]. UGa_3 does not behave as a spin fluctuation system, but is

an itinerant $5f$ electron antiferromagnet. In fitting the transient change in reflectivity for UAl_3 and USn_3 , we needed a two-exponential decay function below T_{sf} , which points to the presence of two relaxation channels below T_{sf} . This arises from the hybridization between f electrons and conduction electrons below T_{sf} . This shows that the ultrafast pump probe technique is sensitive to c - f hybridization in f electron systems. Our T_{sf} is consistent with that obtained from resistivity and susceptibility measurements. We were also able to fit the temperature dependence of the relaxation amplitude and time using the RT model. For UGa_3 , the relaxation time diverges as the temperature approaches the Néel temperature T_N , corresponding to the formation of a spin density wave (SDW) gap near the Fermi level. The results of this chapter have been published in *Physical Review B*, **86**(11), 115103 (2012).

5.2 Experimental Setup

The details of the experimental setup have been given in Section 2.2.2. The laser produced sub-100 fs pulses. The experiments were performed with an average pump power of 2 mW, giving a pump fluence of $\sim 0.9 \mu\text{J}/\text{cm}^2$. Data were taken from 10 K to 300 K. The experiments were performed on single crystals of UX_3 ($X = Al, Ga, Sn$) grown using the standard flux technique, with X used as the flux in each case [12].

5.3 UAl_3 and USn_3

In Figure 5.5 we show $\Delta R/R$ at different temperatures for (a) UAl_3 and (b) USn_3 , as a function of the time delay between the pump and probe pulses. In both UAl_3 and USn_3 , only a fast relaxation of ~ 500 fs, which is typical of regular metals, is observed at high temperatures. At low temperatures, an additional slow, positive picosecond relaxation is observed. Data at low temperatures are fitted to the two-exponential decay function $\Delta R/R(t) = A_{fast}(T) \exp(-t/\tau_{fast}) +$

Figure 5.5: Transient reflection $\Delta R/R$ versus pump-probe time delay at different temperatures for (a) UAl_3 and (b) USn_3 . Thick solid curves denote exponential fits of data, for UAl_3 (at 5 K and 220 K) and USn_3 (at 5 K and 60 K).

$A_{slow}(T) \exp(-t/\tau_{slow})$. This change from one- to two-exponential decay occurs at a particular crossover temperature — ~ 200 K for UAl_3 and ~ 50 K for USn_3 , suggestive of two relaxation channels below this crossover temperature. These crossover temperatures are of the order of the spin fluctuation temperatures T_{sf} obtained in these compounds from temperature-dependent electrical resistivity and magnetic susceptibility measurements (~ 150 K for UAl_3 [6,13] and ~ 50 K for USn_3 [6,26,27]) We thus associate this crossover temperature with the spin fluctuation temperature T_{sf} .

To understand the different characteristic temperatures in UAl_3 and USn_3 , we have also performed band structure calculations in the framework of the density functional theory, by using the WIEN2k linearized augmented plane wave method [28]. The electronic structure calculations were performed by Dr. Jian-Xin Zhu (Los Alamos National Laboratory, USA) on a computer cluster at the Center for Integrated Nanotechnologies, a US DOE Office of Basic Energy Sciences user facility. A generalized gradient approximation [29] was used to treat exchange and correlation. Spin-orbit coupling was included in a second-variational way. The obtained U partial 5*f* DOS, as shown in Figure 5.6, indicates a narrower peak width near the Fermi energy in USn_3 as compared with UAl_3 . In addition, one can see that the splitting between the two major peaks is smaller in USn_3 than in UAl_3 . In view of the fact that the spin-orbit coupling is quite local to the U atoms, one would expect the same effect on both USn_3 and UAl_3 . A reasonable explanation for this difference is a smaller hybridization gap in USn_3 compared to UAl_3 , due to the weakening of the hybridization in USn_3 — a result of the lattice expansion ($a=4.626$ Å in USn_3 versus $a=4.264$ Å in UAl_3) [13]. Though conventional band structure calculations underestimate the correlation effect, the trend of smaller coherence energy scale in USn_3 than in UAl_3 should be robust, as has recently been exemplified in other isostructural actinide compounds [30].

In this context, the two-exponential behavior at low temperature can be explained by the *c-f* hybridization occurring below T_{sf} . Below T_{sf} , the interaction of partially filled *f* shell electrons with conduction electrons leads to the formation of heavy quasiparticles [31]. As the *f* electrons are localized above T_{sf} , relaxation occurs through phonon channels only. Hence only a single exponential decay is expected above T_{sf} . When $T < T_{sf}$, the spin fluctuation channel opens up due to hybridization. Electrons now relax via *both* phonon and spin fluctuation channels resulting in a two-exponential decay behavior. Also, a higher T_{sf} value in UAl_3 compared to USn_3 points to a stronger *c-f* hybridization, which is expected, as *c-f* hybridization tends to decrease as the size of the non-*f* atom increases [3, 32],

Figure 5.6: Uranium 5*f* partial DOS calculated from the LAPW method for UAl_3 and USn_3 , in the magnetic unit cell, in the energy range (-2,2) eV. Note the narrower peak width near the Fermi energy ($E = 0$) in USn_3 compared to UAl_3 .

which causes the lattice expansion as we discussed above.

The presence of the hybridization gap, formed due to hybridization between the conduction electrons and the localized *f* electrons, causes a bottleneck in quasi-particle relaxation. This results in a divergence of the relaxation time at low temperatures. The temperature dependence of the relaxation amplitude and relaxation time can be quantitatively explained by the Rothwarf-Taylor (RT) model explained in Section 2.2.3.

The results of the RT model are as follows [21,33]: From the amplitude $A(T)$, one obtains the density of thermally excited EHPs n_T via the relation

$$n_T(T) \propto \mathcal{A}(T)^{-1} - 1 \quad (5.1)$$

where $\mathcal{A}(T)$ is the normalized amplitude ($\mathcal{A}(T) = A(T)/A(T \rightarrow 0)$). Then we fit the experimental $n_T(T)$ to the expression [21]

$$n_T(T) \propto \sqrt{T} \exp(-\Delta/T), \quad (5.2)$$

where the hybridization gap Δ is temperature independent (or very weakly temperature dependent) and can be obtained from the fitting. Moreover, for a constant

pump intensity, the temperature dependence of n_T also governs the temperature dependence of τ^{-1} , given by,

$$\tau^{-1}(T) = \Gamma[\delta(\beta n_T + 1)^{-1} + 2n_T](\Delta + \alpha T\Delta^4) \quad (5.3)$$

where Γ , δ , β and α are T -independent fitting parameters.

Figure 5.7: Temperature dependence of (a) amplitudes and (b) relaxation times for UAl_3 . Solid lines are fits to the RT model of the slow component. The shaded regions represent the temperature region above T_{sf} where, though a two-exponential fit is better, a one-exponential fit suffices.

Figure 5.8: Temperature dependence of (a) amplitudes and (b) relaxation times for USn_3 . Solid lines are fits to the RT model of the slow component. The shaded regions represent the temperature region above T_{sf} where, though a two-exponential fit is better, a one-exponential fit suffices.

