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**Photoexcited Carrier Relaxation in High Temperature Superconductors probed by Ultrafast Optical Spectroscopy**

**Doctoral Thesis**

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This work would not have been possible without the creative input and encouragement of many people. Whereas it is nearly impossible to list everybody who made a contribution, there are those who deserve special acknowledgment, since without them none of this work could have come together.

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Abstract

This thesis presents measurements of ultrafast carrier relaxation dynamics in materials with a small energy gap in electronic density of states by means of femtosecond time-resolved optical spectroscopy. In these experiments, a femtosecond laser pump pulse excites electron-hole pairs via an interband transition in the material, thereby changing its optical properties. The quasiparticle relaxation and recombination processes are monitored by measuring the resulting photoinduced absorption as a function of time after photoexcitation. Therefore the technique enables direct real-time measurements of non-equilibrium quasiparticle recombination dynamics.

It is shown that the presence of a gap in the low energy excitation spectra creates a relaxation bottleneck, with carrier relaxation being determined by the magnitude of the energy gap. In a superconductor, the opening of a gap, as temperature is decreased through $T_c$, is manifested by a rapid increase in the amplitude and relaxation time of the photoinduced absorption from femtosecond to picosecond range. We show that by analyzing the temperature dependence of the photoinduced absorption in high-$T_c$ superconductors or other systems with a small energy gap in electronic density of states one can determine the temperature dependence and magnitude of the gap in the material under investigation.

In experiments on high-$T_c$ superconductors, photoinduced absorption on the nanosecond timescale was also observed. Because of its anomalous temperature dependence, which cannot be accounted for by simple bolometric model, it is attributed to photoinduced absorption from in-gap localized states. It is shown that the temperature dependence of this long lived photoinduced absorption is also determined by the temperature dependence of the energy gap.

We applied the femtosecond time-resolved optical spectroscopy to study the energy gap evolution in the high-$T_c$ superconductor $\text{Ca}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ over a wide range of doping. In strongly underdoped samples the data imply the presence of a temperature independent energy gap $\Delta^p$, which is found to be inversely proportional to doping. From the absence of anomalies in the relaxation time and amplitude of the picosecond component we argue that the pseudogap behavior arises due to the presence of pairing above $T_c$. Near optimum doping and in the overdoped region we find evidence for the co-existence of two distinct energy gaps: a temperature independent pseudogap $\Delta^p$ and a mean–field-like temperature dependent gap $\Delta_c(T)$. The data suggest the origin of the two-gap behavior is in the microscopic spatial inhomogeneity of the material.

Finally, we used this technique to study the quasi one-dimensional charge-density wave semiconductor $\text{K}_0.3\text{MoO}_3$. Similar to high-$T_c$ superconductors, a fast photoinduced absorption was found whose amplitude and relaxation time shows anomalies at $T_c = 183$ K concurrent with the opening of the Peierls gap. Above $T_c$ its amplitude
gradually drops near \( \sim 240 \) K, which is attributed to the presence of a pseudogap in the single particle excitation spectrum. In addition, photoinduced reflectivity oscillations were observed in real time, whose frequency, amplitude and damping time were found to be in agreement with the charge-density-wave amplitude mode determined in frequency-domain measurements. A temperature dependent overdamped absorption transient is also observed and on the basis of the temperature dependence of its amplitude and damping it is tentatively attributed to relaxation of the phason mode. A long lived photoinduced absorption was observed in this compound also, and is attributed to the presence of in-gap localizes states, similarly as in high-\( T_c \) superconductors.

**KEY WORDS:** High-\( T_c \) superconductivity, carrier relaxation dynamics, femtosecond time-resolved optical spectroscopy, charge density waves.

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Chapter 1

Introduction.

Ever since the discovery of high temperature superconductivity in 1986 [1], these materials have been probably the most extensively studied materials in the field of solid state physics both from the fundamental and applied point of view. Considerable effort has been put into comprehending the pairing mechanism which gives rise to critical temperatures much higher than expected from conventional electron-phonon mechanisms [2]. Until 1986 the highest critical temperature of 23 K was achieved in Nb₃Ge, whereas the current record holder is Hg₂Ba₂Ca₂Cu₃O₁₀−δ with \( T_c = 134 \) K at ambient pressure. The critical temperature in Hg₂Ba₂Ca₂Cu₃O₁₀−δ can be raised up to 164 K by applying high pressure [3].

In this chapter we briefly review some of the most important properties of high temperature superconductors, focusing on the changes in a low energy excitation spectrum associated with the appearance of the superconducting gap and the pseudogap.¹ The pseudogap at temperatures far above critical temperature \( T_c \) was consistently observed by various experimental techniques [4, 5] susceptible to the changes in low energy density of states. Since the pseudogap behavior has been observed in virtually all high-\( T_c \) superconductors including bismuthates, it appears to be a general feature of these materials. Therefore, by understanding the origin of the pseudogap one might elucidate the pairing mechanism in high-\( T_c \) superconductors. After introducing some of the theoretical proposals (section 1.1.3) that treat superconducting as well as normal state properties of high-\( T_c \) superconductors we briefly outline the scope of the thesis in section 1.2.

1.1 Physical properties of high-\( T_c \) superconductors.

In this section we briefly review some structural and electronic properties common to high-\( T_c \) superconducting cuprates, which are believed to be crucial for the occurrence of superconductivity at such high temperatures. The peculiarities of the CaYBCO

¹ The term pseudo-gap is commonly used for depression in the density of states near Fermi energy observed above the (superconducting) phase transition when a real gap is formed.
(Ca\textsubscript{x}Y\textsubscript{1–x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7–δ}) system, on which most of the experiments reported in this thesis were performed are given in section 2.2.

It should be, however, stated that superconductivity at high temperatures is not limited to cuprates only. Besides bismuthates Ba\textsubscript{1–x}K\textsubscript{x}BiO\textsubscript{3} and BaPb\textsubscript{1–x}Bi\textsubscript{x}O\textsubscript{3} with \(T_c \leq 34\) K [6], superconductivity at 90 K was recently reported in sodium doped WO\textsubscript{3} [7, 8], although at the time of writing it still needs to be confirmed.

1.1.1 Structural properties of high-\(T_c\) cuprates.

High-\(T_c\) superconducting cuprates are layered perovskites. They have highly anisotropic, layered structure, as can be seen in Fig. 1.1. In all of these systems, copper oxide planes (CuO\textsubscript{2}) form a common structural element, which is thought to dominate the superconducting properties. Depending on the choice of stoichiometry, the crystallographic unit cell contains varying number of CuO\textsubscript{2} planes. The neighboring CuO\textsubscript{2} planes are bridged by cation layer, whereas groups of CuO\textsubscript{2} planes are separated with layers containing oxygen ions together with cations of various elements. Most frequently these are rare-earth ions, heavy metal ions and ions of the second column elements [9]. The dimensions of the unit cell [see Fig. 1.1] in c- axis vary strongly (approx. 1.2 nm in Ca\textsubscript{x}Y\textsubscript{1–x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7–δ} and Tl\textsubscript{1–x}Pb\textsubscript{x}Sr\textsubscript{2}Ca\textsubscript{y}Y\textsubscript{1–y}Cu\textsubscript{2}O\textsubscript{7}), depending on the number of CuO\textsubscript{2} layers, whereas in a- or b- axis directions the lattice parameters are fairly constant ~ 0.4 nm.

The anisotropy in the crystal structure is reflected in the strong anisotropy in the measured physical quantities in normal and superconducting state. For example, anisotropy in the normal state resistivity \(\rho_c/\rho_{ab}\) ranges from ~ 100 in La\textsubscript{2–x}Sr\textsubscript{x}CuO\textsubscript{4+δ} to ~ \(10^5\) in Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8+δ} [10]. Also, the magnetic penetration depth \(\lambda\) and superconducting coherence length \(\xi\) are strongly anisotropic. In YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}, for instance \(\xi_{ab} \sim 1.5\text{nm}\) and \(\xi_c \sim 0.4\text{ nm}\) was estimated.

1.1.2 Electronic properties.

All the cuprates contain as an essential structural element one or more copper oxide planes (CuO\textsubscript{2}) - see Fig. 1.1. Charge reservoir (CR) layers above and below the CuO\textsubscript{2} planes can accept or donate electrons to CuO\textsubscript{2} planes. This can be achieved by chemical substitution of different-valence ions (like in La\textsubscript{2–x}Sr\textsubscript{x}CuO\textsubscript{4+δ}), by changing the oxygen stoichiometry in CR layers (like in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7–δ}), by ion substitution with isovalent ions of different ionic radius, or by combination of the three.

High-\(T_c\) superconductivity in both electron or hole doped materials was found, the majority of the materials being hole-type conductors. Here we shall focus on the hole-doped materials.

\(\xi\) are determined by measuring the upper critical field \(H_{c2}(H \perp ij) = \frac{\Phi_0}{2\pi\xi_i\xi_j}\), where \(\Phi_0\) is the magnetic flux quantum. Since \(H_{c2}\) was found to diverge as \(T \to 0\) the coherence lengths might be also substantially smaller.
1.1. Physical properties of high-$T_c$ superconductors.

Figure 1.1: Schematic structures of two copper oxides a) $\text{Ca}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and b) $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_y\text{Y}_{1-y}\text{Cu}_2\text{O}_7$. Both unit cells consist of two $\text{CuO}_2$ planes with $\text{Y}$ or $\text{Ca}$ ion in between. The difference is in the charge reservoirs, which in case of $\text{Ca}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ are $\text{CuO}$ chains, whereas in $\text{Tl}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_y\text{Y}_{1-y}\text{Cu}_2\text{O}_7$ there are $(\text{Tl},\text{Pb})\text{O}$ planes.

A schematic phase diagram as a function of doping is given in Figure 1.2. As can be seen, superconductivity is limited to a narrow range of doping. Undoped materials are for historical reasons usually referred to as parent compounds, and below the Néel temperature $T_N$ are antiferromagnetic (AF) insulators. As hole concentration $p$ (measured in holes per Cu ion in $\text{CuO}_2$ plane [11]) increases, $T_N$ decreases and at approximately $p = 0.05$ there is no long-range antiferromagnetic order. In the range of doping from $0.05 \lesssim p \lesssim 0.25$ the materials exhibit superconductivity at low temperatures. The maximum critical temperature that depends on the particular compound and on the number of $\text{CuO}_2$ planes per unit cell, is achieved at $p \sim 0.15$; this doping level is usually referred to as optimum doping. Below and above this doping level the material is underdoped and overdoped respectively. When the hole concentration is further increased (above $p \sim 0.25$) superconductivity vanishes and the material behaves, according to transport properties, as a more or less ordinary metal [10].

Physics of undoped materials.

Band structure calculations for the undoped material indicate that it should be metallic, but in reality it is insulating [12]. It is not a failure of the details of the calculations, since chemical valency considerations also imply that it should be
metallic. Namely, in undoped material there is odd number of electrons per unit cell indicating half filled valence band. Due to strong Coulomb repulsion on Cu $d_{x^2-y^2}$ they are believed to be Mott-Hubbard insulators. The electronic structure of CuO$_2$ plane is described by models generalizing the Hubbard Hamiltonian [13] where the bands originate from copper $d_{x^2-y^2}$ and oxygen $p_x$, $p_y$ orbitals [14]. The common feature in all the models is that the Hubbard mechanism splits the Cu d-band into two (upper and lower Hubbard band) with a large correlation gap of $\sim 8$ eV. The highest occupied band (sometimes referred to as charge-transfer band) is about 1.7 eV below the upper Hubbard band and is derived from predominantly O p-bands. In the range of energies of charge transfer band some other bands might be present, originating from surrounding layers that are not included in a three-band Hubbard model [15].

Below the Néel temperature $T_N$ the unpaired holes of the Cu$^{2+}$ ions are antiferromagnetically coupled via the oxygen O$^{2-}$ superexchange. The maximum Néel temperature is of the order of several hundred K (in YBa$_2$Cu$_3$O$_6$ $T_N \sim 420$ K). By doping with holes $T_N$ decreases rapidly. As doping is increased the semiconducting behavior with small energy gap is inferred from resistivity data [16]. Despite that it appears that the density of states at Fermi level is finite and the photoconductivity [17] data implies the states at $E_F$ to be localized. Localized holes in this Fermi glass [18]
move via thermally activated hopping to extended states with the hopping barrier of approximately 0.1 eV \[17\]. The localization might arise due to disorder caused by non-stoichiometry – Anderson localization \[18\]. However, polaron formation can also give rise to the observed effects. The latter can be inferred from the presence of local modes deduced from photoinduced absorption spectra \[19\], the large absorption \[20\] and photoinduced absorption in mid-infrared \[21\], amongst other.

Superconducting state properties.

One of the early questions was whether there are Cooper pairs in these materials or some new exotic form of superconductivity takes place. This question was soon answered experimentally in favor to Cooper pairs with zero net momentum measuring the AC Josephson effect \[22\] and flux quantization \[23\]. Moreover, the Knight shift was observed to go to zero as \( T \to 0 \) \[24\] implying that the pair is most likely singlet. Soon after the discovery it was shown that high temperature superconductors (HTSC) are extreme type-II superconductors with very short coherence lengths of the order of a unit cell. Therefore, if one calculates the number of Cooper pairs that exist within the radius of one pair one obtains the number of the order of 1-10, in contrast to \( 10^6 \) in conventional superconductors. As a consequence of the short coherence length, large thermodynamical fluctuations are expected in HTSC \[25\].

It was suggested by several authors (see for example Ref. \[26\]) that in order to understand high-\( T_c \) superconductivity one should start by examining normal state properties. On the other hand, also the superconducting state properties in these materials are strongly anomalous.

One of the most interesting properties of HTSC is temperature dependence of the electronic specific heat \[27\]. Unlike in conventional superconductors, where there is a step-like increase in electronic specific heat \( c_p \) as temperature is lowered through \( T_c \) \[2\], \( c_p \) shows strongly anomalous behavior in the cuprates. In the least anisotropic HTSC \( \mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_{7-\delta} \) in optimally doped sample \((\delta = 0.08)\) \( c_p \) shows similar behavior at \( T_c \) as the \( \lambda \)-transition of \( ^4\mathrm{He} \) \[28\]. In other (more anisotropic) cuprates the peak is symmetrical and the jump at \( T_c \) vanishes. Moreover, the magnetic field dependence of the electronic specific heat shows that the peak does not (or in some cases weakly) shift in temperature with increasing magnetic field \[27\]. This behavior is expected in the case of a weakly interacting Bose gas \[27\], but not for a BCS like superconductor.

Secondly, we should mention that the temperature dependence of the upper critical field \( H_{c2} \) shows a divergence as the temperature is decreased towards 0 K \[29, 30, 31\] in practically all HTSC cuprates, in overdoped and underdoped materials and also in non-cuprate HTSC \( \mathrm{Ba}_{1-x}\mathrm{K}_x\mathrm{BiO}_3 \) \[32\]. It is also surprising that the upper critical field determined from resistivity measurements and from specific heat measurements differ by 100 %.

Since these quite unusual anomalies have been quite generally observed in HTSC it follows that the theory of high-\( T_c \) superconductivity should treat these anomalies as
well. Below we review some additional important properties of the superconducting state that might shed some light on the physics of cuprates.

We should mention that due to non-homogeneity and disorder (intrinsic or extrinsic) there is substantial evidence of phase-separation in cuprates [33, 34]. It was first observed in the structural studies of La$_{1-x}$Sr$_x$CuO$_4$ using extended X-ray absorption fine structure spectroscopy (EXAFS) [35], and neutron pair distribution function [36], where two co-existing sets of Cu-O inter-atomic distances were found in CuO$_2$ plane as well as in the out-of plane Cu-O distance. The phase separation was found to be dynamic [36]. A static analogue of the dynamic stripe phase was found in the copper oxide material La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$, with x=0.12, from neutron diffraction [37] implying rows of charge being separated by insulating AF regions (in which neighboring atomic spins oppose each other). However, since there is substantial evidence for the presence of localized states in the vicinity of the Fermi energy ($E_F$) [38, 39] it was argued [34] that the two phases might correspond to carrier rich metallic regions and carrier poor polaronic areas. Since the stripes occur preferentially at lower temperatures, there is still no consensus whether the stripes help or hurt superconductivity in these materials [40].

At the end of the discussion on superconducting properties we should mention another important ongoing discussion - the symmetry of the order parameter. It was shown by phase sensitive experiments [41] that the order parameter has a d-wave symmetry (nodes on the Fermi surface with change of sign in order parameter). However, other phase sensitive experiments show HTSC to have mixed s+d wave order parameter [42] or show the order parameter to be of predominantly s-wave symmetry [43], so there is still no final consensus on this issue, especially considering that other experimental results, like NMR and photoemission, can be interpreted both ways.

Normal state properties.

Like in superconducting properties, there is still no consensus on the theoretical nor experimental understanding of the normal state properties of HTSC. One of the most controversial issues is Fermi liquid vs. non-Fermi liquid behavior. Angle resolved photoemission spectroscopy data on optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [44, 45], YBa$_2$Cu$_3$O$_7$ [46], Nd$_{1-x}$Ce$_x$CuO$_4$ [47], as well as on underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [48] appear to show a large Fermi surface. Such large Fermi surface (FS) is consistent with the Luttinger theorem which states that the area enclosed by the Fermi surface is independent of the interaction and should be equal to the free carrier concentration. As a function of doping $x$, the FS is expected to vary as $1 - x$. On the other hand, transport measurements like resistivity [4] show that the conductivity is proportional to doping $x$ implying that HTSC are more like doped semiconductors. This is supported also by the low temperature resistivity measurements in high magnetic fields [49], where the upturn in resistivity on decreasing temperature is observed.

There are several other anomalous normal state properties of the cuprates. The
1.1. Physical properties of high-$T_c$ superconductors.

Temperature dependence of resistivity is linear over large temperature range near optimal doping [10], the Hall coefficient is T-dependent [50], the T-dependence of the nuclear magnetic resonance (NMR) spin-lattice relaxation time does not follow the Korringa law [51, 52], just to mention a few. Moreover, various physical properties that are determined by low energy excitation spectrum show anomalies corresponding to a reduction in the density of states near Fermi energy at temperatures far above $T_c$. The decrease in the density of states near $E_F$ is usually referred to as a pseudogap. By now a pseudogap in the large part of the phase diagram has been consistently observed by numerous experimental techniques in all the HTSC. It was first observed in underdoped YBa$_2$Cu$_3$O$_{6+x}$ by NMR measurements [52], where instead of temperature independent Pauli susceptibility a decrease in the Knight shift was observed. Since NMR probes the spin channel it was used to support the hypothesis of a spin gap. Further experiments probing the charge channel revealed that the pseudogap exists in both the spin and the charge channels. For a review on experimental evidence for the pseudogap in HTSC the reader is referred to Refs. [4, 5].

It is shown experimentally that the temperature(-s), where the anomalies in physical properties are observed increase as we go to more underdoped samples [see Fig. 1.2]. The pseudogap "onset" temperatures$^3$ (where the anomalies are observed) strongly depend on the criterion used, the experimental technique, and often also on the theoretical model used to interpret the data. Therefore, different phase diagrams have been proposed on the basis of the data, with several crossover temperatures indicated (e.g. $T^o$ and $T^*$ from NMR data, where at $T^o$ Knight shift changes from being T-independent to decreasing linearly with decreasing T, and below $T^*$ it decreases faster than linear with temperature [53]). In order to obtain more qualitative picture, the pseudogap magnitude(-s) are often analyzed as a function of doping. Again, substantial differences depending on the criterion and the model used can be found in literature. Common to all the data is that in underdoped materials the pseudogap increases as doping is decreased [54, 55], whereas in overdoped it seems to follow $T_c$ (in overdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ for example energy pseudogap $\Delta_p$ follows $2\Delta_p/kT_c \sim 9.5$ [5]). The magnitude of the pseudogap again depends on the experimental technique and the criterion used to determine it, however it seems that in general the magnitude of the spin gap is lower than the magnitude of the charge gap.

1.1.3 Microscopic models of high-$T_c$ superconductivity.

Since the discovery of HTSC [1] several microscopic models have been put forward. Here we mention just a few and refer the reader to Refs. [9, 56, 57] for further details. Since pseudogap has been observed in virtually all HTSC (including bismuthates) it is believed to play an important role in the mechanism of superconductivity in HTSC.

$^3$ It is a crossover and not a phase transition temperature since no singularities in thermodynamic quantities were observed at this temperature.
Several models involve preformed pairs [58]. First, there is a bi-polaron model proposed by Alexandrov et al. [59] where Bose-Einstein condensation (BEC) occurs at $T_c$ and the pseudogap comes as a natural extension due to existence of pre-formed pairs above $T_c$, with binding energy corresponding to the pseudogap magnitude.

A similar preformed pairing model based on microstripes (one dimensional charge stripes separated by AF stripes) is given by Emery et al. [60]. Here, pairing in charge stripes is a result of spin gap in the AF stripes through so called magnetic proximity effect. The pseudogap associated with the spin gap appears at some temperature $T^*$, and below this temperature there are only one-dimensional superconducting correlations. When the temperature is lowered through $T_c$ Josephson coupling between metallic stripes becomes large enough to achieve phase coherence.

Another model based on spin-charge separation was proposed by Anderson [26]. According to resonating valence bond (RVB) model [26] the separation of spin and charge in CuO$_2$ planes causes the c-axis transport to be incoherent. However if holons (the charge carrying excitations) could form pairs, tunneling between the planes becomes coherent, thereby lowering the ground-state energy giving rise to superconductivity.

Since properties of the parent antiferromagnetic compound are well accounted for by Hubbard model, a simplified Hubbard model with excluding the possibility of doubly occupied states - so called t-J model - was proposed to account for normal state properties of cuprates. Indeed several normal state properties like transport and optical properties [61] were well accounted for, however it is not clear whether it leads to superconductivity [62].

We should mention also the nearly antiferromagnetic Fermi liquid (NAFL) model proposed by Pines at al. [53]. In the NAFL model the dominant interaction between quasiparticles arises from spin fluctuations characterized by the peak in the susceptibility at wavevector $Q=(\frac{\pi}{a}, \frac{\pi}{a})$, where $a$ is the dimension of the unit cell [see Fig. 1.1]. This peak corresponds to the 41 meV anomaly in spin excitation spectra observed in neutron scattering experiments [63, 64, 65]. Since its doping dependence was found to follow the doping dependence of $T_c$ in underdoped YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) [65] it infers some magnetic pairing mechanism. In the NAFL model only quasiparticles in some parts of FS are strongly affected by AF fluctuations (so called hot quasiparticles as opposed to cold quasiparticles which are not strongly affected by AF fluctuations), forming a pseudogap above $T_c$. Superconductivity occurs when the cold quasiparticles form a gap [53]. An important prediction of the model is the d-wave symmetry of the order parameter.
1.2 Scope of the dissertation.

Early femtosecond pump-probe experiments performed on high temperature superconductors [66, 67, 68] have shown that the amplitude and relaxation time of the photoinduced reflectivity (or transmission) transient is strongly affected by the appearance of the superconducting gap in the single particle density of states. Later, similar experiments showed that there is also some long-lived nanosecond dynamics strongly affected by the closure of the superconducting gap [69]. The effect was attributed to the presence of localized states in the vicinity of the Fermi surface, suggesting that in HTSC two types of carriers coexist, both being responsible for the occurrence of superconductivity at high temperatures. Moreover, the preliminary pump-probe measurements on underdoped HTSC [70] showed no anomalies at $T_c$ in the relaxation time and amplitude of the fast transient, suggesting the presence of the gap in the density of states well above $T_c$.

To determine the temperature and doping dependence of the energy gap(-s) in such a multi-component system from frequency-domain spectroscopy means extracting gap information by deconvolution of all the different spectral components. This inevitably leads to ambiguity in the interpretation of the data, as highlighted by the numerous controversies regarding the interpretation of infrared, Raman and photoemission spectra amongst others. As an experimental alternative, time-domain spectroscopy (TDS) can distinguish between different excitations by their different relaxation dynamics, potentially giving new and complementary information on the low energy electronic structure.

In chapter 2 we present the experimental technique, describe the experimental set-up used in our laboratory, and show how time-resolved data was analyzed in the following chapters. The last section of the chapter 2 is devoted to bolometric effects present when performing pump-probe experiments.

In chapter 3, we give a brief introduction to the theoretical understanding of the photoexcitation and relaxation processes, focusing on the early work on metals, conventional superconductors and some aspects of semiconductor studies. In section 3.3 we summarize the experimental results using femtosecond pump-probe technique on HTSC that were published prior to this study. Several models were proposed to account for the observed effects, however none could account for a vast amount of data that has been provided over the last decade. Systematic investigation of HTSC and related compounds as a function of temperature, probe frequency, and especially as a function of doping, have provided enough data to construct models (Kabanov, Refs. [71] and [72]) that could successfully explain the results obtained on various materials exhibiting a gap in the low energy density of states. In sections 3.4 and 3.5 we present the two models focusing on the fast picosecond (ps) dynamics and slow nanosecond (ns) dynamics respectively, and make a comparisons with the published data.
In chapter 4 the data on high $T_c$ superconductor $\text{Ca}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ over a wide range of doping is presented. We have analyzed the data using the adopted theoretical models. It enabled us to obtain important information about the gap evolution in HTSC. The implications of the results are discussed and compared to the data obtained by other spectroscopic techniques.

The main feature of the adopted theoretical models is that the photoexcited carrier dynamics is completely governed by the temperature dependence and magnitude of the gap. It is quite general and can be applied also to other gapped materials. Therefore, in chapter 5, we present data taken on the quasi one-dimensional charge density wave semiconductor $\text{K}_{0.3}\text{MoO}_3$, in which the temperature evolution of the low energy gap has been extensively studied over the years and is generally accepted. The data were found to be consistent with the theoretical predictions of the model, and in addition several new features have emerged, completing the picture we adopted for HTSC.
Chapter 2

Experimental.

In this chapter we first focus on the experimental technique [73], details about the light sources used in our laboratory and detection of small changes in optical properties. We describe the method of analyzing the time-resolved optical data used in the following chapters and discuss laser heating effects that should be taken into consideration when performing the data analysis. In section 2.2 we present some details on preparation and sample characterization of a high-\(T_c\) superconductor CaYBCO, on which most of the experiments were performed. Details about quasi 1D CDW semiconductor \(K_{0.3}\)MoO\(_3\) are given in chapter 5.

2.1 Femtosecond time-resolved optical spectroscopy: Experimental.

Time resolved optical spectroscopy involves measurement of a transient change of the optical transmission \(T\) or reflectivity \(R\) of a thin film or a single crystal. The technique is usually referred to as a "pump-probe" technique, and as the name suggests it is a two step process. In the first step the material under investigation is excited by an ultrashort laser pulse and in the second the differential reflectivity or transmission \((\Delta R/R\) or \(\Delta T/T\)) of the second probe optical pulse is measured as a function of time delay after the pump pulse. A typical experimental setup is shown schematically in Figure 2.1. A mode-locked laser is used to generate light pulses with the pulselength \(\tau_p\) ranging from 10-200 fs.

Typical values of the pump pulse energies that we use are in the range of 0.1-5 nJ. In these experiments, where 0.1 nJ pulses are focused on \(~60\) \(\mu\)m diameter spot (fluence of the order of 2\(\mu\)J/cm\(^2\)), the perturbation caused by the photoexcited carriers can be assumed to be small. When the material under investigation is a metal, the criterion for small perturbation corresponds to a small increase of the electronic temperature after photoexcitation, \(\Delta T_e\), compared to equilibrium temperature. In the case of superconductors or other materials exhibiting a gap \(2\Delta\) in the low energy excitation spectrum, the criterion for small perturbation is the ratio of the
photoexcited carrier density (roughly the absorbed energy per unit cell divided by the gap energy - discussed in section 3.4.1) to the characteristic quasiparticle density $2N(0)\Delta$, where $N(0)$ is the density of states at Fermi energy. In our experiments this ratio is typically $10^{-4} - 10^{-3}$ [71]. Other laser systems were also used in the past [74, 75], such as the colliding pulse modelocked (CPM) dye laser and amplified lasers. In these experiments pump pulse energies may be up to three orders of magnitude higher (as high as several $\mu$J giving fluences in mJ/cm$^2$).

![Photoinduced transmission setup](image)

Figure 2.1: A typical time-resolved photoinduced transmission setup. A similar setup is also used for measuring the photoinduced reflectivity, except that the reflected probe beam is detected in that case.

The probe beam, which is usually (but not always) at the same wavelength as the pump beam, is suitably delayed in time in a Michelson interferometer and significantly attenuated, typically by a factor of 100. Usually the additional photoexcitation by the probe beam can be neglected.

The changes $\Delta R/R$ or $\Delta T/T$ are small ($10^{-6}$-$10^{-4}$ in low photoexcitation experiments and correspondingly higher at high photoexcitations - up to $10^{-2}$), so high-frequency lock-in detection at $\nu \sim 100$ kHz or more is usually used to reduce laser noise [76]. It is most often sufficient to modulate only the pump beam and detect the probe light with a lock-in detector; still dual modulation techniques are sometimes necessary when bad surface quality of the sample prevents pump scattered light from being sufficiently rejected.
2.1.1 The 50 fs laser system.

The essential component of the femtosecond time-resolved optical system is a stable source of femtosecond laser pulses. In this section we discuss the basic principles of the Ti:sapphire mode-locked laser used in our experiments, and briefly describe the autocorrelation method for measuring the pulse length. It is however, beyond the scope of this work to give an extensive description of the details, therefore for a detailed treatment we refer to the vast number of books and references on this subject [77].

In the experiments performed in our laboratory we used two Ti:sapphire laser systems. At the time when no commercial femtosecond Ti:sapphire laser was available we used a home constructed one. It was an Ar-ion pumped Ti:sapphire, which used saturable absorber to stabilize modelocking; in detail it is described elsewhere [78]. This section only briefly describes our new Ti:sapphire oscillator (Mira Seed by Coherent) where pulsed operation is achieved by Kerr-lens modelocking [77].

Mira-Seed Oscillator.

A schematic of the laser used in this investigation in presented in Figure 2.2. The Ti:sapphire crystal is pumped through the focusing lens L1 by 8 W multi-line Ar-ion laser TEM$_{00}$ beam.

![Figure 2.2: A schematic of the Ti:sapphire laser used in our experiments. Code: M1-M9: mirrors, BP1,BP2: Brewster prisms, BRF: birefringent filter, L: focusing lens. The auxiliary cavity is shown with a dashed line.](image-url)

The dashed line represents the auxiliary cavity that is used only during initial alignment [79], whereas the solid line represents the main cavity. Once Mira-Seed lases in continuous wave (CW) mode, the prism BP1 is repositioned into the beam path for the pulsed (modelocked) operation.

The cavity consists of several parts, each having a specific role needed for pulsed operation. Starting at the end high reflector mirror M7 there is a folded two prism
element with the negative group velocity dispersion (GVD) consisted of Brewster prisms BP1, BP2 and mirror M6. In the case no birefringent filter (BRF) is in the cavity one can adjust the bandwidth from 30-50 nm by moving BP2. However, when tunable frequency from 780-840 nm is desired, the BRF is placed in the cavity and the operation is stable when the bandwidth is approximately 30 nm.

The rotation of BRF affects the pulsewidth and the spectral width, since by adjusting the operating wavelength one changes the position where the center of the beam strikes the BP2 and subsequently the overall GVD. In order to maintain the same bandwidth as the wavelength is changed the prism should be translated to "follow" the beam.

The central part of the laser is the Ti:sapphire crystal, mounted in a water cooled copper block and placed between the two focusing mirrors M4 and M5. The mirror M3 reflects the beam through the reflective starter to the mirror M2 and from there, through the BRF and the slit to the output coupler. At the output there is an additional beam splitter reflecting small amount of the beam to a silicon diode detector. The fast silicon diode is used for monitoring the pulsed/CW operation.

Measuring ultrafast laser pulses.

Ultrafast laser pulses are usually characterized by two sets of measurements: first, in the frequency domain; and in the time domain. For relatively simple pulse shapes (Gaussian temporal profile) the optical peak wavelength $\lambda_M$ and the bandwidth $\Delta \lambda$ ($\Delta \lambda = \text{FWHM}$ - full width at half maximum) are sufficient to give a description of the optical spectrum. The two together with the pulsewidth $\tau_p$ give the complete pulse description.

The measurement of the optical spectrum for sub-100 fs laser pulses which extends over 10’s of nm around 800 nm is easily carried out with an optical spectrum analyzer. It is usually based on a grating and a photodiode array.

Since the pulses are in a femtosecond range, they are clearly beyond the speed of standard electronics. Therefore the most common procedure to measure the pulsewidth is an autocorrelator.

Schematic of the autocorrelator used in our laboratory is shown in Figure 2.3. The autocorrelator is basically the Michelson interferometer with a frequency doubling crystal (BBO—BaB$_2$O$_4$) inserted to facilitate measuring the intensity correlation function of the incident pulses. The incoming laser pulse at the center frequency $\omega$ is split in two legs of the Michelson interferometer by a 50/50 beamsplitter. Subsequently, the two pulses are crossed in BBO by using the lens. We delay one pulse with respect to the other by changing the position of one of the retroreflectors mounted on a mechanical shaker. Crystal is oriented in a way to fulfill the phase matching condition

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1 In order to start Kerr lens mode-locking high power fluctuations need to be induced in the cavity. This is done by periodically changing the cavity length with the reflective starter [see Ref. [79]].

2 An aperture (slit) is placed in the cavity to induce losses in the CW operation. It does not affect the pulsed operation, since its beam diameter is narrower due to Kerr-lensing [77].
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Figure 2.3: A schematic of the autocorrelator used to measure sub-ps pulselengths. Code: RR1,RR2: roof-top retroreflectors; BS: 50/50 beamsplitter; L: focusing lens; BBO: BaB\(_2\)O\(_4\) crystal used for second harmonic generation (SHG); F: filter used to eliminate component at \(\omega\); S: an additional slit to block the light at \(2\omega\) generated individually by each of the beams crossed in BBO; PMT: photo-multiplier tube; OSC: oscilloscope; SH: mechanical shaker.

[80] for second harmonic generation. The intensity of the light at \(2\omega\) is proportional to the autocorrelation function of the pulse intensity \(I_{2\omega}(\tau) \propto \int I_\omega(t+\tau)I_\omega(t)\,dt\), where \(\tau\) is the time delay between the pulses. The light at \(\omega\) is filtered out by a suitable filter. Although the phase matching condition for generation of light at \(2\omega\) by individual beams is not fulfilled, additional slit is placed in front of the photomultiplier tube (PMT) to reject these contributions to the signal.

By scanning the time delay \(\tau\) with mechanical shaker and measuring the current generated by PMT using an oscilloscope one obtains the autocorrelation function. The FWHM of the autocorrelation function \(\tau_{AC}\), calibrated with known change of length in one of the arms of the Michelson interferometer, is wider than the pulselength. To determine the actual pulselength, however, one needs additional information about the shape of the original pulse. We usually assume the Gaussian shape where \(\tau_{AC} = \sqrt{2}\tau_p\).

Practical considerations.

The controls frequently used during daily operation are accessible with the laser cover in place. These are controls of the pump beam, high reflector M7, Brewster prism BP2 position, birefringent plate BRF angle and the position and the width of the hard aperture (slit).

The laser being installed the daily turn-on operation follows. After turning on the system - i.e. the Ar-ion laser and the cooling water for the Ti:sapphire crystal - it is necessary to wait for about 30 minutes for the system to thermalize. Afterwards the
Chapter 2. Experimental.