Since, below T_{sf} , the second relaxation component appears, we attribute it to relaxation across the hybridization gap, and use the RT model to fit the amplitude

and relaxation time below T_{sf} in UAl_3 and USn_3 . The inset of Figure 5.7(a) shows $n_T(T)$ obtained from $A_{slow}(T)$ using Equation (5.1), with the solid line being the fit to Equation (5.2), with the fitting parameter $\Delta \approx (230 \pm 10)$ K. The fitted values of $n_T(T)$ are then inserted into Equation (5.3) to fit the experimental values of $\tau_{slow}(T)$, shown in Figure 5.7(b). Similar fits are also done for USn_3 , as shown in Figure 5.8, yielding $\Delta \approx (90 \pm 20)$ K. The good fits show that the slow relaxation component in both UAl_3 and USn_3 can be described by assuming EHPs relaxing across the hybridization gap near the Fermi surface. More interestingly, the extracted hybridization gap in UAl_3 is larger than in USn_3 , in qualitative agreement with the band structure results. This comparison of hybridization gap is also consistent with that of spin fluctuation energy scale T_{sf} discussed above. Our results show that the ultrafast pump-probe technique is sensitive to the hybridization of f -electron orbitals with the conduction electron orbitals.

Note that in both UAl_3 and USn_3 , there exists a temperature range (indicated by the shaded regions in Figs. 5.7 and 5.8) where, though a two-exponential fit is better, a one-exponential fit suffices. The values of τ_{slow} naturally have large error bars there, and the values of A_{slow} approach zero. The gradual change in A_{slow} in UAl_3 and USn_3 , around T_{sf} , is consistent with T_{sf} being a crossover temperature, rather than a sharp phase transition temperature. T_{sf} is also the temperature below which τ_{fast} starts to rise *gradually*, consistent with that seen in other heavy fermions [21].

It is worth mentioning that mixed-valence systems exhibit the same behavior as spin fluctuation systems by having a susceptibility maximum at some crossover temperature (T_{sf} in spin fluctuation and T_{max} in mixed valence). However, the sign of magnetoresistivity (MR) is opposite — negative in spin fluctuation systems and positive in mixed-valence systems. For example, in $UCoGa_5$, a normal positive behavior of MR was observed, which the authors used to rule out the possibility of spin fluctuation as a mechanism for the susceptibility maximum, and supports the idea of valence instability in this compound [34]. Since the MRs in UAl_3 and

USn_3 are positive [13,27], one might rule out UAl_3 and USn_3 being spin fluctuation systems as well, though the authors there did not suggest this. Theoretical work that links a negative MR to spin fluctuations was carried out using a self-consistent renormalized spin fluctuation theory [35] — however the theory was developed for weakly ferromagnetic metals, which UAl_3 and USn_3 are obviously not. On the other hand, static (specific heat) and dynamic (spin-lattice relaxation time T_1) properties measured on USn_3 showed that these properties in the heavy-fermion state can be described in a quantitatively consistent way via a spin fluctuation model, albeit with a temperature-dependent effective Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, in order to explain the crossover from an incoherent, localized state to a coherent, heavy-fermion state [36].

Moreover, though the U $5f$ electrons are largely thought to be itinerant/delocalized in character, some degree of localization was seen in certain U compounds. For example, though the $5f$ states of α -U metal and US are largely itinerant, those in USe are localized to a greater extent, whereas those in UTe are almost entirely localized [37]. Electron energy-loss spectroscopy and spin-orbit sum rule analysis showed that the $5f$ states in URu_2Si_2 are moderately localized, though not as much as USe and UTe [37]. However, electronic structure calculation of URu_2Si_2 showed that a completely itinerant picture is sufficient to provide an excellent explanation of the low-temperature data of the paramagnetic and antiferromagnetic phases [38,39]. The itinerant band picture is adequate for the monocarbide UC, and acceptable for the mononitride UN [40]. Furthermore, we note that the fast component of dynamics has a very different temperature dependence of relaxation between UAl_3 and USn_3 [compare Figs. 5.7(b) and 5.8(b)]. Since this energy scale ($1/\tau_{fast}$) is larger than that involved in the slow dynamics, the understanding of the fast dynamics may help identify the relevance of spin fluctuations, mixed valence, and dual nature in these heavy-fermion systems — how these different descriptions can explain the crossover from a single- to double-exponential relaxation behavior in our pump-probe data requires further theoretical and experimental work.

5.4 UGa_3

We now turn to the relaxation dynamics of UGa_3 . UGa_3 is not a spin fluctuation system — it is a SDW system with Néel temperature $T_N=65$ K. It is a moderate heavy fermion with Sommerfeld coefficient $52 \text{ mJ/K}^2\cdot\text{mol}$ [22], and is reported to follow a modified Curie-Weiss law behavior [41] with $T^*=2080$ K which is indicative of strong hybridization in this compound. The $5f$ electrons in UGa_3 can be considered itinerant because of the large hybridization of $5f$ orbitals with conduction electron orbitals. Neutron scattering [42] and resistivity [4, 41] data revealed an antiferromagnetic transition at ~ 70 K. Kaczorowski [43] summarized the properties of UGa_3 and found it to fulfil all the main criteria for itinerant magnetism. Further evidence for itinerancy of $5f$ electrons in UGa_3 comes from data of angular correlation of the electron-positron annihilation radiation and is supported by electronic structure calculations within the local density approximation [28, 44].

The photoinduced change in reflectivity, as shown in Figure 5.9, can be fitted with a single exponential decay $\Delta R/R(t) = A(T) \exp(-t/\tau)$. The extracted relaxation amplitude $A(T)$ and time $\tau(T)$ are shown in Figure 5.10(a) and Figure 5.10(b), respectively. Upon entering the SDW phase, $A(T)$ increases with decreasing temperature. However, instead of monotonically increasing as in UAl_3 and USn_3 , $A(T)$ now attains a maximum at ~ 40 K and starts decreasing with decreasing temperature [see Figure 5.10(a)]. Concurrently, τ exhibits a quasi-divergence at T_N , consistent with that observed in itinerant antiferromagnets $UNiGa_5$ and $UPtGa_5$, where the opening up of the SDW gap causes a bottleneck in quasi-particle relaxation [18, 19]. In contrast to $UNiGa_5$ and $UPtGa_5$, however, where τ increases with decreasing temperature at low temperatures, τ in UGa_3 shows a (1) shoulder (or change in curvature) at 40 K, and (2) decrease with decreasing temperature. An anomaly at a spin-reorientation temperature $T_{sr} = 40$ K has been reported in other measurements of UGa_3 , whether in the presence of a magnetic field (nuclear magnetic resonance, neutron scattering, magnetic susceptibility, Mössbauer) [14, 45–49], or in the absence of a magnetic field (thermal

conductivity and neutron scattering) [14, 45, 50]. This anomaly has been associated with a reorientation of the ordered magnetic moments [14, 46, 48–50], which induces strong modifications of the uranium $5f$ orbitals [47]. The magnetic moments, oriented along the $[110]$ axis below 40 K, reorient into the $[111]$ direction at 40 K [43, 50, 51]. The fact that the transition is observed in the absence of magnetic field is an indication that the bump we see at 40 K in our pump probe measurement is not an artifact, but corresponds to the moment reorientation as has been reported in other measurements mentioned above.

Figure 5.9: Photoinduced change in reflectivity $\Delta R/R$ versus pump-probe time delay at different temperatures of UGa_3 . Thick blue (cyan) curves denote one-exponential fits of data at $T = 40$ K (48 K).