CW output power should be optimized by means of adjusting the overlap between the pump beam and CW Ti:sapphire mode using the pump beam controls and high reflector M7. In CW operation the slit should be fully open; the average power achieved by optimization is approximately 1 W at 800 nm with the birefringent plate in the cavity. To start modelocking you turn on the galvanometer of the reflective starter and then gradually decrease the slit width while monitoring the signal from the fast silicon detector on the scope. The modelocking starts when the slit width is narrowed so much that the average output power drops to approximately 600 mW. After that, it is necessary to turn off the galvanometer and optimize the pulse stability and the length by adjusting the slit and pump beam position while monitoring the output from the diode and measuring autocorrelation trace. The pulsewidth at the output is approximately 90-100 fs, and since the pulses are chirped (chirp – variation of the instantaneous frequency with time), additional external element with negative GVD can be used to compress them down to 20 fs. Since the beam passes through several optical elements before hitting the sample, the pulse is broadened due to positive dispersion in the glass, $\frac{\partial^2 k(\omega)}{\partial \omega^2} > 0$. Therefore we pre-chirp the pulses to compensate positive dispersion in the glass to achieve approximately 50-60 fs pulses on the sample.

The laser in air-conditioned laboratory, after initial setup does not need any further adjustments during the day. Yet, the main problem we deal with is dust. On pump optics it modifies the pump wavefront, while dust on other optics within the cavity it disturbs the wavefront and affects the self-modulation in the Ti:sapphire crystal. Therefore the laser optics should be cleaned after every 10-14 days of operation.

2.1.2 Lock-in detection.

Since in our experiment the measured changes in optical constants are of the order of $10^{-5}$ the lock-in detection should be used to extract the data from laser noise. The power spectrum of laser intensity noise is known to be of 1/f type, where f stands for frequency. Noise amplitude in audio range is quite high but is negligible at frequencies above 100 kHz.

A general approach to eliminate noise is to modulate a signal at a frequency where noise is low and use a narrow band amplifier whose maximum gain frequency is equal to the modulation frequency. Such a narrow-band amplifier is called lock-in amplifier [81]; now the commercial lock-in amplifiers operate at modulating frequencies more than 1 MHz which is good enough to successfully eliminate the laser noise.

In present experiment we modulate the pump laser beam at modulation frequency $\omega_M \sim 200$ kHz using an acusto-optic modulator [76]. The reflected (or transmitted) probe beam is detected by means of a photodiode [82] and the signal is fed to the lock-in amplifier [83], which is phase locked to the acusto-optic modulator. Lock-in amplifier discards all signals which are not at exactly the same frequency $\omega_M$ and
in-phase with the modulation. Therefore it detects modulations in the received \textit{probe} intensity caused by the \textit{pump} beam only. By changing the time constant of the phase detector $\tau_l$, you determine the effective width of the frequency interval of the signal — the longer is the time constant the narrower is the frequency width and consequently the lower is the noise. Typical time constant used in this experiment is $\tau_l = 1$ s, therefore the effective frequency width of the amplifier is approximately 1 Hz in the frequency region where laser noise is negligible. This enables us to measure the relative changes in reflectivity or transmissivity of the order of $10^{-6}$. It should be noted that the signal is being normalized with respect to the DC signal amplitude on the photodiode at every data-point to discard the errors due to long-term fluctuation of the \textit{probe} beam intensity.

Another important feature of the technique is the output of the lock-in amplifier. It consists of two signals. The usually discussed one is in phase with the modulation $\omega_M$ and gives the time-resolved signal together with the photoinduced offset due to some long lived contribution to photoinduced signal with the typical time-scale from nanoseconds to microseconds (discussed in section 2.1.4). The second signal gives the photoinduced signal that is out-of-phase with the modulation. This signal picks up all the dynamics that cannot follow the modulation — with timescales of the order of 10 $\mu$s (corresponding to 100 kHz modulation). Usually there is no interest in the second signal, since it describes some very slow dynamics that can be measured by means of some other experimental technique. However, slow nanosecond to microsecond dynamics will be discussed in this work, therefore we should note that any T-dependent dynamics on this timescale should be observed as a temperature dependent effect in addition to T-independent offset.

### 2.1.3 Experimental Setup.

A schematic diagram of the setup used in the experiments discussed in the following chapters is given in Figure 2.4. As presented above, we use the Mira Seed Ti:sapphire oscillator which produces 90-100 fs pulses with a repetition rate of 88 MHz (Separation between two adjacent pulses is 12.8 ns.). The pump beam is modulated by an acousto-optic modulator (AOM), with 100% modulation. Since AOM consists of two-inch high dispersive flint glass, the pulses significantly broaden. Therefore we pre-chirp the pulses by means of a folded two prism setup with negative GVD in order to achieve the shortest pulsewidth at the sample. The mirror M1 is slightly tilted to change the height of the reflected beam to hit the mirror M2 which reflects the beam on the beamsplitter BS1. The BS1 is actually a glass plate reflecting 4 % of light in the \textit{probe} channel, whereas the majority of light is transmitted and serves as the \textit{pump}. In the \textit{pump} as well as in the \textit{probe} beam paths there are several additional optical elements placed before the 150 mm lens L1 used to focus the beams on the same spot of the sample. In both channels the Soleil-Babinet polarization rotators are used to measure the polarization dependence of the photoinduced signals. The
acousto-optic modulator is used to modulate the pump beam, while in order to get
the same pulsewidth in the probe channel we use the same material as used in AOM
to compensate the pre-chirp. To measure the intensity of the transmitted (reflected)
light we use a photodiode. In order to reject the scattered light from the pump beam
we place a pinhole in front of it. Since all the experiments are performed with the
pump and probe polarizations crossed, we use an additional cube polarizer to reject
the scattered light from the pump beam. A CCD camera is used to monitor the
beams overlap on the sample. The overlap is adjusted by the mirror M3.

The sample is glued with G.E. varnish (Oxford Instruments) on the sample holder,
which is mounted on a cold finger of the helium flow optical cryostat \[84\]. In this
cryostat temperatures from 4-350 K can be achieved in vacuum of less than \(10^{-6}\)
mbar (at room temperature). The temperature sensor (RhFe) is placed on the cold
finger. It was calibrated using additional sensor attached at the place of the sample
on sample holder.
2.1. Femtosecond time-resolved optical spectroscopy: Experimental.

The retroreflector RR2 is mounted on the linear positioner driven with a DC-motor with 0.06 μm resolution. The temporal resolution of our setup is therefore limited by the pulsewidth of the laser and is approximately 50-60 fs.

2.1.4 Data Analysis.

A typical time-resolved photoinduced transmission signal on near optimally doped YBa$_2$Cu$_3$O$_{7-δ}$ (YBCO) in the range from -6 ps to 13 ps (open squares) is presented in Figure 2.5. The signal is zero when the pump beam is blocked (A), however there is a non-zero long lived component present even at 12 ns after the pump pulse, seen as a signal at negative time delays, when the pump is unblocked (B). Besides the very slow component there is also a fast transient present, with a rise time of approximately 300 fs and a decay time of approximately 2 ps.

![Figure 2.5](image)

**Figure 2.5:** The time-resolved photoinduced opacity taken at the cryostat temperature 80 K on near optimally doped YBa$_2$Cu$_3$O$_{7-δ}$ with $T_c = 90$ K (solid squares). Also there is the fit (solid line) using a sum of the slow (dotted line) and fast (dashed line) component, with the effective rise time $\tau \sim 300$ fs.

In these experiments usually the temperature dependence of the photoinduced transmission (of reflectivity) is measured. The data is analyzed in terms of amplitudes and relaxation times of the signals. The fast component amplitude is indicated approximately by the difference between points C and D. On the other hand, the magnitude of the slow component due to single pump pulse cannot be directly measured since it does not relax in 12.8 ns - the separation between two successive pump pulses - resulting in the signal pile-up. The pile-up amplitude is indicated
by the difference between signal values in points B and A respectively. In the data analysis performed in the following chapters the difference between signal values D and B is taken as a magnitude of the single pump pulse contribution to the slow component, and the difference between signal values B and A as a pile-up of the slow component.

Since the timescale of the slow component $\tau_L \gg 10$ ns it can be considered as a constant in the range of several 10 ps after photoexcitation and fitted by the step function with finite rise-time. The fast component, on the other hand, was found to be reasonably well reproduced by a single exponential decay with a characteristic relaxation time in the range of 0.5 - 5 ps depending on the doping and temperature [71, 66, 68, 85]. The fit used in Figure 2.5 is therefore a sum of the two (fast and slow) components.

In the case of single exponential decay the fast component in the photoinduced change of transmission is a solution of

$$\frac{\partial A(t)}{\partial t} = -\frac{A(t)}{\tau_R} + g(t) ; \quad A(t) \equiv \Delta T(t)/T, \quad (2.1)$$

with $\tau_R$ being the relaxation time and $g(t) = B \exp(2t^2/\tau_p^2)$ representing the photoexcitation with Gaussian pump pulse with pulsewidth $\tau_p$. Since the probe pulse also has a finite pulsewidth, the measured $\tilde{A}(t)$ is a convolution of $A(t)$ with $g(t)$. However, since this affects the rise time of the signal only, $\tilde{A}(t)$ can be approximated with the solution of the Eq.(2.1) with the effective rise-time $\sigma$

$$\tilde{A}(t) \approx A e^{-\frac{t}{\tau_R}} \left[ 1 - \text{erf}\left( \frac{-4t\tau_R + \sigma^2}{2\sqrt{2}\sigma\tau_R} \right) \right]. \quad (2.2)$$

Here $A$ is the amplitude of the transient with relaxation time $\tau_R$ and $\text{erf}(x) = \int_0^x \exp(-t^2)dt$. In the case when the photoinduced signal follows photoexcitation instantly, the effective rise-time would be $\sigma \approx \sqrt{2}\tau_p$. However, if there is an additional relaxation process after photoexcitation leading to photoinduced transmission change, $\sigma$ increases.

As can be seen in Figure 2.5, the signal can be reproduced quite well using the sum of a step function and a single exponential decay both with a rise-time of $\sim 0.3$ ps. It should be noted here that most of experiments are performed with the pump and probe polarizations crossed; otherwise additional terms can contribute to the signal close to zero time delay. These terms, usually called as "coherent artifacts" [86], arise from coherent interactions between the pump and the probe beam. Physically, the interference between the pump and probe beam creates a grating in the sample which can diffract light from the pump into the probe beam or vice versa, thus contributing to the signal. Since all our measurements described in the thesis were done in crossed polarization these effects will not be further discussed.

\[ ^3 \text{From now on calligraphic letters (e.g. } \mathcal{A}, \mathcal{B} \text{) are used for amplitudes of the photoinduced signals. Usually } T \text{ is used for transmission and } R \text{ for reflectivity amplitude.} \]
2.1.5 Heating Effects.

Laser heating of the sample\(^4\) is an important problem in these experiments and has often been discussed in the literature [73, 87, 88, 89, 90]. When trying to evaluate heating effects one should first consider the processes and typical timescales in question [91]. The energy relaxation of photoexcited carriers in metals is theoretically [92] and experimentally [93] well understood and will be described in detail in section 3.1.2. Here we just summarize the results.

The photoexcitation of electron-hole pairs via an interband transition is followed by electron-electron (e-e) thermalization which takes place within femtoseconds, whereas the electronic energy relaxation is determined by electron-phonon relaxation processes. The electron-phonon (e-ph) relaxation time was calculated by Allen [92] to be \(\tau_{e-ph} = \frac{T_e}{3\lambda(\omega^2)}\), where \(T_e\) is the carrier temperature after photoexcitation and initial e-e thermalization, \(\lambda\) the electron-phonon coupling constant and \(\omega\) the phonon frequency. For photoexcitation intensities used in our experiments \(\tau_{e-ph}\) was estimated to be less than 40 fs in YBa\(_2\)Cu\(_3\)O\(_{7-x}\) meaning that in 100 fs or so after the photoexcitation the electronic and phononic systems in the illuminated spot can be described by the same, somewhat elevated temperature with respect to the rest of the sample. Further relaxation is determined by heat diffusion out of the illuminated spot. Temporal evolution of the temperature increase due to absorption of the laser pulse has typical \(1/\sqrt{t}\) decay [88]. Since the temperature increase does not completely relax by the time next pump pulse is absorbed (\(\sim 12\) ns) this results in the temperature increase pile-up. Therefore the probed volume temperature is higher than the bulk one (temperature of the cold finger). Since the magnitude is the same as if it was the result of the heating induced by CW laser we talk about steady-state heating. Of course each pulse separately induces also some time-dependent temperature increase. In this case we talk about transient heating. The two effects have to be estimated separately. In our experimental configuration (using helium flow optical cryostat [84]) as we shall see the steady-state temperature increase due to "temperature increase pile-up" is far more pronounced.

Steady-state heating.

We can model the steady-state heating due to the pump laser beam considering the heating by the CW laser of the same average fluence. Since the thickness of the substrate or single crystal (\(\sim 0.3\) mm) is typically much larger than the absorption length (\(\sim 80\) nm) the temperature rise can be calculated using a simple steady-state heat diffusion model, where the Gaussian laser beam with the average laser power \(P_L\) is focused into a spot of the diameter \(d\) (the Gaussian beam waist) on the semi-infinite solid with reflectivity \(R\), absorption coefficient \(\alpha\), specific heat \(c\), density \(\rho_s\) and thermal conductivities \(\kappa_x\), \(\kappa_y\), \(\kappa_z\). With \(z = 0\) on the surface, and the center of

\(^4\) The increase in temperature refers to the increase of the lattice temperature unless stated otherwise.
the Gaussian beam being chosen as the origin of the coordinate system the boundary condition is that the temperature at \( z = \infty \) is equal to the temperature of the cold finger. Since we deal with temperature rises of the order of 5 K and the bulk temperatures \( > 20 \) \( \text{K} \), we can usually neglect the energy loss due to thermal radiation. Using this model we obtain the expression\(^5\) for the temperature rise

\[
\Delta T(x, y, z) = \frac{\alpha (1 - R)}{2\pi^2 d^2 k_x k_y k_z} \int_0^{2\pi} \int_0^{\infty} \rho \, d\rho \, d\phi \, e^{-\frac{1}{d} \left( \frac{\sqrt{k_x^2 + k_y^2} \cos \phi}{k_x} \right)^2 - \left( \frac{\sqrt{k_x^2 + k_y^2} \sin \phi}{k_y} \right)^2} \times \left[ e^{\frac{k_z}{2} \int_0^\infty e^{-\alpha z} \frac{1}{\sqrt{\rho^2 + z^2}} \, d\rho} + e^{-\alpha z} \int_{-\infty}^\infty e^{-\frac{k_z}{2} \int_0^\infty} \frac{1}{\sqrt{\rho^2 + z^2}} \, d\rho} \right],
\]

(2.3)

where \( k_x = \sqrt{\kappa_x \kappa_z} / P_0 \), \( k_y = \sqrt{\kappa_x \kappa_z} / P_0 \) and \( k_z = \sqrt{\kappa_x \kappa_z} / P_0 \). For \( \text{YBa}_2\text{Cu}_3\text{O}_7-\delta \) single crystals at 80K using \( \alpha = 0.018 \) \( \times 10^9 \) \( \text{m}^{-1} \) [94], \( \kappa_x = \kappa_y = 8 \) W/mK, \( \kappa_z = 2 \) W/mK [95], \( R \sim 0.1 \), \( d \sim 60 \mu\text{m}^6 \) and \( P_L = 10 \) mW the temperature increase \( \Delta T(0, 0, 0) \sim 17 \) K is obtained. In the case of experiments on thin films the heat flow is determined by thermal properties of the substrate, since the film thickness is negligible in comparison with the substrate thickness. Therefore, using the value \( \kappa_x,\kappa_y,\kappa_z \sim 18 \) W/mK for \( \text{SrTiO}_3 \) at 80 K [96] we get \( \Delta T(0, 0, 0) = 3.8 \) K at \( P_L = 10 \) mW.

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\(^5\) The derivation of the formula is presented in Appendix A.

\(^6\) \( d \) can be calculated using the formula for Gaussian beam optics \( d = \frac{\lambda f}{\pi w_0^2} \), where \( f = 15 \) cm is the focal length of the focusing lens, \( \lambda = 800 \) nm and \( w_0 \) is the beam diameter before the lens.
Since temperature within the illuminated spot is non-uniform we are interested in the effective temperature increase, $\Delta T_{\text{eff}}$, namely the average temperature increase sensed by the probe beam. We use numerical integration to solve Eq.(2.3). As expected the temperature variation in the $z$ direction is negligible in the optical skin depth ($\sim 100$ nm), whereas the radial variation is shown in Figure 2.6, compared to the spatial profile of the incoming pump beam. We get the effective temperature rise and its uncertainty (spread of temperatures within probed volume) by integrating

$$\Delta T_{\text{eff}} = \frac{1}{K} \int_{0}^{\infty} \Delta T(r) I(r) r dr$$

and

$$\sigma_{\Delta T_{\text{eff}}}^2 = \frac{1}{K} \int_{0}^{\infty} (\Delta T(r) - \Delta T_{\text{eff}})^2 I(r) r dr .$$

Here $K = \int_{0}^{\infty} I(r) r dr$ and $I(r) \propto \exp(-2r^2/d^2)$ is the spatial profile of the pump beam. For YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals at 80K we get $\Delta T_{\text{eff}} \sim 12K$ and $\sigma_{\Delta T_{\text{eff}}} \sim 4K$ at 10 mW pump power, whereas in thin film $\Delta T_{\text{eff}} \sim 2.7K$ at 10 mW pump power with the $\sigma_{\Delta T_{\text{eff}}}$ far less pronounced. The facts mentioned above are the reason that the pump intensity in all the experiments performed on single crystals was kept below 10 mW (usually $\sim 5$ mW). In high intensity experiments additional optics should be used to increase the pump beam waist in order to decrease $\sigma_{T_{\text{eff}}}$.

Figure 2.7: Experimental determination of $\Delta T_{\text{eff}}$ at temperature close to $T_c$ by measuring $R(T)$ of the illuminated microbridge compared to the non-illuminated one. At $P_L = 40$ mW, $d = 50$ $\mu$m one obtains $\Delta T_{\text{eff}}(80K) \sim 12$ K, which is consistent with the calculated result using Eq.(2.3) giving $\Delta T_{\text{eff}}(80K) \sim 11$ K.
Experimentally CW heating can also be measured and accounted for quite accurately and in agreement with the model. On thin film samples the effect of the laser heating can be measured with a four-point probe resistivity measurement of a thin microbridge made of the same superconductor film. Using this method, the increase in temperature close to \( T_c \) can be determined very accurately as can be seen in Figure 2.7.

![Figure 2.8: The T-dependence of the fast component amplitude in photoinduced transmission \( T \) for a sample with \( T_c = 89K \) using three different laser intensities. The data has been normalized with respect to the laser fluence \( \Phi \). The insert shows low temperature \( T \) vs. \( \Phi \), where \( T \) scales linearly with \( \Phi \) and \( \Phi_0 = 5.5 \times 10^{13} \) photons/cm\(^2\)/pulse.](image)

Although this method works very well with thin films, it is not applicable to single crystals. However, since the temperature dependence of the fast component in near optimally doped superconductors is strongly temperature dependent as shown in Figure 2.8, and it was experimentally shown [71] that the amplitude at low photoexcitation densities is linearly dependent on the pump fluence, one can determine \( \Delta T_{eff} \) quite accurately by ”scaling” the temperature dependence of the fast component amplitude of the photoinduced transmission \( T \) (by normalizing the signal amplitude to the pump fluence and by adjusting the temperature scale due to heating).

In Figure 2.8 we show the temperature dependence of the photoinduced transmission amplitude taken on the same thin film as used in Figure 2.7 at three different laser fluences. \( \Delta T_{eff} = 14 \) K was determined at \( P_L = 40 \) mW, again comparable with the modelled temperature rise. When conducting the same analysis on single crystals

\(^{7}\) The long-lived signal is also strongly \( T \)-dependant near \( T_c \). If the intensity dependence was known, similar analysis could be performed by ”scaling” the long-lived amplitude.
using the temperature dependence of photoinduced reflectivity amplitude we get the result $\Delta T_{eff} = 14 - 20K$ at $P_L = 10 \text{ mW}$, depending on doping [97].

Using one of the above experimental methods together with the model temperature of the sample to within $\pm 3K$ in the temperature range 4 - 300K can be determined. It is important to note that as the thermal constants are different for different superconductors (and substrates), and so different experimental configurations can give rise to heating effects which vary by more than one order of magnitude.

In Table 2.1 we summarize the calculated values of temperature raises for various materials and substrates used in our experiments, compared to the experimentally determined using one of the above mentioned methods.

<table>
<thead>
<tr>
<th>material</th>
<th>$\rho_s$ [kg/m$^3$]</th>
<th>$c$ [J/kgK]</th>
<th>$\kappa_{a,b,c}$ [W/mK]</th>
<th>$\Delta T_{cw}$ [K]</th>
<th>$\Delta T_p$ [K]</th>
<th>$\Delta T_{exp}$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaYBCO</td>
<td>6400</td>
<td>170$^a$</td>
<td>8;8;2$^b$</td>
<td>12</td>
<td>0.18</td>
<td>14</td>
</tr>
<tr>
<td>SrTiO</td>
<td>5110</td>
<td>220$^c$</td>
<td>16$^d$</td>
<td>3</td>
<td>0.15</td>
<td>3.5</td>
</tr>
<tr>
<td>MgO</td>
<td>860</td>
<td>115$^e$</td>
<td>450$^f$</td>
<td>0.1</td>
<td>1.13</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Hg-1223</td>
<td>7090</td>
<td>280$^g$</td>
<td>5$^h$</td>
<td>9.5</td>
<td>0.08</td>
<td>12</td>
</tr>
<tr>
<td>K$_{0.3}$MoO$_3$</td>
<td>4185</td>
<td>480$^i$</td>
<td>7;2;7;0.6$^j$</td>
<td>15.5</td>
<td>0.08</td>
<td>17</td>
</tr>
<tr>
<td>1T-TaS$_2$</td>
<td>5940</td>
<td>260$^k$</td>
<td>5$^l$</td>
<td>9.5</td>
<td>0.11</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 2.1: Calculated values of the temperature increase due to pulsed laser excitation compared to the experimentally determined ones in Ca$_{x}$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ (CaYBCO), SrTiO$_3$, MgO, HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ (Hg-1223), K$_{0.3}$MoO$_3$ and 1T-TaS$_2$. In order to model the temperature increase we used experimentally measured values of specific heat $c$, and thermal conductivities $\kappa_i$ where $a$ and $b$ are parallel to the crystal surface, whereas $c$ is perpendicular (when anisotropy data is available). The densities $\rho_s$, were calculated using published X-ray diffraction data. In all calculations we assumed the average pump laser power to be 10 mW and the pulse length was taken to be 100 fs.

$^a$ at 80 K, from Ref. [98] ; $^b$ at 80 K, from Ref. [95, 97] ; $^c$ at 80 K, from Ref. [96] ; $^d$ at 80 K, from Ref. [99] ; $^e$ at 80 K, from Ref. [100] ; $^f$ at 80 K, from Ref. [101] ; $^g$ at 120 K, from Ref. [102] ; $^h$ at 120 K, from Ref. [103] ; $^i$ at 180 K, from Ref. [104] ; $^j$ at 180 K, from Ref. [105, 106] ; $^k$ at 180 K, from Ref. [107] ; $^l$ at 180 K, from Ref. [108].

It should be mentioned that the modelling is based on the assumption that the thermal contact between the sample and cold finger is good. In our experiments, we attach the samples on the cold finger made of copper using G.E. varnish (Oxford Instruments) - known for its high thermal conductivity at low temperatures. However, in some cases, when the manipulation with the sample is difficult (for instance due to fragility and extremely small size as in case of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$), the thermal coupling is weak. In this case the crystal as a whole heats up and the effective temperature can be much higher than calculated. The effect of this overall heating can be experimentally observed when measuring the signal equilibration on the
lock-in detector after applying the pump beam to the sample. If there is weak thermal coupling between the sample and the cold finger the typical timescale of this "thermalization" process is minutes.

**Transient heating.**

The second type of heating effect is transient heating, where temperature builds up during and after the pump laser excitation and then decreases as $1/\sqrt{t}$. This effect can also be calculated accurately using the heat-diffusion model [87, 88] with transient laser pulses including the anisotropy in thermal conductivity (the derivation is given in Appendix A). For our purpose, the transient increase in temperature $\Delta T_{tr}$ can be estimated using simple relation

$$\Delta T_{tr} = \frac{\Delta W}{mc},$$

where $\Delta W$ is the pulse energy, $c$ the specific heat, and $m$ the mass of the illuminated volume. The effect is much less pronounced as *steady-state heating*, giving the peak transient temperature increases of the order of 0.01 - 0.2 K/mW, again depending on the material.

### 2.2 The high-$T_c$ superconductor CaYBCO.

The high-$T_c$ superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ is by far most intensively studied HTSC. It was discovered [109] less than a year after the initial discovery of high temperature superconductivity in La$_{2-x}$Ba$_x$CuO$_{4+\delta}$ [1] and is the first superconductor with critical temperature exceeding the boiling point of nitrogen. Physical properties of this compound can be changed by changing oxygen content over a wide range without any significant changes in structure. Also, a whole class of compounds with similar physical properties can be obtained by substitution of Y with rare-earth ions like La, Dy, Gd... 

YBa$_2$Cu$_3$O$_{7-\delta}$ is observed in two modifications [110], as far as the crystal structure is concerned [Fig. 2.9]). The orthorhombic Pmmm ($D_{4h}^1$) phase is observed at low temperatures $T \leq 500^\circ C$ for oxygen concentrations $\delta \leq 0.6$. The tetragonal P4/mmm ($D_{4h}^2$) phase is observed at higher temperatures, when oxygen content starts to decrease accompanied by disordering in Cu(1)-O(1) layers. In the undoped material YBa$_2$Cu$_3$O$_6$ the O(1) sites are not populated, and the lattice constants $a$ and $b$ are equal [Figure 2.9]. In the orthorhombic YBa$_2$Cu$_3$O$_7$ only O(1) sites are occupied forming the so called Cu-O chains that are besides the two CuO$_2$ planes (oxygen and copper ions in crystallographic positions O(2), O(3) and Cu(2)) the most important parts of YBCO. At intermediate oxygen concentrations the structure strongly depends on the way, how the oxygen is removed. Quenching from high temperature tetragonal phase at $\delta \geq 0.6$ preserves the tetragonal phase with disordered occupancy of O(1) and
2.2. The high-$T_c$ superconductor CaYBCO.

O'(1) positions, whereas if the samples are prepared by low temperature technique the orthorhombic phase can be achieved up to $\delta \geq 0.8$. In this case, several modifications of the orthorhombic phase occur [111].

Changing the oxygen concentration strongly affects the physical properties [see Figure 2.10]. The undoped YBa$_2$Cu$_3$O$_6$ is insulator with optical gap $E_g \approx 1.5$ eV [17], with Cu$^{2+}$ spins in the CuO$_2$ planes exhibiting long range antiferromagnetic order. The maximum Néel temperature is $\sim 420$ K at $\delta = 1$. As the oxygen concentration in the Cu(1)-O(1) layer increases, the charge transfer from the CuO$_2$ planes to the Cu(1)-O(1) chains [112] causes the Néel temperature to decrease. At $\delta \sim 0.6$ the long range antiferromagnetic order vanishes and there is a phase transition from the Fermi glass to a metallic-like phase. The bands crossing the Fermi surface originate from the CuO$_2$ planes and the emerging Cu-O chains [12]. The material undergoes superconducting transition at $T_c$ that increases as we increase the hole concentration in planes. The maximum $T_c = 93$ K at $\delta \sim 0.07$ and this doping level is usually referred to as optimal doping. When $\delta = 0$ YBa$_2$Cu$_3$O$_7$ is slightly overdoped.

Charge transfer from the CuO$_2$ planes in YBCO can also be achieved by chemical doping, e.g. by partial substitution of Y$^{3+}$ with Ca$^{2+}$ [113, 114, 115], again leading to an increase of the hole concentration in the CuO$_2$ planes. In this part of the phase diagram $T_c$ decreases with increasing doping, and we are talking about the overdoped regime. At Ca doping beyond $x \approx 0.2$ the $T_c$ evolution is not plotted in Fig. 2.10, since the evolution strongly depends on the preparation (also at high doping Ca$^{2+}$ starts to replace Ba$^{2+}$ ions as well).

Figure 2.9: The crystal structure of Ca$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$, with different crystallographic positions enumerated in brackets.
Figure 2.10: Schematic phase diagram of Ca$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ (CaYBCO). The Néel temperature evolution is taken from Ref. [116], and the evolution of $T_c$ is taken from Refs. [117, 114]. In underdoped YBCO a pseudo-gap (PG) in low energy density of states has been observed by many experimental techniques with anomalies appearing at temperatures much above $T_c$ (dashed area) depending on the experimental technique and the criterion.

Similar to other HTSC in underdoped YBCO anomalies in measured physical quantities (change of slope in resistivity, non-linear I-V curves in tunneling, changes in Knight shift...) due to changes in low energy density of states appear at temperatures much above $T_c$. The temperature where the anomalies are observed (usually referred to as $T^*$) depends on the experimental technique and the criterion used. Below this temperature (dashed area in Figure 2.10) a pseudo-gap exists in the density of states.

2.2.1 Sample preparation and characterization.

The YBa$_2$Cu$_3$O$_{7-\delta}$ thin films used in our experiments were prepared at the University of Cambridge on SrTiO and MgO substrates using multi-target sputtering [118] and laser ablation techniques [119]. The original films deposited on 0.3-0.6 mm thick substrates of SrTiO and MgO were near-optimally doped with $0 \leq \delta \leq 0.08$ oriented with c-axis perpendicular to the substrate surface. The thicknesses were ranging from 100 to 150 nm. This is approximately one optical absorption lengths in the visible spectrum enabling us to perform transmissivity studies.

In YBCO the oxygen content can be reversibly changed from $0 \leq \delta \leq 1$ [120] by high temperature annealing in partial $O_2$ atmosphere. Therefore, the underdoped
samples with $\delta \geq 0.08$ were prepared by annealing the optimally doped samples [120, 121]. The oxygen concentration depends on the annealing temperature $T_a$, and partial oxygen pressure. In our case the underdoped samples were prepared by annealing in O$_2$ atmosphere. First, the temperature was increased with rate 2K/min, reaching the annealing temperatures ranging from 400 to 800 °C. In the case of thin films the equilibrium oxygen concentration is established within 60 minutes [121]. After 60 min at $T_a$ the samples were quenched (fast cooled) to a copper block or liquid nitrogen. In the later case special care was taken to prevent the condensation of water on the samples and corresponding sample degradation, when taking the samples from liquid nitrogen. Therefore, after quenching, the dewar containing liquid nitrogen was placed in vacuum until all nitrogen evaporated, and the sample thermalized to room temperature. In this way we prepared the samples with $T_c$-s ranging from 48-90 K. We determined the $T_c$-s and corresponding oxygen contents [122] by measuring AC susceptibility [see Figure 2.11 a)].

Figure 2.11: a) Normalized real part of the AC susceptibility measured on several oxygen depleted YBCO thin films. The oxygen content was deduced from determined $T_c$ in accordance with Ref. [120]. b) DC magnetization curves for single crystals, where Ca and O content were determined by EDX.

Single crystals used in our experiments were grown by Thomas Wolf (Institut für Technische Physik, Karlsruhe) using self flux method in Y or Ca stabilized ZrO$_2$ crucibles [123]. The $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ single crystals with $x = 0$, 0.016, 0.101 and 0.132 had $T_c$-s of 93K, 89.5K, 83 K and 75 K respectively, whereas the underdoped sample with $\delta = 0.14$ had $T_c = 86$ K. The Ca-content was determined by EDX (energy-dispersive x-ray spectroscopy) and neutron diffraction analysis. The oxygen content $\delta$ was adjusted by heat treatment and adjustment of oxygen pressure to give
\[ \delta = (0.006 + 0.5 \, x) \] [124]. \( T_c \) was determined by A.A. Martin (Max Planck Institute, Stuttgart) measuring dc magnetization for each sample as shown in Figure 2.11 b).

### 2.3 Summary.

In this chapter we discussed some of the experimental aspects of femtosecond time-resolved optical pump-probe spectroscopy. We presented the experimental setup used in our laboratory and briefly described the Kerr-lens modelocked Ti:sapphire laser and lock-in detection. Then we showed the way how to analyze the data in terms of amplitudes and typical relaxation times. When analyzing temperature dependences of various signals it is important to know the actual temperature of the probed spot on the sample, therefore we estimated the sample heating effects and revealed that in these experiments the steady state heating is far more important than transient heating. In configuration with high intensity laser sources operating at low repetition rates the situation can be reversed.

In section 2.2 we presented some peculiarities of CaYBCO superconductor, focusing on preparation and characterization of samples used in our investigation.
Chapter 3

The Physics of Femtosecond Pump-Probe Spectroscopy.

The art of pump-probe spectroscopy is the ability to identify the physics of the excitation as well as the relaxation processes, and to understand them well enough that meaningful information can be extracted from the data. This requires the support from other experimental techniques and a detailed knowledge of the physics of the system under investigation.

In this chapter we give a historical experimental and theoretical overview on time-resolved pump-probe spectroscopy. Our interest is focused on metals and superconductors but we omit the wide area of ultrafast research in semiconductors [125]. We first direct to investigations of time-resolved thermomodulation studies of metals performed at room temperature and at high photoexcitation intensities [126]; here we introduce the basic concepts of the technique and discuss the typical timescales of the excitation and relaxation processes. Next, we present Allen’s model [92] describing the initial photoexcited carrier relaxation processes in metals in experiments performed at room temperature. The model predicts that the thermal relaxation of electrons in metals is determined by the electron-phonon relaxation time, which is proportional to the average electron-phonon coupling constant $\lambda$, a very important parameter in the theory of superconductivity [2]. The model was experimentally tested with great success on conventional metallic superconductors [93] giving the electron-phonon coupling constants consistent with $\lambda$-s extracted from other experimental techniques. The femtosecond thermomodulation experiments have also been applied to high-T$_c$ superconductors [74, 75] giving the values of $\lambda$ in these materials of the order of 1.

Further, we present the theory for displacive excitation of coherent phonons [127] which was successfully applied to explain the oscillatory components present in some time-resolved data. In section 3.3 we summarize most of the experimental results on high-T$_c$ superconductors which were published prior to this work. In the last two sections we focus on the materials with a small energy gap in the excitation spectrum, and present the adopted theoretical models for the picosecond [71] and nanosecond [72] components in the differential reflectivity of transmission. According
to the model, the dynamics of the induced signals are determined by the magnitude, anisotropy and the temperature dependence of the gap, and are therefore sufficiently general to be applied for investigation of low-energy electronic structure in high-Tc superconductors as well as charge-density wave insulators.

### 3.1 Femtosecond thermomodulation spectroscopy.

The first time-resolved experiments using picosecond and sub-picosecond laser pulses were named femtosecond thermomodulation experiments [126]; since they are considered to be an extension of the conventional thermomodulation spectroscopy. The conventional thermomodulation spectroscopy is a method which was used for band structure investigations in metals. Since in the conventional optical reflectivity or transmission experiments performed on metals interband transitions are usually masked by free electrons up to the plasma energies - (4-10 eV [128]), modulation spectroscopy is ideal for studying the band structure of metals. Thermomodulation spectroscopy involves periodically perturbing the sample’s temperature and measuring the changes in the optical absorption spectrum occurring in synchronism with the perturbation. Since only the changes in optical spectrum are measured, the modulation spectroscopy is very sensitive to the critical points in band structure, i.e. presence of the narrow bands below $E_F$ giving rise to large joint density of states (JDOS).

The change in temperature modifies the reflectivity of the metal in several ways:

- Firstly, the increase of temperature causes a slight broadening of the occupation of states near the Fermi energy (the Fermi level smearing), thereby blocking some states and opening others for optical transition. This changes the sample’s absorption, which can be sensed as a change in transmission or reflectivity. This purely electronic effect is usually the most pronounced, especially in femtosecond measurements since the electron dynamics is the only one on the fs timescale.

- Secondly, the temperature change causes strain in the sample due to thermal expansion. Since the band structure is determined by the lattice, strain causes the bands to shift in energy therefore influencing optical transitions involving these bands. The rise-time of this effect depends on the electron-phonon coupling, but usually it is of the order of 100 fs. Because this is a lattice effect, determined by the phonon escape time, the relaxation timescale is typically of the order of $\gg 10$ ps. Therefore ns dynamics in time-resolved experiments is usually attributed to lattice heating effects.