We use the model proposed by Kabanov *et al.* [52] to analyze the temperature dependence of relaxation amplitude $A(T)$. The temperature dependence of the relaxation amplitude in the SDW state for an isotropic temperature-*dependent* gap $\Delta_{SDW}(T)$ is given by [writing $\Delta_{SDW}(T)$ as $\Delta(T)$],

$$A(T) = \frac{\epsilon_I / (\Delta(T) + k_B T / 2)}{1 + \zeta \sqrt{\frac{2k_B T}{\pi \Delta(T)}} \exp[-\Delta(T) / k_B T]}, \quad (5.4)$$

where ϵ_I the pump laser intensity per unit cell, ζ is a constant, and $\Delta(T)$ obeys a weak-coupling BCS temperature dependence. The above expression for $A(T)$ de-

Figure 5.10: Temperature dependence of (a) amplitude and (b) relaxation time for UGa_3 obtained from one-exponential fits, with dashed lines in (a) and (b) being fits to the RT model from 40 K to T_N .

scribes a reduction in the photoexcited quasiparticle density with increase in temperature, due to the decrease in gap energy and corresponding enhanced phonon emission during the initial relaxation. A good fit between the experimental $A(T)$ and Equation (5.4) can only be made from T_N down to ~ 40 K, where $T_N = 55$ K is a fitting parameter. The reason for this low value of T_N compared to that from other measurements could be that the SDW gap only gaps part of the Fermi surface which may not be accounted for in Equation (5.4). In the SDW state ($T < T_N$), the temperature dependence of τ can be obtained from Equation (5.3), but can be written in the alternative form [writing $\Delta_{SDW}(T)$ as $\Delta(T)$] [16]

$$\tau^{-1}(T) = \Gamma \{ \delta A(T) + \eta \sqrt{\Delta(T)T} \exp[-\Delta(T)/T] \} \times [\Delta(T) + \alpha T \Delta(T)^4]. \quad (5.5)$$

The fit of $\tau(T)$ to Equation (5.5) is shown in Figure 5.10(b). Once again, a good fit is obtained only from T_N to ~ 30 K, close to T_{sr} . Below T_{sr} , the fit deviates from the experimental data, consistent with the existence of another transition at T_{sr} .

5.5 Conclusion

We have performed time-resolved photoinduced change in reflectivity measurements on three isostructural uranium compounds — UAl_3 , UGa_3 and USn_3 . The values of T_{sf} , a measure of the degree of hybridization, in UAl_3 and USn_3 are consistent with data from other measurements. Our fit of the slow component to the Rothwarf-Taylor model shows that the slow component can be described by assuming electron-hole pairs relaxing across the hybridization gap. We have thus shown the pump probe technique to be sensitive to c- f hybridization. Our data on UGa_3 are consistent with the formation of a SDW gap at $T_N = 55$ K and a reorientation of magnetic moments at $T_{sr} = 40$ K.

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Chapter 6

Ultrafast relaxation dynamics in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{BiFeO}_3$ heterostructure

The temperature dependence of relaxation dynamics in bilayer thin film heterostructure composed of multiferroic BiFeO_3 (BFO) and superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) grown on (001) SrTiO_3 (STO) substrate is studied by time resolved pump probe technique. The differential reflectivity data of the heterostructure is compared with that of YBCO and BFO thin films having the same growth conditions. The superconductivity of YBCO is found to be retained in the heterostructure. We observe speeding up of YBCO dynamics in the superconducting state in the heterostructure. Also, BFO dynamics is seen to be affected by the YBCO underlayer in the superconducting state in the heterostructure.

6.1 Introduction

Perovskite oxides exhibit many useful physical properties such as high temperature superconductivity, ferroelectricity, colossal magnetoresistance and multiferroic properties. Since many of these oxides are epitaxially compatible, it is possible to create heterostructures at the atomic level with unique properties [1]. Complex oxide heterostructures of superconductors are being studied extensively in recent years [2–4], motivated by the expected enhancement in the properties or emergence of a new property, which can be exploited in the development of electronic devices with improved performance and can provide further insight into the different order parameters at the interface.

Multiferroics and high-temperature superconductors are by themselves complex materials with different and often antagonistic order parameters (magnetic & superconducting). We report time-resolved pump-probe studies on a multi-

ferroic/superconductor bilayer thin film heterostructure composed of multiferroic BiFeO₃ (BFO) and superconducting YBa₂Cu₃O_{7- δ} (YBCO) layers. BFO is one of the most studied multiferroic materials because of its room temperature ferroelectricity ($T_C \sim 1103$ K) [5] and antiferromagnetism ($T_N \sim 643$ K) [6]; weak ferromagnetism is also reported in BiFeO₃ film below T_N [7]. We want to know, in bilayer heterostructures containing multiferroics and HTSCs, how the interplay of various interactions in the constituent materials determines its ultimate functionality.

Figure 6.1: Normalized differential reflectivity as a function of time delay at $T = 20$ K for pure YBCO film and LSMO/YBCO bilayer, from Ref. [3]. Solid lines show exponential decay fit to experimental data.

Time-resolved pump-probe ultrafast optical spectroscopy has been widely used in probing nonequilibrium carrier dynamics in correlated electron systems, and in particular, high-temperature superconductors. It has proven to be a useful time-domain tool to probe dynamics of complex structures [3, 8–13] and coexisting [14]/competing [15] phases. Thus ultrafast optical spectroscopy is well suited to study competing interactions in nanocomposites containing high-temperature superconductors. Pump-probe studies on La_{1- x} Sr _{x} MnO₃/YBa₂Cu₃O₇ (LSMO/YBCO) bilayers [3, 8] have shown that interfacing the superconducting film with LSMO results in faster relaxation times when compared to sole superconducting films. Figure 6.1 from Ref. [3] compares the normalized reflectivity data at 20 K for a

YBCO film and a LSMO/YBCO bilayer. It is reported that LSMO layer, due to proximity effect, acts as an effective sink layer for quasiparticles coming from YBCO resulting in a faster relaxation time. According to Sá de Melo, magnetism and superconductivity phases would coexist in a superconductor/ferromagnet heterostructure with layers of thickness in the nanometer range if the magnitude of proximity effects are such that the superconductivity and magnetism are not destroyed [16–18]. Suppression of ferromagnetism in the ferromagnetic layer at an interface with a superconductor has been observed for La_{1-x}Ca_xMnO₃/YBa₂Cu₃O₇ (LCMO/YBCO) [19, 20], and LSMO/YBCO [21, 22] interfaces. In the case of LCMO/YBCO, possible reasons for the suppression of ferromagnetism include “a compensating ferromagnetic moment of YBCO and canting of the interfacial Mn spins due to superexchange across the interface, a modest charge transfer across the interface which pushes the interfacial LCMO layers closer to a charge-ordered antiferromagnetic state, and enhanced fluctuations due to the reduced dimensionality” [20]. In our pump-probe study on BFO/YBCO bilayers, we also see a similar speeding up to YBCO dynamics in the BFO/YBCO bilayers as in LSMO/YBCO bilayers. Note that a weakened ferromagnetism together with superconductivity has been reported for BFO/YBCO bilayers grown on a LSAT substrate [23]. The speeding up of YBCO dynamics in the BFO/YBCO bilayers in the present case could hence be related to the BFO overlayer acting as a trapping layer and/or to the interaction of weak ferromagnetism in BFO and superconductivity in YBCO.

6.2 Experiment

6.2.1 Samples for study

The bilayer thin film heterostructures of BFO and YBCO were deposited on (001) oriented single-crystal SrTiO₃ (STO) (CrysTec GmbH, Berlin Germany) substrates by a pulsed laser deposition (PLD) technique using 248 nm, KrF excimer laser. Two different BFO/YBCO bilayer thin film heterostructures were used in the ex-

periment with BFO thicknesses of 26 nm and 130 nm. YBCO thin films are deposited first since the high growth temperature ($\sim 750^\circ\text{C}$) may degrade BFO thin films. In both cases, two YBCO thin films are grown at the same conditions and BFO is deposited subsequently on one of the films (with simultaneous deposition of BFO on the substrate for comparing dynamics). The other YBCO film is later used for comparing the dynamics.