- Due to the change in temperature the phonon population increases, causing broadening of the reflectivity linewidths as a result of increased scattering. This
effect is believed to be negligible as most of these experiments are performed at room temperature, where the phonon population is already large.

In the case of femtosecond thermomodulation experiments on metals with narrow d-bands photoexcited with sub-picosecond laser pulses, most often only fast picosecond transient changes in reflectivity are analyzed. Therefore only the Fermi level smearing effect on sample’s optical properties is considered.

3.1.1 Photoexcitation and initial thermalization.

As shown in Fig. 3.1 the high intensity pump pulse excites electrons from occupied to unoccupied states. This is followed by initial electron-electron thermalization. The electron-electron thermalization time \( \tau_{\text{e-e}} \sim \frac{\hbar E_F}{2\pi E^2} \) [13], where \( E \) is the carrier energy measured from the Fermi energy \( E_F \), is of the order of several femtoseconds. Since it is fast compared to the pulse duration we can assume the process to be instantaneous. As \( \tau_{\text{e-e}} \) is much faster than the period of a typical phonon vibration, electrons are decoupled from lattice, and the electronic system can be described with the electronic temperature \( T_e \) which differs from the lattice temperature \( T_L \). Because the heat capacity of the electron gas is much smaller than the heat capacity of the lattice, \( T_e \) can be much higher than \( T_L \). In experiments performed with high photoexcitation density pulses \( T_e \) can reach several hundred or even thousand degrees K above \( T_L \).

Figure 3.1: Thermomodulation mechanism: a) photoexcitation, where the arrows represent possible electronic transitions from occupied (hatched) to unoccupied electronic states, results in b) Fermi surface smearing thereby opening some states and blocking others for optical transition. When the change in reflectivity (i.e. absorption \( \Delta \alpha \)) is measured with respect to the probe photon energy \( \omega \) one observes c) a derivative-like feature when the probe energy matches the energy of d-band to \( E_F \) transition. The temporal evolution of the effect can be measured by a femtosecond thermomodulation technique.

Fermi level smearing affects the reflectivity of the delayed probe pulse. In first
approximation it affects the probe optical transition only if the initial or final states lie near $E_F$. The amplitude of the reflectivity change therefore strongly depends on the probe pulse wavelength [Fig 3.1 c]), in metals having the most pronounced wavelength dependence at probe photon energies near $d$–band to $E_F$ transition. The strong dependence of the photoinduced signal amplitude on the wavelength of the probe pulse made these materials especially interesting for studying energy relaxation processes and the experiments gave new insight in non-equilibrium phenomena.

Figure 3.2: a) Picosecond thermomodulation response in Cu after Eesley et al. [129]. By tuning the probe laser energy around 2.15 eV the sign of the fast component changes according to Fig. 3.1. b) Transient reflectivity change in Au as a function of probe photon energy at various time delays from the heating pulse after Schoenlein et al. [131]. Insets: corresponding thermomodulation spectra of Cu and Au at 300K from Brorson [126], where thermomodulation was achieved by heating the sample with current.

The first room-temperature picosecond thermomodulation experiments on Cu were performed by Eesley in 1983 [129]. He used the two sync-pumped dye lasers, a tunable one between 2.03 and 2.17 eV (610 -572 nm) as a probe and the other one at 1.92 eV (645 nm) as a pump. He observed a fast initial signal [Fig. 3.2 a)] being pulse width limited which changed sign at the probe photon energy approximately 2.15 eV in accordance with the conventional thermomodulation as shown in the inset to Fig. 3.2 a). The initial fast signal was followed by a slowly decaying signal which did not change sign as the probe photon energy was changed and was attributed to lattice
effects with typical timescales being determined by heat diffusion. Similar results were found by Fujimoto et al. [130] in W. The first time-resolved measurements of electronic system relaxation were done by Schoenlein in Au [131] and Elsayed in Cu [132], where 60 fs CPM (colliding pulse modelocking) lasers were used as a probe. In Schoenlein’s experiment high intensity pulses from a CPM laser were used to produce a 60 fs broadband continuum enabling them to measure the electron relaxation with < 100 fs resolution over broad energy range [see Fig. 3.2 b)]. The experiment showed the electron decay time to be of the order of 2-3 ps.

It should be noted however that the derivative-like feature observed in the femtosecond and the conventional thermomodulation is much broader than one might expect on the basis of the simple model, which suggests the width of the feature should be of the order of $k_B T_e$. It may be discussed however that neither d-band nor p-like states near $E_F$ are dispersionless, leading to a broadening of the observed feature. Likewise, the broadening might result from an extremely short lifetime of the photoexcited state giving, through the uncertainty principle, $\Delta E \sim 0.5 eV$ with $\tau \sim 1.3$ fs. However, the picture seems to be qualitatively correct, while these measurements opened a new field of time-resolved spectroscopy.

### 3.1.2 Photoexcited electron relaxation processes in metals.

By measuring the temporal dependence of the reflectivity change on the picosecond timescale we can experimentally determine the relaxation time of the photoexcited electronic system. In general two effects should be considered: first, the energy relaxation due to the electron-electron scattering and scattering with other excitations (phonons, plasmons, etc.), and secondly the transport of energy out of the probed volume.

Considering the transport of high energy carriers out of the probed volume, we have to remember that the motion of an individual electron is a random walk. Since the electrons that lie close to the Fermi surface are the principal contributors to the transport, the heat carrying electrons move with the Fermi velocity $v_F$. In the limit of lengths longer than the momentum relaxation length $l_p$, the random walk behavior is averaged and the electron motion is subject to the diffusion equation. On the other hand, on a length scale shorter than $l_p$ the electrons move ballistically with velocities close to $v_F$. In metals the electron-electron scattering length $l_{e-e}$ was found to be $l_{e-e} \propto (E - E_F)^2$ and was calculated for Au [133] to be 80 nm for 1 eV electrons. On the other hand, the electron-phonon scattering length $l_{e-ph}$ is usually inferred from conductivity data. Using the Drude relaxation times one obtains $l_{e-ph} \sim 50$ nm for Au at room temperature. When compared to the characteristic length - optical skin depth, which is of the order of 10 nm in metals, we can see that in pump-probe optical experiments one is probing the ballistic rather than diffusive transport of electrons.

The femtosecond electronic heat transport in thin Au films was experimentally studied by Brorson et al. in 1987 [134], when two types of pump-probe experiments
were performed on films of different thicknesses on sapphire substrates. First the differential reflectivity of the probe at the back surface of the film was measured as the sample was pumped with a 100 fs pulse from the front. By measuring the delay of the rising edge as a function of the film thickness they found that it increases linearly with the film thickness giving an energy transport velocity of \( \sim 10^8 \text{m/s} \), which is the same order of magnitude as \( v_F (1.4 \times 10^8 \text{m/s in Au}) \). The "front pump - front probe" relaxation time measurements revealed that the relaxation time was indeed much shorter in thicker films. This can be understood in the following way. When the sample thickness is large in comparison to the optical skin depth, the transport and the energy relaxation occur simultaneously. In this case, the photoinduced reflectivity decay is very fast since two competing processes remove energy from the probed region of the sample. Conversely, when the sample length is decreased to the order of optical skin depth less transport occurs and the photoinduced reflectivity is primarily due to the energy relaxation. These observations put experimental constraints to the experiments probing the energy relaxation processes in metals. Namely, in order to obtain the intrinsic energy relaxation time, film thicknesses of the order of the optical skin depth should be used.

Motivated by the experimental data \([129, 131, 132]\) the energy relaxation through electron-phonon scattering was theoretically investigated by Allen in 1987 \([92]\). He followed the model of Kaganov et al. \([135]\) considering the system of electrons and phonons with thermal distribution functions \( f_k \) and \( n_Q \) determined by \( T_e \) and \( T_L \) respectively. He assumed that i) diffusion driven by spatial inhomogeneities is negligible, which is a good approximation in case when the mean free path is short, ii) acceleration due to external or internal fields is negligible, and iii) no other collision processes are important. The collision integrals describing the time development of \( f_k \) and \( n_Q \) can be approximated by

\[
\frac{\partial f_k}{\partial t} = -\frac{2\pi}{\hbar N_c} \sum_Q |M_{kk'}|^2 \{ f_k (1-f_{k'}) [(n_Q+1) \delta (\varepsilon_k-\varepsilon_{k'}-\hbar\omega_Q) + n_Q \delta (\varepsilon_k-\varepsilon_{k'}-\hbar\omega_Q)] \\
- (1-f_k) f_{k'} [(n_Q+1) \delta (\varepsilon_k-\varepsilon_{k'}+\hbar\omega_Q) + n_Q \delta (\varepsilon_k-\varepsilon_{k'}-\hbar\omega_Q)]\}
\]

\[
\frac{\partial n_Q}{\partial t} = -\frac{4\pi}{\hbar N_c} \sum_k |M_{kk'}|^2 f_k (1-f_{k'}) [n_Q \delta (\varepsilon_k-\varepsilon_{k'}+\hbar\omega_Q) - (n_Q+1) \delta (\varepsilon_k-\varepsilon_{k'}-\hbar\omega_Q)]
\]

where \( k \) and \( Q \) are the electron and phonon wave vectors respectively, \( N_c \) is the number of the unit cells in the sample and \( M_{kk'} \) is the electron-phonon matrix element normalized to the unit cell of magnitude \((E_F^2 \hbar \omega_D)^{1/2}\). The additional factor 2 in the second equation accounts for electron spin degeneracy. In the model Allen considered other collision processes — electron-electron (e-e) and phonon-phonon (ph-ph) scattering — being active in keeping the distributions \( f_k \) and \( n_Q \) equal to local equilibrium distributions characterized by \( T_e \) and \( T_L \), which depend on time.

\(^1\) In case the geometry of the experiment prevents the electron transport out of the probed volume or if the electron mean free path is short in comparison with the optical skin depth.
3.2 Displacive excitation of coherent phonons.

In pump-probe experiments on a number of conducting and semiconducting materials oscillations have been observed in photoinduced reflectivity or transmission with frequencies corresponding to the optical phonon modes of materials. Several models have been proposed to explain the observed phenomena including impulsive stimulated Raman scattering (ISRS) [138, 139], the nonlinear optical susceptibility mechanism, and the screening of the space-charge fields at the surface of semiconducting samples [140]. In this section, however, we discuss the mechanism proposed for describing oscillatory components in several semiconductors and semimetals, where only A1 symmetry Raman-active modes were observed, even though modes of comparable strength with different symmetries also occur in Raman spectra of these materials. For obvious reasons noted later in the text the model was named displacive excitation of coherent phonons (DECP) [127, 141].

In DECP, after being excited by the pump laser pulse, the electronic system comes to quasi-equilibrium in a time short compared to the oscillation period of the lattice. This quasi-equilibrium is described by elevated electronic temperature $T_e$ with respect to lattice temperature, as in metals, or by density of the photoinduced carriers in the upper band $n_p(t)$, in case of semiconductors, which relax on the ps timescale. Since
both $T_e$ and $n_p$ are scalars they can be coupled only with scalar $A_1$ vibrational modes. In materials with $A_1$ vibrational modes the quasi-equilibrium nuclear $A_1$ coordinates are thereby displaced with no change in lattice symmetry in time short compared to the period of lattice vibration. This gives rise to a coherent vibration of ions about the displaced quasi-equilibrium coordinates. In the following paragraphs we briefly describe the model since the oscillations of $A_1$ symmetry Raman-active modes were observed also in materials under investigation in our experiments.

The basis of DECP is the postulation that the origin of the oscillations in $\Delta R(t)$ is a change in the quasi-equilibrium $A_1$ coordinate $Q_0(t)$ (where $Q_0 = 0$ defines the state before the photoexcitation). The $A_1$ modes are the so called ”breathing modes”, where the ionic displacements do not lower the symmetry. The $A_1$ symmetry displacements have a continuum of possible values. The actual equilibrium value of $A_1$ displacements is determined by minimizing the free energy of the system. Therefore, it follows that the equilibrium positions of the nuclei should be a function of temperature and electronic distribution.

As in metals the photoexcitation is followed by rapid carrier thermalization leading to changes in the electron temperature $\Delta T_e(t)$. Since the materials, where coherent oscillations have thus far been observed (Bi, Sb, Te [141, 142], Ti$_2$O$_3$ [143], YBa$_2$Cu$_3$O$_6$ [144, 145], K$_{0.3}$MoO$_3$ [146], 1T-TaS$_2$ [147]...) are either semimetals or semiconductors, photoexcitation may also produce interband transitions leaving $n_p(t)$ electrons per unit volume in the excited bands. Both, the increase in electronic temperature or the increase in the occupation number of states in bands above $E_F$ may lead to change in the quasi-equilibrium $A_1$ ionic coordinate in timescale short compared to the equilibration time of an ionic system and thereby coherently exciting $A_1$ vibrational mode. Whichever is the dominant source of the observed effect, it leads to a very similar result for $\Delta R(t)$ in DECP. In the following brief derivation we assume that the main source is $n_p(t)$.

The equation describing the rate of change of $n_p(t)$ in the sample is
\[ \frac{dn_p(t)}{dt} = \rho P(t) - \beta n_p(t) \quad . \quad (3.2) \]
The first term on the right describes the rate of generation of the carriers in the excited band which is assumed to be proportional to the pump pulse temporal profile $P(t) = E_{\text{pump}} g(t)$ and $\rho$ is the proportionality constant. The second term, however, is the rate of the transfer of electrons back to the ground state. The source of excitation of the $A_1$ mode is the dependence of the equilibrium $A_1$ coordinate $Q_0(t)$ on $n_p(t)$. It is reasonable to take this dependence to be linear $Q_0(t) = \kappa n_p(t)$, with $Q_0 = 0$ before photoexcitation takes place. The equation governing the time dependence of the coordinate $Q(t)$ is then
\[ \frac{d^2Q(t)}{dt^2} = -\omega_0^2 [Q(t) - Q_0(t)] - 2\gamma \frac{dQ(t)}{dt} \quad , \quad (3.3) \]
where $\omega_0$ is the angular frequency, and $\gamma$ the damping of the $A_1$ mode. Assuming
that the pulse duration is short compared to the $A_1$ mode phonon cycle, we can approximate $g(t)$ with a $\delta$-function giving the exponential time dependence of $n_p(t) \propto e^{-\beta t}$. Then the time dependence of the coordinate $Q(t)$ is given by:

$$Q(t) = \frac{\omega_0^2 \kappa \rho E_{pump}}{(\omega_0^2 + \beta^2 - 2\beta \gamma)} \left[ e^{-\beta t} - e^{-\gamma t} \left( \cos(t) - \frac{\beta - \gamma}{\beta + \gamma} \sin(t) \right) \right]$$  \hspace{1cm} (3.4)

where $\gamma = \sqrt{\omega_0^2 - \gamma^2}$. If $R$ is the unperturbed reflectivity before the arrival of the pump pulse, then the differential reflectivity change due to the photoexcitation can be written as

$$\frac{\Delta R(t)}{R} = \frac{1}{R} \left[ \frac{\partial R}{\partial n_p}(t) + \frac{\partial R}{\partial T_e} \Delta T_e(t) + \frac{\partial R}{\partial Q} Q(t) \right].$$  \hspace{1cm} (3.5)

By writing the reflectivity in terms of complex dielectric function and using Eqs. (3.4) and (3.5) we get the time dependence of the photoinduced reflectivity

$$\frac{\Delta R(t)}{R} = \tilde{A} e^{-\beta t} + \tilde{B} \frac{\omega_0^2}{(\omega_0^2 + \beta^2 - 2\beta \gamma)} \left[ e^{-\beta t} - e^{-\gamma t} \left( \cos(t) - \frac{\beta - \gamma}{\beta + \gamma} \sin(t) \right) \right],$$  \hspace{1cm} (3.6)

with

$$\tilde{A} = \frac{1}{R} \left[ \left( \frac{\partial R}{\partial \epsilon_1} \right) \left( \frac{\partial \epsilon_1}{\partial n_p}(t) \right) + \left( \frac{\partial R}{\partial \epsilon_2} \right) \left( \frac{\partial \epsilon_2}{\partial n_p}(t) \right) \right] \rho E_{pump}$$

$$\tilde{B} = \frac{1}{R} \left[ \left( \frac{\partial R}{\partial \epsilon_1} \right) \left( \frac{\partial \epsilon_1}{\partial Q} \right) + \left( \frac{\partial R}{\partial \epsilon_2} \right) \left( \frac{\partial \epsilon_2}{\partial Q} \right) \right] \kappa \rho E_{pump}.$$

The fit to the differential reflectivity taken at low temperatures on 2D charge density wave insulator $1T$-$TaS_2$ using Eq. (3.6) is shown in Figure 3.3 giving an excellent agreement with the theory.

In DECP the oscillations in reflectivity $R$ are excited with a $\cos(t)$ dependence, where $t = 0$ is the time of arrival of the probe pulse. The phase shifts from a simple $\cos(t)$ were found to be rather small, since $\omega_0$ is usually an order of magnitude larger than $\beta$ and $\gamma$ [127]. Of course, large values of $\beta$ can contribute a $\sin(t)$ term if the term $\beta - \gamma$ is not negligibly small [Eq.(3.6)]. An important prediction of DECP model is also the linear dependence of the oscillatory amplitude on the pump pulse integrated intensity that has also been experimentally confirmed [127, 146]. The main difference between DECP and ISRS or other nonlinear impulsive excitation mechanisms is that in case of DECP the $A_1$ symmetry modes should be the only ones observed. With extremely short 10 fs laser pulses now commercially available high frequency limit for the observation of coherent phonons was raised to several hundreds of cm$^{-1}$ enabling measurements of a whole spectrum of $A_1$ symmetry mode oscillations [148].


Figure 3.3: The photoinduced reflectivity signal $\Delta R/R(t)$ taken at 30 K on 2D CDW material 1T-TaS$_2$ (full squares connected by a dotted line) together with the fit using Eq.(3.6) (solid line). The two components are also plotted separately, dashed line representing $n_p(t)$ and dotted line representing the oscillatory part only corresponding to $Q(t)$. The value of $\omega_0$ and $\gamma$ correspond to the published value of $A_1$ amplitude mode frequency and damping [149].

### 3.3 Summary of previous pump-probe experiments on HTSC.

In this section we make a summary of the experimental data obtained on various HTSC prior to this work. We first focus on experiments performed at room temperatures using high photoexcitation density setup to investigate the electron-phonon coupling constants using Allen’s theory [92]. In the subsequent subsection we present the data obtained at intermediate photoexcitation densities where oscillations in reflectivity transients were observed in insulating as well as superconducting samples, and were attributed to the coherent phonon generation through the DECP mechanism. In the final subsection we point to the main features in the temperature dependences of the photoinduced transients obtained in experiments with low photoexcitation densities. We focus on anomalies in the relaxation time and signal amplitude, which accompany the superconducting transition. These anomalies will be a matter of discussion in the following sections.
3.3.1 Femtosecond thermomodulation spectroscopy on HTSC.

Motivated by femtosecond thermomodulation measurements of $e$-$ph$ coupling constant in conventional superconductors several groups applied the same technique in studies of the electron-phonon coupling constants in high temperature superconductors [74, 75]. By fitting relaxation of the fast reflectivity transient with single exponential decay in these high photoexcitation density experiments performed at room temperature – which was shown for metals and metallic superconductors (see section 3.1) to be the time of energy relaxation from electronic system to phonons $\tau_{e-ph}$ – electron-phonon coupling constants $\lambda$ was experimentally determined. These experiments were performed on YBa$_2$Cu$_3$O$_{7-\delta}$ [75], Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$ [74]. On YBCO $\tau_{e-ph}$ was found to be $\simeq 100$ fs for initial carrier temperatures $T_e = E_I/C_e$ in the range 3000 K [75] and $\tau_{e-ph} \simeq 60$ fs for $T_e \simeq 410$ K [74]. Here $E_I$ is the energy density per unit volume deposited by the laser pulse and $C_e$ is the electronic specific heat. Using the Allen formula [92], $\tau_{e-ph} = \frac{T_e}{3\lambda\langle \omega^2 \rangle}$, and an estimated mean-square phonon frequency $\langle \omega^2 \rangle$, $\lambda$ was determined to be in the range $0.9 < \lambda < 1$ both in YBa$_2$Cu$_3$O$_{7-\delta}$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$.

The probe wavelength dependence of the photoinduced reflectivity amplitude on YBa$_2$Cu$_3$O$_{7-\delta}$ [75] shows, similarly to metals, a derivative like feature centered around 2.05 eV. The effect was associated with the Fermi level smearing of the in-plane O(2p) derived band with the holes being excited from Cu(3d) band lying about 2 eV lower in energy.

In the following years several experiments were performed to investigate the doping dependence of the Fermi energy and $e$-$ph$ coupling constant by measuring the dependence of the photoinduced signal on doping at constant probe energy of 2 eV. In YBCO the doping was changed by Pr substitution of Y [150, 151] and by changing the oxygen content [87, 151, 152], while in Bi$_2$Sr$_2$Ca$_{1-y}$Y$_y$Cu$_2$O$_8$ by Y doping [87]. Common to these data is the decrease of the photoinduced reflectivity amplitude and eventually a change in sign while increasing the probe pulse photon energy from 1.96 eV. It was associated with a shift of the Fermi level position with respect to the center of the Cu(3d) band with doping. The data infer the Cu(3d)-$E_F$ energy difference to be $\sim 2.07$ eV in optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$, in agreement with the wavelength dependence data from Ref. [75].

As far as the relaxation time is concerned, the room temperature $\tau_{e-ph}$ was found to increase as the doping is decreased (in underdoped samples) [151, 152]. This was attributed [151, 152] to the decrease of the electron-phonon coupling constant $\lambda$ from $\sim 1$ in optimally doped samples to $\sim 0.2$ in strongly underdoped ones. However, it should be noted that as we go to strongly underdoped samples, the metallic picture assumed by the Fermi level smearing mechanism is highly questionable. As we go to insulating YBa$_2$Cu$_3$O$_6$ where Fermi smearing cannot occur, the relaxation time of the induced transmission is further increased. The mechanism for the observed transient in insulating YBa$_2$Cu$_3$O$_6$ is suggested to be spectral hole burning.
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3.3.2 Photoinduced DECP observations on HTSC.

The oscillatory component in the photoinduced transients were first observed on insulating YBa$_2$Cu$_3$O$_{6+x}$ [144]. An oscillation with a period of 237 fs was measured, corresponding to the Raman active mode of $A_{1g}$ symmetry at 142 cm$^{-1}$. Later Albrecht et al. [145] performed experiments at somewhat higher pump intensities and observed two $A_{1g}$ modes at 120 and 150 cm$^{-1}$ in an optimally doped superconducting sample at temperatures below and above $T_c$. An important feature in the temperature dependence is a sharp increase in the phonon dephasing times for both modes upon cooling through the critical temperature; no such changes were observed at low temperatures in the insulating samples. The increase in the dephasing time below $T_c$ can be understood in terms of decreased coupling of the modes to the electronic system due to appearance of the superconducting gap.

An important question, as far as DECP oscillations are concerned is their origin, namely is the oscillatory signal due to an increase in $\Delta T_e$ or due to $n_p$ as discussed in section 3.2. It appears that the relative amplitude of the oscillations is much stronger in the undoped material [152] favoring the $n_p$ mechanism. Similarly, the T-dependence of the Ba mode amplitude at 120 cm$^{-1}$ in the superconducting sample shows a rapid increase below $T_c$ [145]. This suggests the relaxation bottleneck in the photoexcited carrier relaxation caused by the appearance of the superconducting gap. In this case again we can speak about the "$n_p$ mechanism."

3.3.3 T-dependence of the photoinduced transients on HTSC.

In this subsection we summarize the main features that were consistently observed in temperature dependence measurements of the photoinduced transmission and reflectivity of several different HTSC. We focus especially on the anomalies at $T_c$ that were observed in optimally doped samples in the amplitude and the relaxation time of the fast picosecond component, and the magnitude of the slow component [see section 2.1.4].

Let us focus first on the fast ps component, where the general features of the data can be seen in Figure 3.4. A set of time-resolved photoinduced transmission traces in the near-optimally doped YBa$_2$Cu$_3$O$_7$ sample with $T_c = 90$ K are shown in Figure 3.4 a) together with the fits using the sum of a single exponential decay modelling the fast component and a step function to describe the slow component with nanosecond decay. The data clearly show that both the lifetime [Figure 3.4 b)] and its amplitude [Figure 3.4 c)] are strongly temperature dependent on near optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$. The relaxation time $\tau_R$ is nearly constant below $T_c$, shows a clear maximum slightly below $T_c$ and drops to a much lower value above $T_c$. The amplitude of the fast transient shows nearly no T-dependence up to 0.8 $T_c$ followed by a rapid drop at $T_c$. Above $T_c$ the signal amplitude slowly drops until
3.3. Summary of previous pump-probe experiments on HTSC.

Figure 3.4: a) A set of time-resolved photoinduced transmission traces in an near optimally doped ($\delta \approx 0$, $T_c = 90$K) YBa$_2$Cu$_3$O$_{7-\delta}$ thin film on SrTiO substrate with the long-lived pile-up component subtracted to enable the comparison of the fast component. The straight lines are fits to the data using single exponential decay with $\tau_R$ in the range 0.5 - 3 ps and a step function representing the long-lived component (see the Section 2.1.4). From the fit one obtains b) the temperature dependence of the relaxation time (solid squares) and c) the amplitude of the fast component $T$ (also solid squares). The data represented by open circles have been obtained on undoped YBa$_2$Cu$_3$O$_6$ sample.

it is hardly resolved at temperatures above 150 K. The data taken on the undoped YBa$_2$Cu$_3$O$_6$ sample [70] are shown for comparison, exhibiting no anomalies in either amplitude or relaxation time of the fast transient.

The first observations of this effect were reported by Han et al. [66] on YBCO and by Chwalek et al. [67], who presented the data obtained on YBa$_2$Cu$_3$O$_{7-\delta}$ and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$. Later that year Eesley et al. [68] presented the analysis of the relaxation time on Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$, finding that the temperature dependence of amplitude closely follows the observed behavior on YBa$_2$Cu$_3$O$_{7-\delta}$ [66]. Later Reitze et al. [153] studied Pr doped YBCO. They discovered that below $T_c$ the signal consists of two picosecond components of opposite sign. The relaxation time of the component associated with superconducting state (the component that vanished above $T_c$) showed a divergence as the temperature was raised up to $T_c$ as shown by earlier experiments on YBa$_2$Cu$_3$O$_{7-\delta}$ [66] and Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ [68]. Similar results on Bi$_2$Sr$_2$Ca$_{1-y}$Y$_y$Cu$_2$O$_8$ [87, 154], HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ [155], and on electron doped
cuprate Nd_{1.85}Ce_{0.15}CuO_{4-y} [156] came out in the following years.

Although several theoretical interpretations of experimental results were done [66, 158, 159], none of them was widely accepted. Common to all of them is an agreement that the fast component below T_c is somehow connected with the changes in low-energy excitation spectrum associated with the formation of the energy gap below T_c. Here we should mention also the experiment performed by Gong et al. [160], who measured the reflectivity transients of a current biased microbridge far below T_c. At temperatures far below T_c they found a strong decrease in the relaxation time as the microbridge was driven normal by biasing it with current, above the critical current. This way they confirmed that the anomaly in the relaxation time corresponds to the opening of the superconducting gap.

Chwalek et al. [67] argued that the origin of the observed effect was electronic in origin and the states being probed lie near E_F, however no explicit mechanism was proposed. Han et al. [66], on the other hand, observed that the amplitude of the transient below T_c roughly follows the $[1 - (T/T_c)^4]$ behavior and interpreted the data in terms of the two-fluid model. They proposed that the change in the transmission on the ps timescale at 2 eV is due to partial restoration of the Drude contribution to $\sigma(\omega)$. According to this hypothesis the fast signal above T_c was due to the presence of the same mechanism in the metallic state. They proposed the decay of the signal to be determined by the order parameter relaxation governed by Rothwarf and Taylor equations [161], which is determined by the relaxation time of the phonons with energy higher than magnitude of the gap, $2\Delta$. The strong increase in the relaxation time as T_c was approached from below was attributed to generation of acoustic phonons causing the phonon decay time to increase. Eesley et al. [68] also found good agreement with the theoretical prediction for the relaxation of the order parameter, $\tau_R \sim T/\Delta (T)$, as was theoretically studied by Tinkham and Clarke [162] and Schmid and Schön [163] and experimentally confirmed by Schuller and Gray [164] in superconducting Al. It was argued however that the temperature dependence of the relaxation time in HTSC strongly depends on photoexcitation intensity, therefore no final conclusion on this issue was made [157].

Reitze et al. [153] performed experiments on YBCO at a different probe wavelength as used by Han et al. [66] and found a change of sign in the signal at T_c. They argued that a simple redistribution of the oscillator strength at optical frequencies in the two-fluid model proposed by Han et al. [66] was insufficient to explain neither the magnitude nor the change of sign in the signal at T_c observed at certain probe wavelengths.

In addition to the above mentioned explanations for the observed anomalies, Mazin et al. [159] proposed that DECP could account not only for the small oscillatory contribution to the signal (observed on YBCO [145] as discussed above), but also for the non-oscillatory signal in the superconducting state. They performed LDA calculations to argue that in the superconducting state the dependence of reflectivity on the photoinduced carrier concentration [constant $\hat{A}$ in Eq.(3.6)] is far
less pronounced than its dependence on phonon equilibrium coordinate [constant $\tilde{B}$ in Eq.(3.6)]. Although the model can explain the increase in the amplitude of the fast transient at $T_c$ upon cooling from high temperatures, and the change of sign in the signal at $T_c$ observed at certain probe wavelengths, it cannot account for the increase in the relaxation time as $T_c$ is approached from below.

When describing experimental data on the fast ps transients taken below and above $T_c$ in these materials we should briefly discuss the sign of the photoinduced transmission or reflectivity. Although no systematic study of dependence of photoinduced signal on probe wavelength has been done so far, apart from the femtosecond thermomodulation measurements at room temperature presented in section 3.3.1, we can compile the data taken on the near optimally doped YBCO from different groups [69, 70, 66, 67, 153, 157, 158] using probe photon energies from 1.96 to 2.03 eV. The sign change in the differential reflectivity from positive, below 1.98 eV, to negative, observed above 2 eV, strongly opposes the models proposed by Han et al. [66] and Mazin et al. [159], and shows that the photoinduced changes strongly depend on the details of the band structure.

Figure 3.5: The temperature dependence of the amplitude of the slow component $\mathcal{D}$ ($D-B$ in Figure 2.5) in the differential transmittance on the near optimally doped YBCO compared to the data taken on the insulating YBCO sample (open circles). The solid circles are from Stevens et al. [69], while the solid diamonds are from Mihailovic et al. [70]. The solid line is the activation fit $e^{-A/T}$ to the data with the activation energy $A = 3.5 \ k_B T_c$, whereas the dotted line is a guide to the eye. The data of Stevens et al. was shifted in temperature by 10 K due to heating.
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Beside the fast ps component, the slower component in the relaxation [see Figure 2.5] was observed in virtually all the experiments on superconducting samples. It was usually attributed to bolometric effects [68]. The first notion of a possible non-bolometric origin of this component was given by Thomas et al. [87]. They measured the signal up to 500 ps and found the temporal evolution not to be consistent with the predicted bolometric response (see section 2.1.5). Moreover, they found the characteristic time of this photoinduced absorption to be in the \( \mu s \) range, as they observed induced absorption even after 160 \( \mu s \) (i.e. at negative time delays). They attributed it to photoinduced self-trapped states.

A detailed study of the slow component on YBCO was done by Stevens et al. [69], who measured its T-dependence. The temperature dependence of the slow component amplitude \( D \) on YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) is shown in Figure 3.5. It can be seen that it has a strong temperature dependence and is, similarly to the fast component, sensitive to the superconducting transition. It is important to state that the slow component was studied in single crystals, thin films on different substrates, and even freestanding thin films - all with quite different thermal properties - and the observed effect in all cases is qualitatively the same. The data taken on an insulating YBa\(_2\)Cu\(_3\)O\(_6\) film on the same substrate (open circles) is shown for comparison exhibiting no anomaly around 90 K. Therefore a simple thermal origin of the slow component can be rejected; so we can assume it to be electronic in origin. From its temperature dependence that is well fitted with the activated behavior \( D \propto e^{-A/T} \), Stevens et al. [69] proposed the long lived component to be due to localized unpaired hole states near \( E_F \) with population being thermally activated.

Finally, we should also mention the previous measurements on slightly underdoped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) obtained in our laboratory that show a distinctly different temperature dependence as those on optimally doped samples [70]. As opposed to the data on optimally doped samples, in underdoped sample the amplitude starts to drop at temperatures much higher than \( T_c \), with no anomaly at \( T_c \), falling off very slowly. Secondly, there is no anomaly in the relaxation time at \( T_c \) - moreover the relaxation time seems to be T-independent. Since the increase in amplitude below \( T_c \) was associated with energy gap formation and pairing, these observations naturally lead us to the idea of possible pairing above \( T_c \).

3.4 Femtosecond spectroscopy in materials with a small energy gap.

In this section we present the model [71] describing the temperature dependences of the amplitudes and relaxation times of the photoinduced transients in the experiments performed with low photoexcitation densities on materials exhibiting a gap in the low energy excitation spectrum. Theoretical investigation has been motivated by unusual temperature dependence of amplitudes and relaxation times in high temperature
superconductors summarized in section 3.3.3. The main result of the model is that the temperature dependence of the relaxation processes entirely depends on the magnitude and the temperature dependence of the gap in the low energy excitation spectrum. Although the model was developed for superconductors, it is sufficiently general that it can be used also for charge density wave materials and other materials with a small energy gap near Fermi energy.

We first give the main idea of the model, then derive the analytical expressions for the temperature dependence of the photoinduced amplitudes of the fast transients for the case of T-independent gap and a BCS-like\(^2\) T-dependent gap. We first assume that the gap is isotropic (i.e. s-wave), and then discuss the case when the gap is highly anisotropic (i.e. d-wave). Later on we present a derivation of the temperature dependence of the relaxation time and conclude with some discussion.

### 3.4.1 The basis of the model.

Our assumption is that the Fermi liquid picture holds as well for HTSC and treat them similarly to metallic conventional superconductors. The assumption is based on room-temperature femtosecond thermomodulation measurements, where the behavior in HTSC [74, 75] follows the behavior in metallic superconductors as described in section 3.3.1.

The basis of the model is shown in Figure 3.6. The photoexcitation and initial relaxation processes are given by 1 and 2 respectively, whereas the probe process is given by 3. Below we discuss the three processes separately.

1. A pump pulse with photon energy 1.5 eV excites carriers from occupied states below \(E_F\) to unoccupied states in bands 1.5 eV above.

2. The initial phase of the photoexcited carrier relaxation after absorption of the pump laser photon proceeds rapidly. The photoexcitation is followed by carrier thermalization through electron-electron scattering with a characteristic time \(\tau_{e-e} \sim \frac{\hbar E_F}{2k_B E_F}\) for intraband relaxation, where \(E\) is the carrier energy measured from the Fermi energy \(E_F\). Electron-electron relaxation time has been experimentally measured in \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\) [165] in range of energies 1.4 – 3 eV above \(E_F\) and was found to be on the order of 10 fs. In the initial thermalization process, a quasiparticle avalanche multiplication due to electron-electron collisions takes place as long as \(\tau_{e-e}\) is less than the electron-phonon (\(e-ph\)) relaxation time \(\tau_{e-ph}\). Experimentally \(\tau_{e-ph}\) was determined on \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) [75] as well as on \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}\) and \(\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}\) [74] by time resolved experiments using intense laser pulses, giving \(\tau_{e-ph} \sim 100\) fs. Given that, \(e-ph\) relaxation becomes important when the quasiparticle energy

\(^2\) When discussing a BCS-like gap we assume a gap that closes at \(T_c\) in mean-field-like fashion. For simplicity, in the following analysis BCS temperature dependence of the gap magnitude (see Ref. [2]) is used.
Figure 3.6: Schematic of the photoexcitation, carrier relaxation and photoinduced absorption processes in materials with a small energy gap. Interband photoexcitation (step 1) is followed by an ultrafast initial relaxation (step 2). The gap in the density of states creates a relaxation bottleneck. The probe pulse measures through the photoinduced absorption (step 3) the time evolution of the photoexcited carrier density.

is reduced below \( E = \sqrt{\frac{\hbar E_F}{2\pi \tau_{e-ph}}} \approx 30 - 50 \text{ meV} \), assuming \( E_F \approx 0.1 - 0.2 \text{ eV} \) in these materials.