The structure and crystalline quality of synthesized thin films were studied by a high resolution x-ray diffractometer (Smartlab, Rigaku Corporation, Japan). The topographic imaging and the piezoresponse force microscopy (PFM) measurements were carried out on an atomic force microscope (Asylum Research, USA, MFP-3D). Further, we confirmed the T_c of our samples by taking magnetization data using a Magnetic Property Measurement System (MPMS, Quantum Design).

6.2.1.1 BFO(~ 26 nm)/YBCO(~ 100 nm)/STO

A BFO(26 nm)/YBCO bilayer and corresponding YBCO film were grown by He Mi from Prof. Tom Wu's group, Nanyang Technological University, Singapore. The YBCO bottom layer with a thickness of ~ 100 nm was grown in 150 mTorr oxygen at a substrate temperature of 750°C , and then the BFO thin film layer of thickness ~ 26 nm was deposited on top of the YBCO layer at 75 mTorr and 700°C .

Figure 6.2: X-ray diffraction patterns of (a) BFO(26 nm)/YBCO bilayer and (b) corresponding YBCO thin film.

Figure 6.2 displays the x-ray diffraction spectrum for the BFO(26 nm)/YBCO

Figure 6.3: (a) $2 \times 2 \mu\text{m}^2$ topographic AFM image of the BFO(26 nm) grown on YBCO/STO, and (b) corresponding piezoresponse phase image. Yellow (bright) and purple (dark) correspond to the original up and down domains, respectively.

Figure 6.4: Magnetization vs temperature measured on BFO(26 nm)/YBCO bi-layer and corresponding YBCO thin film.

bilayer and corresponding YBCO thin film grown on STO substrates. No impurity phase was observed but only (00l)-type diffraction peaks indicating the epitaxial growth of samples. The $2 \times 2 \mu\text{m}^2$ topographic AFM image and the corresponding out-of-plane PFM image are depicted in Figure 6.3(a) and Figure 6.3(b), respectively. Due to strain relaxation, the surface morphology of YBCO thin films is not smooth enough leading to a root mean square roughness¹ (R_{rms}) of ~ 11 nm of the BFO(26 nm)/YBCO bilayer thin film. In a PFM image, yellow and purple colours represent spontaneous polarization component pointing ‘up’ and ‘down’, respectively [24]. Hence Figure 6.3(b), with the purple domain dominating, indicates that a majority of the ferroelectric domains are pointing ‘down’ for the

¹Here the roughness is not a problem for reflectivity measurements of the sample under study since it is of nanometer scale.

BFO(26 nm)/YBCO bilayer sample. The temperature-dependent magnetization of the BFO(26 nm)/YBCO bilayer and YBCO are depicted in Figure 6.4, where a magnified view near the transition demonstrates the onset of superconductivity at $T_c \sim 90$ K in both films. It shows that after depositing the BFO thin film on YBCO/STO, T_c does not change.

6.2.1.2 BFO(~ 130 nm)/YBCO(~ 100 nm)/STO

A BFO(130 nm)/YBCO bilayer and corresponding YBCO film were grown by Dr. Lu Chengliang from Prof. Tom Wu's group, Nanyang Technological University, Singapore. The YBCO bottom layer of thickness ~ 100 nm was grown in 150 mTorr oxygen at a substrate temperature of 780°C, and the BFO thin film layer of thickness ~ 130 nm was deposited on top of YBCO layer at 80 mTorr and 670°C. Fig-

Figure 6.5: X-ray diffraction patterns of (a) BFO(130nm)/YBCO bilayer and (b) corresponding YBCO thin film.

ure 6.5 displays the x-ray diffraction spectrum for the BFO(130 nm)/YBCO bilayer and corresponding YBCO thin film grown on STO substrates. No impurity phase was observed but only (00l)-type diffraction peaks indicating the epitaxial growth of samples. The $5 \times 5 \mu\text{m}^2$ topographic AFM image and the corresponding out-of-plane PFM image are depicted in Figure 6.6(a) and Figure 6.6(b), respectively. The root mean square roughness (R_{rms}) is ~ 19 nm for BFO(130 nm)/YBCO bilayer thin film. Figure 6.3(b), with the purple domain dominating, indicates that majority of the ferroelectric domains are pointing ‘down’ for the BFO(130 nm)/YBCO

Figure 6.6: (a) $5 \times 5 \mu\text{m}^2$ topographic AFM image of the BFO(130 nm) grown on YBCO/STO, and (b) corresponding piezoresponse phase image. Yellow (bright) and purple (dark) correspond to the original up and down domains, respectively.

bilayer sample. The temperature-dependent magnetization of YBCO shown in Figure 6.7 demonstrates the onset of superconductivity at $T_c \sim 90$ K. This YBCO is of better quality than the previous one, comparing their XRD spectra and M-T curves.

Figure 6.7: Magnetization vs temperature measured on YBCO thin film corresponding to BFO(130 nm)/YBCO bilayer.

6.2.2 Experimental setup

The experimental setup is detailed in Section 2.2.2. The experiments were performed with an average pump power of 2 mW, giving a pump fluence of $0.9 \mu\text{J}/\text{cm}^2$. Data were taken from 10 K to 120 K. The optical penetration depth of 800 nm laser radiation in YBCO is of the order of 100 nm [25]; whereas for BFO, the pene-

tration depth is about $10\text{ }\mu\text{m}$ [26]. Thus, the laser probe beam in our pump-probe experiment can reach the interface, and perhaps is sensitive to the carrier dynamics there.

6.3 Results & Discussions

We performed pump-probe measurements on BFO/YBCO bilayer heterostructures of different BFO thickness. The results of the measurements and discussions are detailed below.

6.3.1 BFO($\sim 26\text{ nm}$)/YBCO($\sim 100\text{ nm}$)/STO

Figure 6.8: Time dependence of photoinduced reflectivity of YBCO thin film.

Figure 6.8 and Figure 6.9 show the photoinduced reflectivity $\Delta R/R$ as a function of pump-probe time delay of the YBCO thin film and BFO(26 nm)/YBCO bilayer thin film respectively, at different temperatures below and above T_c . The YBCO film shows fast relaxation dynamics ($\sim$ a few ps) as has been previously reported [27–30].

We observe that the photoresponse of the BFO(26 nm)/YBCO bilayer thin film shown in Figure 6.9 is different from that of YBCO thin film. The negative peak in reflectivity for the BFO(26 nm)/YBCO bilayer can be due to multiple reflections from thin heterostructures. The reflectivity data of the BFO(26 nm)/YBCO bilayer

Figure 6.9: Time dependence of photoinduced reflectivity of BFO(26 nm)/YBCO bilayer thin film.

Figure 6.10: Comparison of differential reflectivity as function of pump-probe time delay normalized to peak value for the BFO(26 nm)/YBCO bilayer and YBCO thin films at (a) 35 K, (b) 50 K, (c) 80 K and (d) 100 K. Dashed lines are guide to the eye.

can be compared with that of the YBCO film to understand the effects of the BFO overlayer on the dynamics of YBCO. The amplitude drops in the presence of a BFO overlayer. Comparing Figure 6.8 and Figure 6.9, we can see that the dynamics in the BFO(26 nm)/YBCO bilayer is not single-exponential. Figure 6.10 compares the differential reflectivity data of BFO(26 nm)/YBCO bilayer and YBCO films

normalized to the peak value which has a similar trend as in Figure 6.1. Comparing the signals, the presence of a BFO layer is seen to speed up the relaxation dynamics of YBCO as compared to the pristine superconducting film.