In the experiments taken into consideration here the laser intensities are significantly lower than in femtosecond thermomodulation measurements [75, 74], and the photoexcited electronic temperature \( T_e \) is only a few K in excess of the lattice temperature, i.e. \( T_e \approx T \). This gives the \( e-ph \) relaxation time [see Eq.(3.1)] \( \tau_{e-ph} = \frac{\pi \hbar k_B T_e}{3 \hbar \Lambda^2 \alpha_e^2} \approx 10 \text{ fs} \). Under these near-equilibrium conditions, where the carrier temperature being near the lattice temperature, this value of \( \tau_{e-ph} \) is comparable to the relaxation time determined from infrared reflectivity measurements. For energies of the order of \( 30 - 50 \text{ meV} \), \( \tau \approx 16 \text{ fs} \) was found [166] at room temperature, in good agreement with the above estimated \( \tau_{e-ph} \approx 10 \text{ fs} \). To summarize, in the absence of gap in the density of states the photoexcitation is followed by rapid carrier relaxation resulting in slightly elevated electron-phonon temperature within \( \approx 100 \text{ fs} \).

On the other hand, when the gap with magnitude \( 2\Delta \) is present in the low energy density of states, phonons with energies less than \( 2\Delta \) cannot contribute to the relaxation of carriers just above the gap, therefore the situation is strongly modified and a bottleneck in the relaxation occurs after \( t \approx 100 \text{ fs} \). As a result quasiparticles accumulate near the gap, forming a non-equilibrium distribution.
Since typical values of the energy gap in HTSC are of the order of $2\Delta \sim 30 - 50$ meV, each photon creates $30 \sim 40$ quasiparticles given by $E_{\text{pump}}/2\Delta$, where $E_{\text{pump}} = 1.5$ eV is the laser pump photon energy. As the final relaxation step across the gap is strongly suppressed [161], the quasiparticles together with high frequency phonons (with $h\omega > 2\Delta$) form a near-steady state distribution. The quasiparticle recombination dynamics of this system is governed by the emission and re-absorption of the high frequency phonons.\(^3\) Phonons with $h\omega < 2\Delta$ do not participate in the direct relaxation of the quasiparticles, since in this case the quasiparticle final states would lie in the gap. In the case of a mean-field-like gap, upon increasing temperature closer to $T_c$, more low-energy phonons become available for re-absorption and the recombination mechanism becomes less and less efficient, thereby the relaxation time increases.

Considering the probe process, we are interested in photoinduced changes of transmission or reflectivity – on the picosecond timescale. Since we are dealing with weak perturbations, we can assume that the photoinduced transmission $\Delta T/T$ (or reflectivity $\Delta R/R$) is in the linear approximation proportional to photoinduced absorption $\Delta A/A$. Through Fermi golden rule the photoinduced absorption is due to changes in the initial or final state carrier density. As the relaxation of quasiparticles high above $E_F$ is of the order of 10 fs, we can assume (similar assumption is made also in femtosecond thermomodulation experiments) that the main changes in absorption involve photoexcited carriers above the gap as initial or final states for absorption. Since the probe laser photon energy $E_{\text{probe}}$ is typically well above the plasma frequency in high-$T_c$ superconductors, we make an approximation that the photoinduced absorption is given by the Fermi golden rule, with photoinduced quasiparticles above the gap as initial states and with final unoccupied states well above the Fermi energy in a band, which lies approximately at $E_2 \sim E_{\text{probe}}$ (Figure 3.6). The amplitude of the photoinduced absorption $A$ (step 3 in Figure 3.6) is proportional to the number of photoexcited quasiparticles $n_{pe}$ and by measuring the photoinduced transmission $\Delta T/T$ (or reflectivity $\Delta R/R$) the temporal evolution of the photoexcited carrier density $n_{pe}$ is probed. The photoinduced transmission amplitude $T$ is thus weighted by the dipole matrix element and the joint density of states, so $T \propto -n_{pe}\rho_f |M_{ij}|^2$, where $n_{pe}$ is the photoexcited carrier density, $\rho_f$ is the final density of unoccupied states, and $M_{ij}$ is the dipole matrix element.

There are several experimental observations that speak in favor to this simplified picture. In the model we assume, that the photoinduced signal builds up during initial relaxation processes [see Figure 3.6], where both $\tau_{e-e}$ and $\tau_{e-ph}$ were found to increase on decreasing temperature – see Refs. [165] and [92] respectively. This

\(^3\) A quantitative justification for the assumption that phonons play a dominant role in the quasiparticle relaxation will be given in section 3.4.4.
is manifested as an increase in the risetime of the fast optical transient, which was observed already in the first time-resolved measurements on YBCO [66, 67], giving the risetime of 200-300 fs at temperatures below $T_c$ [66].

Secondly, we should consider the sign of the photoinduced transmission (or reflectivity). In the model we consider that the photoexcited carriers above the gap are initial states in the probe process resulting in increased absorption (increased opacity) — as is the case in YBCO at 1.5 eV probe photon energy. However, the sign of $\Delta A/A$ (and correspondingly $\Delta T/T$ and $\Delta R/R$) could also be opposite in case the initial states lie 1.5 eV below $E_F$ and the states above the gap are final states in absorption process. Indeed, as discussed in section 3.3.3, the sign of the photoinduced transmission or reflectivity transient changes with the probe photon energy.

Another important experimental evidence in favor of the above described model was recently obtained on one dimensional charge density wave (CDW) insulator K$_{0.3}$MoO$_3$ [146] (see section 5.2). The dipolar nature of the probe process was confirmed while measuring the dependence of the photoinduced reflectivity amplitude on the probe pulse polarization. It has a $\cos^2(\phi)$ dependence, where $\phi$ is the angle between the probe pulse polarization and the crystal axis. This observation is possible due to the low monoclinic symmetry of K$_{0.3}$MoO$_3$ crystal. In materials with higher symmetry, a higher degeneracy of electronic bands is expected (larger number of energy bands of different symmetry per energy interval). Therefore the anisotropy in the signal is expected to be much less pronounced. On YBa$_2$Cu$_3$O$_y$ for example, there is almost no in-plane anisotropy [69], whereas the ratio of the signal with the probe polarized parallel to the c-axis and perpendicular to it was found to be approximately 5 [69]. It should be said here, that changing the pump beam polarization or photon energy does not affect the photoinduced signal [69, 146] giving further confirmation of the model.

According to the above, measuring the change in reflectivity (transmission) with respect to time after the photoexcitation one probes the temporal dependence of the photoexcited carrier density, $n_{pe}(t) \sim \Delta T(t)/T$. Since the relaxation process depends strongly on the magnitude of the gap as well as on lattice temperature, $n_{pe}(t)$ should be strongly $T$-dependent. The derivations of the $T$-dependence of the amplitude and relaxation time of the photoexcited picosecond transients for different gaps is presented in next subsections.

### 3.4.2 T-dependence of the photoexcited quasiparticle density.

In this subsection we give the derivation of the temperature dependence of the photoexcited carrier density for different temperature dependences of the low energy gap. At low photoexcitation intensities the photoexcited carrier density is substantially lower than the characteristic quasiparticle density in a superconductor $2N(0)\Delta$, where $N(0)$ is the density of states at Fermi energy, $E_F$. Therefore a laser pulse makes only a weak perturbation in the superconductor [71, 69, 66]. In the
calculation we assume a 100 fs pump laser pulse at 1.5 eV photon energy, with the energy of 0.1 nJ focused in a \( \sim 60 \mu \text{m} \) diameter spot on the high-T\(_c\) superconductor YBCO.

Using these parameters the number of photogenerated quasiparticles is \( n_{pe} \lesssim 3 \times 10^{-3} \) per unit cell [71]. On the other hand, the typical carrier concentration (relevant for superconductivity) in a high temperature superconductor is \( n_0 = 2N(0)\Delta \simeq 0.2 - 0.4 \) per unit cell. The number of photoexcited quasiparticles is small compared to the characteristic quasiparticle density \( n_{pe}/n_0 \lesssim 10^{-2} \) so the weak photoexcitation approximation is clearly justified and the photoexcited quasiparticles make only a weak perturbation of the distribution functions.

In experiments two different regimes were observed. In the samples near optimal doping the gap seems to close at \( T_c \), whereas in underdoped samples the pseudogap seems to persist also at higher temperatures. Therefore we have considered two cases; in one the gap closes at \( T_c \) (For simplicity we have used BCS temperature dependence.), whereas in the other the gap is assumed to be \( T \)-independent. Here the term temperature-independent gap means that the gap does not vanish at \( T_c \), but persists above \( T_c \) (It does not exclude the possibility of weak temperature dependence.). As far as the gap anisotropy is concerned, we assume in the first approximation the gap to be isotropic. Secondly, because of many theoretical and experimental studies on the possibility of d-wave symmetry order parameter in HTSC, we estimate the implications of a strong gap anisotropy on the temperature and photoexcitation intensity dependence of the fast transient amplitude.

**Isotropic gap.**

Assuming that the energy gap is isotropic, one can approximate non-equilibrium phonon \( (n_{\omega q}) \) and quasiparticle \( (f_\varepsilon) \) distribution functions as follows [167]:

\[
n_{\omega q} = \begin{cases} 
\frac{1}{\exp\left(\frac{\hbar \omega_q}{k_B T}\right) - 1}, & \hbar \omega_q < 2\Delta \\
\frac{1}{\exp\left(\frac{\hbar \omega_q}{k_B T'}\right) - 1}, & \hbar \omega_q > 2\Delta 
\end{cases}
\]

(3.7)

\[
f_\varepsilon = \frac{1}{\exp\left(\frac{\varepsilon}{k_B T}\right) + 1},
\]

(3.8)

where \( T \) is the lattice temperature and \( T' \) is the temperature of quasiparticles and high frequency phonons with \( \hbar \omega_q > 2\Delta \). The number of photoexcited quasiparticles \( n_{pe} \) can be calculated as the difference between the numbers of thermally excited quasiparticles (per unit cell) after and before photoexcitation characterized by temperatures \( T' \) and \( T \). The number of photoexcited carriers \( n_{pe}(= n_{T'} - n_T) \) can be obtained directly considering energy conservation.

To differentiate between \( T \)-independent and \( T \)-dependent mean-field-like gap we use notation \( \Delta^p \) for the temperature independent gap and \( \Delta_c(T) \) for the \( T \)-dependent
gap that closes at $T_c$. In case of arguments that hold for both cases symbol $\Delta$ without subscripts is used (e.g. $\Delta (0)$ is the gap magnitude at $T = 0$ K).

Let us first assume that $\Delta = \Delta^p$ is temperature independent and large in comparison to $k_B T$. Since the magnitude of the gap $\Delta^p$ is of the order of several 10 meV, which corresponds to temperatures of a few hundred kelvins, we can assume that quasiparticles are non-degenerate and $f_\varepsilon$ can be approximated as $f_\varepsilon \sim \exp (-\varepsilon/k_B T)$. Similarly we can approximate $n_{\omega_q} \sim \exp (-h\omega_q/k_B T)$. When considering the temperature-independent (pseudo-)gap, we take the quasiparticle density of states given by

$$N(E) = \begin{cases} 0, & E < \Delta^p \\ N(0), & E > \Delta^p. \end{cases}$$

Strictly speaking the model density of states corresponds to the real gap, however $\Delta^p$ should be understood as an energy where the relaxation of photoexcited quasiparticles in inhibited. The density of states below $\Delta^p$ could be finite but the relaxation through these states is suppressed (e.g. relaxation through localized states) therefore they are not available for the relaxation.

Further, we assume that the phonon spectral density is constant at large frequencies ($\omega > 2\Delta^p$). In this case the quasiparticle energy and the energy of high frequency phonons at temperature $T$ are given by

$$E_T = 2N(0)\Delta^p T \exp (-\Delta^p / k_B T),$$

$$E_T^{ph} = \frac{2\nu \Delta^p T}{c} \exp (-2\Delta^p / k_B T),$$

respectively. Here $\nu$ is the number of high frequency phonon modes (per unit cell) and $c$ is the phonon cutoff frequency. Since we assume that after photoexcitation the high energy phonons and quasiparticles are described by the same temperature, we write the conservation of energy as

$$\mathcal E_I = \left( E_{T'} + E_{T'}^{ph} \right) - \left( E_T + E_T^{ph} \right)$$

(3.9)

where $\mathcal E_I$ is the energy density per unit cell deposited by the incident pump laser pulse. Since quasiparticle density is given by $n_T = 2N(0) T \exp (-\Delta^p / k_B T)$, by making the approximation that $T \ll \Delta$, Eq.(3.9) can be rewritten in terms of quasiparticle densities at temperatures $T'$ and $T$

$$\left( n_{T'} - n_T \right) \Delta^p + \left( n_{T'}^2 - n_T^2 \right) \frac{\nu \Delta^p}{2\hbar cN(0)^2 k_B T'} = \mathcal E_I.$$  

(3.10)

There are two limiting cases to be considered with respect to the ratio of photoexcited vs. thermally excited quasiparticle densities, $n_{pe}/n_T$.

In the low temperature limit $n_{pe} \gg n_T$, since $n_T$ is exponentially small. In this case $n_{T'} \gg n_T$ and by equaling $n_T$ to 0 in Eq.(3.10) one gets the quadratic equation
for $n_{T'} \ (\simeq n_{pe})$. Since $n_{pe}$ is small, one can neglect the quadratic term in Eq.\( (3.10)\) obtaining

$$n_{pe} = (n_{T'} - n_{T}) = \mathcal{E}_I / \Delta^p. \quad (3.11)$$

It follows that in the low temperature limit the photoinduced signal amplitude $T (\simeq n_{pe})$ is independent of temperature and its magnitude is proportional to photoexcitation intensity $\mathcal{E}_I$.

The second limiting situation is the case when $n_{pe} \ll n_{T}$. Then, taking into account that $n_{pe} = (n_{T'} - n_{T}) \ll n_{T}$ and $n_{T} = 2N(0)k_B T \exp(-\Delta^p / k_B T)$, the number of photogenerated quasiparticles at temperature $T$ is given by

$$n_{pe} = \frac{\mathcal{E}_I / \Delta^p}{1 + \frac{2 \nu}{N(0) \hbar \epsilon} \exp(-\Delta^p / k_B T)} \quad (3.12)$$

It is important to stress that Eq.\( (3.12)\) includes also the solution of Eq.\( (3.10)\) in the low temperature limit given by Eq.\( (3.11)\).

Similar derivation can be applied to determine the $T$-dependence of the number of photoexcited carriers in the case of a temperature dependent mean-field-like gap $\Delta_c(T)$ such that $\Delta_c(T) \rightarrow 0$ as $T \rightarrow T_c$. In our analysis we use BCS functional form for the temperature dependence of the mean-field-like gap magnitude – see Ref. [2]. In this case the approximation that $T \ll \Delta_c(T)$ does not hold as temperature is increased close to $T_c$. By including higher order correction to the quasiparticle distribution function [71] and using the approximation $n_{T} \simeq 2N(0)\sqrt{\pi \Delta_c(T)k_B T / 2E \exp(-\Delta_c(T)/T)}$ [167] with $k_B T \ll \Delta_c(0)$, this results in a slightly modified expression for $n_{pe}$ that again contains both the low and the high temperature limits

$$n_{pe} = \frac{\mathcal{E}_I / (\Delta_c(T) + k_B T/2)}{1 + \frac{2 \nu}{N(0) \hbar \epsilon} \sqrt{2k_B T / \pi \Delta_c(T)} \exp(-\Delta_c(T)/k_B T)} \quad (3.13)$$

Note that in Eqs.\( (3.12)\) and \( (3.13)\) the explicit form of $n_{pe}(T)$ (and hence $\mathcal{A}(T)$ or $T(T)$) depends only on the ratio $k_B T / \Delta(0)$, showing that the intensity of the photoresponse is a universal function of $k_B T / \Delta$ as long as the particular functional form of temperature dependence of $\Delta$ is the same. We plot the temperature evolution of $n_{pe}$ given by expressions \( (3.12), (3.13)\) for different values of $\Delta(0)/k_B T_c$ in Figure 3.7 a) and b). The dimensionless constant $\frac{2 \nu}{N(0) \hbar \epsilon}$ is estimated [see section 4.2 in next chapter] to be in the range of 10-100 for YBCO – in Fig. 3.7 the value 50 is used.

Another important feature of the expressions \( (3.12)\) and \( (3.13)\) is that at $T = 0$, $n_{pe} \propto 1/\Delta(0)$, which allows a determination of $\Delta(0)$ as long as the experimental parameters required to calculate $\mathcal{E}_I$ are recorded sufficiently precisely. At last it should be stressed that the model predicts a linear dependence of the photoinduced transient amplitude on the photoexcitation intensity at low photoexcitations. The

\footnote{Since the main $T$-dependence is in the exponential term Eq.\( (3.13)\) is very similar to Eq.\( (3.12)\) with $\Delta_c(T)$ instead of $\Delta^p$.}
linear dependence of the fast transient amplitude on photoexcitation intensity was shown experimentally [see Figure 2.8] to hold in a range of more than one order of magnitude in intensity, supporting the model.

Since the decay of each phonon involves the creation of two quasiparticles, the number of high frequency phonons is proportional to the square of the number of quasiparticles $n_{q}^2$, at temperature $T'$. At higher pulse energies when $n_{pe}$ becomes large, one would expect a crossover of the photoresponse from a linear dependence on laser power, $n_{pe} \propto I$ to a square root dependence $n_{pe} \propto \sqrt{I}$ at very high intensities.