Figure 6.11: (a) Temperature-dependence of amplitude $|\Delta R/R|(T)$ and (b) temperature-dependence of relaxation time for YBCO film. Dashed lines are guide to the eye.

Figure 6.12: (a) Temperature-dependence of amplitude of fast relaxation component, (b) temperature-dependence of relaxation time of fast relaxation component and (c)-(d) temperature-dependence of slow relaxation component for BFO(26 nm)/YBCO bilayer. Dashed lines are guide to the eye.

The peak value of reflectivity change $|\frac{\Delta R}{R}|(T)$ for YBCO is determined [31] and plotted in Figure 6.11(a). The temperature dependent relaxation time τ plotted in Figure 6.11(b) is extracted using a single-exponential decay fit to the reflectivity

curves. Notice that the amplitude drops approaching 90 K, whereas the relaxation time exhibits an upturn near this temperature. This can be attributed to the superconductivity of YBCO [14].

Figure 6.13: Temperature-dependence of relaxation times for BFO(26 nm)/YBCO and YBCO thin films. Dashed lines are guide to the eye.

The reflectivity data of the BFO(26 nm)/YBCO bilayer is compared quantitatively with that of the YBCO film by fitting the reflectivity curves for BFO(26 nm)/YBCO bilayer with a bi-exponential decay function containing two characteristic relaxation times. Figure 6.12(a)-(d) shows the temperature dependence of the relaxation amplitudes and relaxation times for the BFO(26 nm)/YBCO bilayer. We attribute the fast component to the superconducting order as A_{fast} shows a dip around 90 K and the fast relaxation time τ_{fast} shows a divergence on approaching ~ 90 K. Figure 6.13 compares the relaxation times for BFO(26 nm)/YBCO bilayer and YBCO thin films. It can be seen that the superconducting component relaxes faster in the BFO(26 nm)/YBCO bilayer compared to a pristine YBCO film.

Figures 6.14(a)-(d) show $\Delta R/R$ of BFO(26 nm)/YBCO bilayer and BFO superposed on top of one another, at the same temperature, for long time delays. For such long time delays, the YBCO underlayer, below T_c , suppresses the signal from BFO in the bilayer. We do not see a relaxation component in BFO/STO of dynamics comparable to the slow relaxation component in the BFO(26 nm)/YBCO bilayer. Hence we assume the slow relaxation component in the BFO(26 nm)/YBCO bilayer could be related to a new relaxation channel arising from the interfacing of

Figure 6.14: $\Delta R/R$ as function of pump-probe time delay of BFO(26 nm)/YBCO bilayer and BFO thin films superposed with one another at (a) 35 K, (b) 50 K, (c) 80 K and (d) 100 K.

BFO and YBCO.

6.3.2 BFO(~ 130 nm)/YBCO(~ 100 nm)/STO

Figure 6.15 and Figure 6.16 show the photoinduced reflectivity $\Delta R/R$ as a function of pump-probe time delay of a YBCO thin film and a BFO(130 nm)/YBCO bilayer thin film respectively, at different temperatures below and above T_c . The YBCO film shows fast relaxation dynamics ($\sim$ a few ps) as has been previously reported [27–30].

The reflectivity data of BFO(130 nm)/YBCO bilayer can be compared with that of the YBCO film to understand the effects of a BFO(130 nm) overlayer on the dynamics of YBCO. Comparing Figure 6.15 and Figure 6.16, the main observations are a decrease in relaxation amplitude and a faster relaxation dynamics similar to the previous results on a BFO(26 nm)/YBCO bilayer. Figure 6.17 compares the differential reflectivity data of BFO(130 nm)/YBCO bilayer and YBCO films normalized to the peak value. The presence of a BFO layer is seen to speed up the relaxation dynamics of YBCO compared to the pristine superconducting film

Figure 6.15: Time dependence of photoinduced reflectivity of YBCO thin film.

Figure 6.16: Time dependence of photoinduced reflectivity of BFO(130 nm)/YBCO thin film.

below T_c as in the case of the BFO(26 nm)/YBCO bilayer.

The peak value of reflectivity change $|\frac{\Delta R}{R}|(T)$ for YBCO is determined [31] and plotted in Figure 6.18(a). The temperature dependent relaxation time τ plotted in Figure 6.18(b) is extracted using a single-exponential decay fit to the reflectivity curves. Notice that the amplitude drops approaching 90 K, whereas the relaxation time exhibits an upturn near this temperature. This can be attributed to the superconductivity of YBCO [14].

The reflectivity data of the BFO(130 nm)/YBCO bilayer is compared quantitatively with that of the corresponding YBCO film by fitting the reflectivity curves for BFO(130 nm)/YBCO bilayer with an exponential decay function. Below T_c

Figure 6.17: Comparison of differential reflectivity as function of pump-probe time delay normalized to peak value for the BFO(130 nm)/YBCO bilayer and YBCO thin films at (a) 35 K, (b) 50 K, (c) 80 K and (d) 100 K. Dashed lines are guide to the eye.

Figure 6.18: Temperature-dependence of (a) amplitude $|\Delta R/R|(T)$ and (b) relaxation time for YBCO film. Dashed lines are guide to the eye.

two-exponentials were needed, whereas a single-exponential was enough above T_c . Figure 6.19(a)-(d) show the temperature dependence of the relaxation amplitudes and relaxation times for the BFO(130 nm)/YBCO bilayer thin film. We attribute the fast component to the superconducting order as both the relaxation amplitude and the relaxation time of the fast component show distinct changes near to T_c . Figure 6.20 compares the relaxation times for BFO(130 nm)/YBCO bilayer and YBCO thin films. It can be seen that the superconducting component relaxes

Figure 6.19: Temperature-dependence of (a) relaxation amplitude and (b) relaxation time for fast component and temperature dependence of (c) relaxation amplitude and (d) relaxation time for the slow component of BFO(130 nm)/YBCO bilayer thin film. Solid diamonds show single-exponential parameters. Dashed lines are guide to the eye.

Figure 6.20: Temperature-dependence of relaxation time BFO(130 nm)/YBCO bilayer (τ_{fast}) and corresponding YBCO thin film. Dashed lines are guide to the eye.

faster below T_c in the BFO(130 nm)/YBCO bilayer compared to YBCO film.

Figures 6.21(a)-(d) show $\Delta R/R$ of BFO(130 nm)/YBCO bilayer and BFO superposed on top of one another, at the same temperature, for long time delays. For such long time delays, the YBCO underlayer, below T_c , suppresses the signal from BFO in the bilayer similar to results for the previous samples. Relaxation

Figure 6.21: $\Delta R/R$ as function of pump-probe time delay of BFO(130 nm)/YBCO bilayer and BFO thin films superposed with one another at (a) 35 K, (b) 50 K, (c) 80 K and (d) 100 K.

dynamics comparable to the slow relaxation component in BFO(130 nm)/YBCO bilayer is not observed in either the YBCO film or in the BFO film. We hence assume this slow component to be related to a new relaxation channel arising from interfacing of BFO and YBCO films.

The relaxation in the BFO(26 nm)/YBCO bilayer is two-exponential even above T_c , whereas the relaxation in BFO(130 nm)/YBCO is two-exponential below T_c only. We assume this difference arise because of the different thickness of the BFO overlayer. The BFO layer with thickness ~ 26 nm is maximally strained [32] compared to the BFO layer with thickness ~ 130 nm.

The obvious decrease in the relaxation time of YBCO for BFO/YBCO bilayer compared to YBCO film can be attributed to the presence of the BFO overlayer. The speeding up of YBCO dynamics in the BFO/YBCO bilayer could be due to the BFO overlayer acting as a trapping layer and/or due to the the interaction of weak ferromagnetism in BFO and superconductivity in YBCO. The interface may be causing an increase in the decay of high-frequency phonons to low-frequency phonons, thereby making the relaxation time faster. More theoretical and exper-

imental studies are needed to better understand the physics in these thin film heterostructures. Experimental studies such as strain effects or surface roughness effects on these samples would help in understanding how the properties of the bilayer depend on these parameters and would help in growing optimized bilayer samples. The effect of changing the thickness of BFO layer and YBCO layer on the speeding up of the dynamics is another suggested experimental work which would also help in understanding why the signals are so different with BFO layers of different thickness.

6.4 Conclusion

We performed optical pump-probe reflectivity measurements on YBCO and BFO thin films, and on BFO/YBCO bilayer thin film heterostructures. The results show retaining of the superconductivity of YBCO in the heterostructure. The presence of a BFO overlayer produces an apparent change in the relaxation process. We observe that the BFO overlayer in a BFO/YBCO bilayer speeds up the YBCO dynamics when compared to pristine YBCO dynamics; *i.e.* the BFO affects the YBCO at short time delays. On the other hand, the YBCO underlayer suppresses the BFO signal at long time delays. These results may encourage the use of pump-probe technique for studies on other heterostructures to explore the interactions across the interfaces.

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Chapter 7

Terahertz optical response of YBCO thin films

The chapter begins with an introduction where a brief literature review of previous studies on YBCO thin films in the terahertz (THz) regime is provided and the motivation for undertaking terahertz time-domain spectroscopy (THz-TDS) measurements on YBCO thin films is discussed. This is followed by the details on THz-TDS measurement on YBCO thin films grown on different substrates (MgO and LSAT) and discussion of the results.

7.1 Introduction

The optical properties of superconducting thin films in the terahertz range have been extensively studied as this may lead to more information on the low-energy excitations in the superconducting state of high-temperature superconductors. YBCO is expected to find applications in high-speed photodetectors, and terahertz (THz) digital and communication applications [1] because of the picosecond photoresponse. Many reports on optical conductivity measurements on YBCO thin films performed in the THz frequency region are available [2–9] that provided significant information on the complex optical conductivity of these films.

In this chapter, the results of THz-TDS measurements of YBCO thin films grown on different substrates (MgO and $(\text{LaAlO}_3)_{0.3}\text{-(Sr}_2\text{AlTaO}_6)_{0.7}$ [LSAT]) at different temperatures below and above the superconducting transition temperature T_c in the frequency range from 0.2 THz to 2.5 THz is presented. Averitt *et al.* have reported on terahertz studies of 60 nm-thick $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ thin films ($T_c = 89$ K) grown on 500 μm -thick MgO substrates [6–8]; whereas no terahertz studies on a YBCO film on LSAT substrate have been reported till date to our knowledge.

We carry out this measurement as a starting point for future THz time-domain spectroscopic measurements on BFO/YBCO bilayers and similar heterostructures where the measured complex optical conductivity of the heterostructure can be analyzed and compared with that of the pristine superconducting material to get information on the changes in the dynamics of the superconducting component brought about by other components in the heterostructure. The extracted optical properties such as complex index of refraction and complex optical conductivity of the YBCO thin film samples agree with literature. We also extracted other parameters of interest such as scattering rate, superconducting and normal carrier fractions, and penetration depth by fitting the optical conductivity with the two-fluid model explained in Section 2.3.5.1.

7.2 Experiment

7.2.1 Samples for Terahertz Study

The samples used for this study, YBCO thin films on MgO substrates, are obtained from Q. X. Jia, Los Alamos National Laboratory, USA. The samples are optimally-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c \sim 81 \text{ K}$ ¹, $\sim 60 \text{ nm}$ thick), grown on $\sim 0.5 \text{ mm}$ -thick MgO substrate. The sample dimension is $10 \text{ mm} \times 10 \text{ mm}$. The reason for low value for T_c could be strain.

Figure 7.1: Magnetization vs temperature measured on (a) YBCO thin film grown on MgO substrate and (b) YBCO thin film grown on LSAT substrate.

¹The low value of T_c could be due to strain/lattice mismatch.

We also studied the terahertz response of a YBCO thin film on LSAT substrate grown by He Mi from Prof. Tom Wu's group, Nanyang Technological University, Singapore. The sample is optimally-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c \sim 90$ K, ~ 60 nm thick²), grown on ~ 1 mm-thick LSAT substrate. The sample dimension is $5 \text{ mm} \times 5 \text{ mm}$.

7.2.2 Experiment

THz-TDS transmission measurements are carried out on YBCO thin films in the terahertz frequency range using a Teraview TPS Spectra 3000 Spectrometer [10] at a resolution of 1.2 cm^{-1} . Experimental details are given in Section 2.3.3. The measurements are performed in the temperature range of $10 \text{ K} - 120 \text{ K}$ at 10 K intervals. A measurement is also made at room temperature. The frequency range of measurements is 0.2 THz to 2.5 THz . For measuring the YBCO thin film sample, the *sample on substrate-substrate* configuration is used. The substrate is also measured in the same frequency range at the above temperatures with the reference pulse measured in vacuum (*sample-vacuum* configuration). The Fabry-Perot term in the data analysis of the substrate equals 1 as we consider no multiple reflections in the substrate. The procedure method to extract the complex optical conductivity is described in detail in Section 2.3.4.

7.3 Results & Discussions

7.3.1 YBCO thin film grown on MgO substrate

First, the complex refractive index ($\tilde{n} = n + ik$) of the substrates at different temperatures is extracted from the THz-TDS measurement of the substrate with the reference signal being vacuum. The frequency dependence of the complex index of refraction $\tilde{n}(\nu)$ of the substrate is needed for extracting the complex optical

²The thickness rate for YBCO growth is given as 1 nm per 100 pulse. Given that 6000 pulses have been used, the thickness of the YBCO thin film is estimated to be $\sim 60 \text{ nm}$.

conductivity $\tilde{\sigma}$ of the YBCO thin film.

Figure 7.2: Index of refraction at different temperatures as function of frequency obtained from THz-TDS measurements of MgO substrate.

Figure 7.2 shows the real part of refractive index $n(\nu)$ of the ~ 0.5 mm-thick MgO substrate at different temperatures. The refractive index values that we obtained are in good agreement with reported refractive index values of a MgO substrate in the THz frequency range [11,12]. The obtained refractive index is fitted with a quadratic function of frequency ν [$n(\nu) = a\nu^2 + b\nu + c$] to use later in the extraction of complex optical conductivity $\tilde{\sigma}(\nu)$ of the YBCO thin film grown on MgO substrate.

Figure 7.3: Time-domain THz electric field transmitted through YBCO thin film grown on MgO substrate.

Figure 7.3 displays the transmitted THz waveforms through the YBCO thin

film grown on a MgO substrate in the time domain, at several temperatures below and above T_c . An decrease in the transmitted THz amplitude is observed as the sample becomes superconducting which is due to increased reflection of incident radiation as the sample becomes more conducting.

Figure 7.4: (a) Transmission amplitude and (b) transmission phase of the THz signal transmitted through the YBCO thin film on MgO substrate.

Figure 7.4(a) and Figure 7.4(b) show the extracted amplitude (the ratio of the sample to reference amplitude in frequency domain) and phase (the phase difference between the sample and reference signals in the frequency domain) of the complex transmission function. We can see that there are obvious changes as the sample enters the superconducting phase — a decrease in amplitude that can be related to an increased in reflection as the sample becomes more conducting accompanied by an increase in absorption that is reflected by an increase in phase.

Figure 7.5(a) and Figure 7.5(b) show respectively, at temperatures below and above T_c , $n(\nu)$ and $k(\nu)$ obtained from the complex transmission function by the calculation explained in Section 2.3.4. The obtained values agree well with reported values in the THz frequency range [13].

Figure 7.6 and Figure 7.7 show, respectively, the real part $\sigma_1(\nu)$ and imaginary part $\sigma_2(\nu)$ of the frequency-dependent optical conductivity at temperatures below and above T_c . The extracted $\sigma_1(\nu)$ and $\sigma_2(\nu)$ agree well with the reported THz optical conductivity values of YBCO [6–8].

First, consider $\sigma_1(\nu)$ given in Figure 7.6. At temperatures above T_c , the fre-

Figure 7.5: (a) Real part $n(\nu)$ and (b) imaginary part $k(\nu)$ of complex index of refraction of YBCO thin film on MgO substrate at temperatures below and above T_c .

Figure 7.6: Real part $\sigma_1(\nu)$ of optical conductivity of YBCO thin film on MgO substrate at temperatures below and above T_c .

quency dependence of σ_1 is very weak and increases upon cooling as the scattering rate is getting lower, whereas ω_p and $x_n(T)$ are almost unchanged. Below T_c , σ_1 decreases with decreasing temperature. This is caused by a decrease in $x_n(T)$ with decreasing temperature as more quasiparticles are transferred to the superconducting condensate. The real part σ_1 is entirely due to a contribution from a normal fraction.

One can easily identify the phase transition from $\sigma_2(\nu)$ given in Figure 7.7. Above T_c , there is hardly any change of σ_2 as the density of superconducting carriers is zero above T_c . The imaginary part σ_2 increases with decrease in temperature because of an increase in $x_s(T)$. We can observe the well known $1/\omega$ dependence of

Figure 7.7: Imaginary part $\sigma_2(\nu)$ of optical conductivity of YBCO thin film on MgO substrate at temperatures below and above T_c as a function of frequency.

σ_2 below T_c due to the superconducting condensate fraction even though there is a non-zero contribution from a normal fraction as well. In calculating the imaginary part of conductivity, we have used the high-frequency dielectric constant of YBCO ($\epsilon_\infty = 5$) [14].

Figure 7.8: Two-fluid model fit to experimentally obtained frequency dependent conductivity at (a) 60 K and (b) 100 K. The dashed line in (a) is contribution from the superconducting carrier fraction whereas the dotted line denotes the contribution from normal carrier fraction.

The experimental values of $\sigma_1(\nu)$ and $\sigma_2(\nu)$ are fitted with a two-fluid model (Equation 2.27) to obtain ω_p , temperature dependence of Γ and temperature dependence of $x_n(T)$ and $x_s(T)$. Figure 7.8(a) and Figure 7.8(b) show the two-fluid model fit to the conductivity data at temperatures 60 K and 100 K, respectively.

The dashed line in Figure 7.8(a) denotes the contribution from a superconducting carrier fraction to $\sigma_2(\nu)$ at 60 K, whereas the dotted line denotes the contribution from the normal carrier fraction. Above T_c , as shown in Figure 7.8(b), $\sigma_2(\nu)$ has a contribution only from the normal carrier fraction since $x_s(T > T_c) = 0$. The obtained values of scattering rate from the fit to the two-fluid model are shown in Figure 7.9(a). We can see that the scattering rate decreases with decreasing temperature and almost saturates at low temperature. We get the plasma frequency $\omega_p \approx (1150 \pm 35) \times 10^{12} \text{ s}^{-1}$ from a two-fluid model fit to experimental data which agrees with reported values obtained from photoexcitation studies [1,9]. The ratio $N/(m^*/m_0) \approx 4.2 \times 10^{20} \text{ cm}^{-3}$ is obtained from the plasma frequency value using the relation $\omega_p^2 = \frac{ne^2}{\varepsilon_0 m^*}$, where m_0 is the electron rest mass. From the plasma frequency, we can also obtain the penetration depth at ‘zero-temperature’ $\lambda_L(0)$ using the relation $\omega_p = \frac{c}{\lambda_L(0)}$. We get $\lambda_L(0) \approx (260 \pm 10) \text{ nm}$. This value of $\lambda_L(0)$ is of the same order as reported in THz-TDS measurements of YBCO films [9,15].

Figure 7.9: (a) Scattering rate as a function of temperature. (b) Circles: superconducting fraction and squares: normal fraction, as a function of temperature. Triangles: normal fraction with contribution from residual normal fluid subtracted. Dotted lines are guide to the eye.

Figure 7.9(b) show $x_s(T)$ and $x_n(T)$ obtained from two-fluid fit to the data. Note that the $x_n(T)$ decreases with decrease in temperature below T_c , whereas $x_s(T)$ increases with decreasing temperature below T_c .

We notice that the normal carrier fraction deep inside the SC state is substantially high. Since our sample is a thin film, probably there are impurities

contributing to a residual normal fluid density which might lead to a non-zero normal fraction at low temperature [16]. Also, in two-fluid model, we assume sum of the superconducting and normal carrier fractions to be unity ($x_n + x_s = 1$) at all temperatures which could be inadequate.

We fit the obtained temperature dependent normal fraction $x_n(T)$ to the relation $(t^2 [1 - x_n(0)] + x_n(0))$ [16] where $x_n(0)$ is the residual normal fluid fraction and $t = \frac{T}{T_c}$. We get $x_n(0) = 0.45 \pm 0.02$. The normal fraction is replotted with $x_n(T) = \left(\frac{T}{T_c}\right)^2$ (triangles) in Figure 7.9(b) where the contribution from the residual normal fluid is not present.

Figure 7.10: Penetration depth $\lambda_L(T)$ as function of temperature obtained by fitting imaginary conductivity with Equation (2.32). The solid line is the interpolation line.

The imaginary part $\sigma_2(\nu)$ is fitted with Equation (2.32) to obtain the London penetration depth as function of temperature which is displayed in Figure 7.10. We get a $\lambda_L(0)$ value of ≈ 350 nm by interpolation which is of the same order as obtained from ω_p value. The $\lambda_L(0)$ value ≈ 350 nm was obtained from fitting imaginary conductivity with Equation (2.32) which is an approximation in the limit $\omega\tau \ll 1$. In our case, $\omega\tau$ is not strictly $\ll 1$. Therefore we have a discrepancy compared to the value obtained from plasma-frequency.

Figure 7.11 shows the measured $\tilde{\sigma}(T)$ at ~ 0.5 THz. The circles and squares are the experimental values for $\sigma_1(T)$ and $\sigma_2(T)$, respectively. These results are in agreement with previous THz studies [6, 7] and are similar to the theoretical calcu-

Figure 7.11: Circles, experimental σ_1 at ~ 0.5 THz; squares, experimental σ_2 at ~ 0.5 THz.

lation shown in Figure 2.28. The sudden increase in σ_2 below T_c can be attributed to an increase in $x_s(T)$. Above T_c , the decrease in Γ with decreasing temperature results in a corresponding increase in $\sigma_1(T)$. This increase is overcome by the decrease in σ_1 corresponding to a decrease $x_n(T)$ below T_c , resulting in a peak in $\sigma_1(T)$ near to T_c . We know the imaginary part of optical conductivity normalized to conductivity in the normal state $\sigma_2(T)/\sigma_n$ saturates at low temperatures at the value $\pi\Delta(0)/\hbar\omega$ [17]. We obtain the zero-temperature gap value $2\Delta(0) \sim 20$ meV from the above relation using the saturation value of the imaginary conductivity obtained by interpolation. A gap value $\Delta = 14 \pm 2$ meV has been reported for YBCO from tunneling, far infrared and Andreev reflection measurements [18, 19].

7.3.2 YBCO thin film grown on LSAT substrate

Figure 7.12 shows the index of refraction of the ~ 1 mm-thick LSAT substrate at different temperatures. Compared to MgO, there is hardly any temperature dependence. The refractive index values that we obtained are in good agreement with reported refractive index values of LSAT substrate in THz regime [12]. $n(\nu)$ and $k(\nu)$ are fitted with a quadratic function of frequency $[y = a\nu^2 + b\nu + c]$ which is used later in extracting $\tilde{\sigma}(\nu)$ of YBCO film.

Figure 7.13 displays the transmitted THz field through the YBCO thin film

Figure 7.12: (a) Real part $n(\nu)$ and (b) imaginary part $k(\nu)$ of the complex index of refraction at different temperatures obtained from THz-TDS measurements of LSAT substrate.

Figure 7.13: Time-domain THz electric field transmitted through YBCO thin film grown on LSAT substrate.

grown on a LSAT substrate in the time domain at temperatures below and above T_c . As the sample becomes more conducting on entering the superconducting phase, we see a sudden decrease in the amplitude of the time-domain THz field.

Figure 7.14(a) and Figure 7.14(b) respectively show the extracted amplitude and phase of the complex transmission function of the YBCO film. We can see that there are obvious changes as the sample enters the superconducting phase — a decrease in amplitude that can be related to an increased in reflection as the sample becomes more conducting accompanied by an increase in absorption that is reflected by an increase in phase. But, note that the phase is negative and it crosses zero, different from the phase of YBCO on a MgO substrate. The zero-crossing

Figure 7.14: (a) Transmission amplitude and (b) transmission phase of the THz signal transmitted through the YBCO thin film grown on LSAT substrate.

of phase is interesting as we do not see this mentioned anywhere in the literature. Another YBCO sample grown on LSAT substrate also shows phase crossing zero at a non-zero frequency. We are still investigating the reason for this behavior.

Figure 7.15: (a) Real part $n(\nu)$ and (b) imaginary part $k(\nu)$ of complex index of refraction of YBCO thin film on LSAT substrate at temperatures below and above T_c .

Figure 7.15(a) and Figure 7.15(b) show, at temperatures below and above T_c , $n(\nu)$ and $k(\nu)$ obtained from the complex transmission function by the calculation explained in Section 2.3.4. The obtained values are in agreement with reported values [13]. $\tilde{n}$ and $\tilde{\sigma}$ discussed later have been calculated only in the frequency range 1 THz–2 THz to avoid the zero-crossing of the phase.

Figure 7.16 and Figure 7.17 show $\sigma_1(\nu)$ and $\sigma_2(\nu)$ at temperatures below and above T_c . The extracted $\sigma_1(\nu)$ and $\sigma_2(\nu)$ are of the same order as that of YBCO

Figure 7.16: Real part $\sigma_1(\nu)$ of optical conductivity of YBCO thin film on LSAT substrate at temperatures below and above T_c .

Figure 7.17: Imaginary part $\sigma_2(\nu)$ of optical conductivity of YBCO thin film on LSAT substrate at temperatures below and above T_c .

on a MgO substrate and have almost similar frequency dependence.

Figure 7.18 shows the measured complex conductivity as function of temperature at 1 THz. The circles and squares are the experimental values for σ_1 and σ_2 , respectively. We see that the temperature dependence of conductivity is similar to that in Figure 7.11. We get a zero-temperature gap value $2\Delta(0) \sim 30$ meV using the saturation value of the imaginary conductivity obtained by interpolation, which is slightly greater than that of a YBCO film on a MgO substrate. The accuracy of extracted parameters from THz-TDS results of the YBCO film on a LSAT substrate is yet to be confirmed as we are still investigating the reason for zero-crossing of phase. The zero-crossing may affect the accuracy in the measurement. In case

Figure 7.18: Circles, experimental σ_1 at 1 THz; squares, experimental σ_2 at 1 THz. The dotted lines are guide to the eye.

of YBCO grown on MgO substrate, there is no zero-crossing. This zero-crossing below T_c is observed by different users with different samples on LSAT substrate where the two of the samples are grown by PLD and one by dc sputtering. We still do not know the reason for the zero-crossing, whether it is an interface effect or not.

7.4 Conclusion

We performed terahertz time-domain spectroscopy measurements on YBCO films grown on MgO and LSAT substrates. Our data agrees with the literature on optical conductivity measurements of YBCO in the THz regime. This would be used as an outset to a detailed study on terahertz dynamics of heterostructures such as a BFO/YBCO bilayer.

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Chapter 8

Concluding Remarks & Future Work

Femtosecond pump-probe studies were performed to study the photoinduced dynamics of complex systems such as the high-temperature superconductor Bi-2212, spin fluctuation systems with strong hybridization between conducting electrons and f-electrons and most importantly, a multiferroic/superconductor bilayer heterostructure BFO/YBCO with competing interactions at the interface. We see that femtosecond pump-probe measurements are a very useful tool to study such complex materials. We also performed THz-TDS measurements on a YBCO thin film grown on a MgO substrate.

We studied the temperature dependence of the photoinduced dynamics of Bi-2212 in the overdoped regime using an ultrafast pump-probe technique. We observed that the pseudogap phase exists in the sample. Our data support the *two-gap* scenario where both the superconducting gap and pseudogap coexist in the superconducting state. Our results also point to an increased scattering rate between electrons and spin-fluctuations as the sample enters the pseudogap phase. We also performed polarization dependent studies on underdoped, optimally doped and overdoped samples of Bi-2212. We see a clear polarization dependence. We are still working on the theoretical explanation for the observed polarization dependence.

We studied the photoinduced dynamics of UX_3 ($X = \text{Al, Sn, Ga}$) single crystals as a function of temperature. For UGa_3 , the quasidivergence of the relaxation time near the Néel temperature T_N indicates the formation of a spin density wave gap. The relaxation dynamics shows a gradual change from single-exponential to two-exponential behavior below the spin fluctuation temperature T_{sf} for UAl_3 and USn_3 , showing that ultrafast spectroscopy is sensitive to c- f Kondo hybridization in the f -electron systems.

Further we studied ultrafast relaxation dynamics of a BFO/YBCO bilayer heterostructure and compared it with the relaxation dynamics of a pristine YBCO thin film. We found that the superconductivity of YBCO is retained in the heterostructure. The most interesting result is a speeding up of YBCO dynamics in the superconducting state in the heterostructure because of the BFO overlayer. We also observed that BFO dynamics is affected by the YBCO underlayer in the superconducting state in the heterostructure. We are still working on the theoretical explanation for the observed speeding up of superconducting dynamics.

We performed THz-TDS measurements on a YBCO thin film grown on MgO and LSAT substrates. Our results agree with literature. Though similar studies have already been reported, we conducted this experiment as a starting point for future terahertz studies on BFO/YBCO bilayer and similar heterostructures. We are interested to know how the parameters like optical conductivity, superconducting and normal carrier fraction, penetration depth *etc.* change when BFO is deposited on top of a YBCO film. Our group will also be performing OPTP measurements on these samples.