### Anisotropic gap with nodes.

If the gap is strongly anisotropic and contains nodes on the Fermi surface - such as for $d$-wave or strongly anisotropic $s$-wave pairing - there is no clear gap in the energy spectrum. Nevertheless the quasiparticle density of states (DOS) still has a strong energy dependence and a separation of low and high energy quasiparticles still exists, albeit it is less pronounced than in the case of an isotropic gap. For an anisotropic gap with nodes one can approximate the quasiparticle DOS as a function of energy $\varepsilon (\varepsilon = E - E_F)$ as:

$$N(\varepsilon) = N(0) \left( \frac{\varepsilon}{\Delta_a} \right)^\eta (\varepsilon \ll \Delta_a),$$

where $\Delta_a$ is the characteristic energy scale separating the low and high-energy quasiparticles and the exponent $\eta$ depends on the topology of the nodes on the Fermi surface. For a two dimensional Fermi surface (with nodes) $\eta = 1$, while for a three-dimensional one $\eta = 2$.

In the high temperature limit, when the energy relaxation is determined by the high energy phonons decay, we expect, apart from more complicated expressions with more parameters, the temperature dependence to be very similar to the s-wave case. In the low temperature limit, when the energy is accumulated in the quasiparticle system, the difference in the temperature and intensity dependences between s-wave and d-wave prediction should be observed.

The calculation [71] gives the expression for the number of photogenerated quasiparticles as a function of temperature

$$n_{pe} = \frac{2GN(0)(k_BT)^{\eta+1}}{\Delta_a^{\eta}} \left[ \left( 1 + \frac{E_I^\eta \Delta_a}{2FN(0)(k_BT)^{\eta+2}} \right)^{\frac{\eta+1}{\eta+2}} - 1 \right],$$

where the numerical factor $F$ and $G$ are given by $F = \int_0^\infty \frac{x^{\eta+1}}{\exp(x)+1}dx$ and $G(\eta) = F(\eta + 1)$.

A feature of the model prediction for a $d$-wave gap, which is particularly important for the comparison with the experiment, is the peculiar sub-linear dependence of $n_{pe}$ on the laser pump intensity, $n_{pe} \sim \mathcal{E}_I^{\frac{\eta+1}{\eta+2}}$ at low temperatures. In the high temperature limit, on the other hand, we can expand the term in brackets [Eq.(3.15)] to obtain a
3.4. Femtosecond spectroscopy in materials with a small energy gap.

Figure 3.7: The predicted $T$-dependence of the photoexcited carrier density in the case of a) a mean-field-like $T$-dependent gap given by Eq.(3.13), b) a $T$-independent gap given by Eq.(3.12). In both cases the value of the dimensionless constant $B = \frac{2\mu}{N(0)k_B} \approx \frac{1}{2}$ was estimated be 50. c) The predicted $T$-dependence of $n_{pe}$ in the case of an anisotropic gap with nodes using Eq.(3.15): 2-D FS (solid line for $\Delta_a = \Delta_0$, dotted line for $\Delta_a = \Delta_{BCS}(T)$) and 3-D FS (dashed line for $\Delta_a = \Delta_0$, dotted line for $\Delta_a = \Delta_{BCS}(T)$). Inset: The two curves for $\Delta_a = \Delta_0$ in the wider temperature range.
crossover to linear behavior with a temperature-dependent slope

\[ n_{pe} = \frac{2G \eta + 1}{k_B T \eta + 2}. \]  

(3.16)

It should be pointed out that in the high temperature limit the phonon contribution becomes increasingly important and the decrease of the number of photogenerated quasiparticles with temperature will eventually become exponential, like in the case of an isotropic T-independent gap.

In Figure 3.7 c) the low temperature expression for the photoinduced carrier density in the case of gap with nodes is plotted with \( \eta = 2 \) (3D DOS, solid line) and \( \eta = 1 \) (2D DOS, dashed line) and the same values of \( N(0) \) and \( \mathcal{E}_I \) as used in panels a) and b) for an isotropic gap. We consider both the T-independent and the BCS-like T-dependent gap. In both cases \( (\eta = 2 \text{ and } \eta = 1) \) the two dependences are quite similar at low temperatures, showing the decrease in the photoexcited carrier density already at low temperatures in contrast to the T-independence at low temperatures in case of isotropic gap. In the case of the T-dependent gap (e.g. of BCS form) in Eq.(3.15) the curves for \( n_{pe} \) show an upturn from the T-independent gap case as \( T_c \) is approached (only close to \( T_c \) the effect of temperature dependence of the gap on \( n_{pe} \) should be observed). However, close to the superconducting transition temperature \( n_{pe} \) is already small compared to the number of phonons so the high temperature solution should be used. Near \( T_c \) therefore, \( n_{pe} \) for the BCS-like T-dependent d-wave gap should behave similarly to the case of an isotropic gap. In inset to Figure 3.7 c) the T-dependence of \( n_{pe} \) for the T-independent gap is plotted; at higher temperatures instead of an exponential fall-off with increasing temperature (the isotopic gap case) the photoexcited quasiparticle number decreases according to the power law.

From the above analysis we can say that from the data on amplitude of the photoinduced transient the difference between the s-wave and d-wave (or strongly anisotropic s-wave) gap symmetry can be observed at low temperatures only. Instead of a linear dependence of the fast transient amplitude on photoexcitation intensity, as observed in all the data available to date, the dependence should be sub-linear in a d-wave case. Secondly, in a d-wave case the signal magnitude should decrease with increasing temperature already at low temperatures - which has also not been observed. Instead, the signal was found to slightly increase with increasing temperature. The time-resolved data seem to support an isotropic gap.

### 3.4.3 The quasiparticle relaxation rates.

In this section we discuss the temperature dependences of the relaxation time, focusing on the anomaly observed near \( T_c \) [see Figure 3.4]. As already discussed, the relaxation rate of the photoinduced quasiparticles near \( T_c \) is dominated by energy transfer from high-frequency phonons with \( \hbar \omega > 2\Delta \) to phonons with \( \hbar \omega < 2\Delta \).

To describe the relaxation of non-equilibrium quasiparticles in this case we
consider the kinetic equation for phonons taking into account phonon-phonon scattering [168]

$$\frac{\partial n_\omega}{\partial t} = I_{ph-\text{ph}}\{n_\omega\}.$$ \hspace{1cm} (3.17)

Here phonon-phonon scattering integral has the following form

$$I_{ph-\text{ph}}\{n_\omega\} = 2\pi \sum_{q_1,q_2} |w_{q_1,q_2}|^2 \left\{ \frac{1}{2} \left[ (n_\omega+1)n_{\omega_1}n_{\omega_2} - n_\omega (n_\omega+1)(n_{\omega_2}+1) \right] \delta (\omega-\omega_1-\omega_2) 
+ [(n_\omega+1)(n_{\omega_1}+1)n_{\omega_2} - n\omega n_{\omega_1}(n_{\omega_2}+1)] \delta (\omega_2-\omega-\omega_1) \right\}, \hspace{1cm} (3.18)$$

with $w_{q_1,q_2}$ being the anharmonic coupling constants and $n_\omega$ the phonon distribution function. We neglect the electron-phonon scattering integral, since at temperatures close to $T_c$ the relative contribution of quasiparticles to the relaxation of phonons is small due to relatively small number of quasiparticles compared to the number of phonon modes $N(0) \ll \nu$. Electron-phonon collisions can play an important role only at temperatures $T'$ (non-equilibrium temperature of the quasiparticle-high frequency phonon system after photoexcitation) much lower than $T_c$. But since (as shown in Figure 3.4) $T(\propto n_{pe})$ is nearly constant at low temperature -- $T'$ cannot be small.

The energy relaxation time can be obtained by considering the rate of change of number of low energy phonons that can be calculated by multiplying Eq.(3.17) with $\omega_q$ and sum over $q$, satisfying the condition $0 < \omega_q < 2\Delta(T)$. We make the approximation that the anharmonic coupling constant is momentum independent $w_{q_1,q_2} = w$. The resulting equation describing the relaxation of $T'$ is given by (detailed derivation is given in Ref. [71]):

$$\frac{\partial T}{\partial t} = \frac{1}{\tau_{ph}} (T' - T) \hspace{1cm} (3.19)$$

$$\frac{1}{\tau_{ph}} = \frac{9\pi \nu^2 \omega^2 k_B T' \Delta(T)}{(\hbar c)^3}. \hspace{1cm} (3.20)$$

Eq.(3.19) is rather similar to the one derived by Allen [92] for the temperature relaxation in the electron-phonon system in normal metals, except that it describes the phonon energy relaxation modified by a gap in the quasiparticle spectrum.

The phonon-phonon relaxation time [Eq.(3.20)] can be expressed in terms of an experimental parameter, namely the Raman phonon linewidth $\Gamma_\omega$ giving (see Ref. [71]) the following form:

$$\frac{1}{\tau_{ph}} = \frac{12\Gamma_\omega k_B T' \Delta(T)}{\hbar \omega^2}. \hspace{1cm} (3.21)$$

The relaxation time for the temperature dependent gap $\Delta_c(T)$ is expected to show a divergence $\tau_{ph} \propto 1/\Delta_c(T) \rightarrow \infty$ due to the gap closing as $T_c$ is approached from
below. A divergence in relaxation time at \( T_c \) was indeed observed in optimally doped cuprates [66, 68, 85]. A similar divergence of the relaxation time was calculated previously by Tinkham [162] and Schmidt and Schön [163], albeit for somewhat differently created nonequilibrium situations.

The typical relaxation timescale \( \tau_{ph} \) given by the formula Eq.(3.21) is very close to the experimentally observed values. From the data on the Raman linewidth of the \( \text{A}_1g\)-symmetry apical O(4) phonon mode in YBCO - already shown to be particularly anharmonic [169] - \( \Gamma_{\omega} \approx 13 \text{ cm}^{-1} \) and \( \omega \approx 500 \text{ cm}^{-1} \) at \( T' \approx T = T_c/2 \), and using \( \Delta \approx (T_c/2) \approx 200 \text{ cm}^{-1} \) one obtains\(^5\) \( \tau_{ph} = 1.3 \text{ ps} \).

At low temperatures the quasiparticle temperature \( T' \) is much higher than the lattice temperature \( T \) and the formula is expected to fail. However, from the temperature dependence of the transient amplitude \( T \) [Figure 3.4 c)] we see that the number of photogenerated quasiparticles (which is proportional to \( T \)) is nearly constant at low temperatures. \( T' \) can therefore be estimated from Eq.(3.11). Taking into account that the number of thermally excited quasiparticles is \( n_T \approx 2N(0)\Delta(0)\exp(-\Delta(T)/k_BT) \) one gets the expression for the non-equilibrium temperature \( T' \):

\[
k_BT' \approx \Delta(T)/\ln \left\{ 1/(\mathcal{E}_I/2N(0)\Delta(0)^2 + \exp(-\Delta(T)/k_BT)) \right\}.
\]

At low temperatures \( T' \approx \Delta(T)/k_B\ln \left\{ (2N(0)\Delta(0)^2/\mathcal{E}_I) \right\} \approx T_c/2 \), while in the high temperature limit the exponent in the logarithm becomes large and \( T' \approx T \). Combining Eqs.(3.21) and (3.22) one gets an expression for the quasiparticle relaxation time as a function of lattice temperature \( T \) and photoexcitation energy density \( \mathcal{E}_I \) which is valid for all temperatures \( 0 < T < T_c \).

\[
\frac{1}{\tau_{ph}} = \frac{12\Gamma_{\omega} \Delta(T)^2}{\hbar \omega^2 \ln \left\{ 1/(\mathcal{E}_I/2N(0)\Delta(0)^2 + \exp(-\Delta(T)/k_BT)) \right\}}.
\]

To enable a comparison of expression 3.23 with experiments we use Raman data on high-frequency optical phonon linewidths, a value of gap frequency of 200 cm\(^{-1}\) \( (2\Delta(0) \approx 9k_BT_c) \), the values of \( N(0) = 2.2 - 5 \text{ eV}^{-1}\text{cell}^{-1}\text{spin}^{-1} \), and the BCS functional form for \( \Delta(T) = \Delta_c(T) \). \( \mathcal{E}_I \) is calculated using the pulse energy of 0.1 nJ incident on a 100 nm thick film with a spot size of \( \sim 60 \mu m \) diameter. We obtain the temperature dependence of the relaxation time \( \tau_{ph} \) as shown by the solid line in Figure 3.8. The comparison of the theory [Eq.(3.23)] with data for optimally doped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) samples [66, 85] shows good agreement, especially near \( T_c \), with no adjustable parameters.

Some experimental data on Bi\(_2\)Sr\(_2\)Ca\(_{1-y}\)Y\(_y\)Cu\(_2\)O\(_8\) [154] and HgBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8+x}\) [155] show an upturn in the relaxation time at low temperatures, which is also partly present in the data in Fig. 3.8. Although Eq.(3.23) is derived for temperatures close to \( T_c \), an upturn at low temperature is expected if we reduce the energy density per pulse \( \mathcal{E}_I \). (In fact in the limit of \( \mathcal{E}_I \to 0 \), Eq.(3.23) gives \( \tau_{ph} \propto 1/T \) at low \( T \).)

\(^5\) 1 eV corresponds to 8044 cm\(^{-1}\) (spectroscopy units).
Figure 3.8: The relaxation time \( \tau \) as a function of temperature for a temperature-dependent gap [Eq. (3.23)]. The data are for near-optimally doped samples \( (T_c = 90\, K) \) from Han et al. [66] (full circles) and Demsar et al. [181] (open circles).

At the end we make a brief quantitative comparison of the relaxation rates for a gapped and gapless material. Comparing the relaxation time of a gapped material with the one in normal metal described by Allen’s formula [92] (see section 3.1.2) one obtains:

\[
\frac{\tau_{ph}}{\tau_{e-ph}} \sim \frac{\lambda h^3 \nu^4}{4\pi (k_B T)^2 \Delta \Gamma}.
\] (3.24)

Inserting experimental values for \( \omega \) and \( \Gamma \) we find the anharmonic phonon decay time in a high-\( T_c \) superconductor to be approximately two orders of magnitude larger than electron-phonon relaxation in a gapless material as \( \tau_{ph}/\tau_{e-ph} \sim 60 - 200 \) for \( T \simeq T_c \) as expected.

### 3.4.4 Discussion and criticism.

The analysis was made assuming that the rate limiting step for quasiparticle relaxation is anharmonic decay of high-energy phonons, while the direct electron-phonon relaxation was assumed to be small. To justify this quantitatively, one has to calculate the direct electron-phonon relaxation rate \( \tau_1 \). The derivation was made using the usual electron-phonon collision integral (see Appendix in Ref. [71] for details) giving

\[
\frac{1}{\tau_1} = \frac{\pi N(0) \lambda \Delta_c(T) c}{2\nu}.
\] (3.25)
We see that the electron-phonon relaxation rate [Eq.(3.21)], when compared to the phonon relaxation rate is reduced by the factor \( N(0)h_c/\nu \ll 1 \), so

\[
\frac{\tau_{ph}}{\tau_1} = \frac{\pi \hbar^2 N(0)\lambda \omega^2}{24\nu \Gamma \omega k_B T} < 1 ,
\]

(3.26)

and can therefore be neglected. However if the number of phonon modes involved in relaxation is significantly smaller than estimated, the ratio \( \tau_{ph}/\tau_1 \) may approach unity. In this case the electron-phonon collisions can also contribute to the phonon relaxation. However, the temperature dependence of the relaxation rate \( 1/\tau_1 \) is very similar to the anharmonic relaxation rate \( 1/\tau_{ph} \); both being proportional to \( \Delta_c(T) \) so the two contributions to the relaxation may be difficult to separate experimentally.

The expression for the relaxation time \( \tau_{ph} \) [Eq.(3.23)] without any fitting parameters fits the YBCO data very well [Figure 3.8], so it appears to be reasonable to assume that anharmonic relaxation described by Eqs.(3.21) and (3.23) is dominant in near optimally doped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\).

Another feature of the model that needs to be discussed is the assumption that high energy phonons govern the relaxation of photoexcited quasiparticles. This assumption is based on the ratio of the phonon specific heat with respect to the specific heat of some other collective modes (e.g. magnons..). Since the number of high-energy phonon modes \( \nu \) for YBCO is of the order of \( 20 - 36 \) (depending on the magnitude of the gap \( 2\Delta_c(0) \)), the phonon specific heat is much higher than for example specific heat of magnons with the number of modes of the order of \( 2 - 4 \). However, the energies of the pseudogap in heavily underdoped samples (see chapter 4) obtained from the fit to the model and/or implied from other optical measurements [166, 170] are of the order of the phonon cut-off frequency \( \omega_c \), so the effective number of high energy phonon modes \( \nu \) decreases. Therefore, some additional high energy collective modes (e.g. magnons) might contribute to the relaxation. What is important is the fact that the predicted temperature dependences of amplitudes and the relaxation times are the same for all high energy excitations with Bose distribution [Eq.(3.7)]. Only the dimensionless constant \( B = \frac{2\nu}{N(0)h_c} \) is affected.

At the end we should discuss the effect of gap anisotropy on the relaxation time of the measured fast transient. First, in case of the \( d \)-wave gap we would expect a distribution of relaxation times, contrary to the exponential decay that was found in most of the experiments - supporting the isotropic gap. Secondly, no single divergence of \( \tau \) at \( T_c \) should be observed. The important question that still needs to be theoretically investigated is the magnitude of the relaxation time in case of the \( d \)-wave gap. One could argue that the relaxation should be metallic like, since no clear gap in the DOS exists in this case. Kinematic constraints, on the other hand, might introduce a mechanism for slow quasiparticle recombination dynamics in nodes as proposed by Feenstra et al. [171].
3.5 Slow-component in photoinduced absorption.

As already discussed in section 3.3.3 in addition to the quasiparticle response that occurs on the picosecond timescale a distinct slower response was also consistently observed on YBa$_2$Cu$_3$O$_7$–δ [69], Bi$_2$Sr$_2$CaCu$_2$O$_8$, and Bi$_2$Y$_x$Ca$_{1-x}$SrCu$_2$O$_8$ [87], and more recently on the charge-density-wave quasi one-dimensional Peierls semiconductor K$_{0.3}$MoO$_3$ [146]. It was shown to be of non-bolometric origin (detailed analysis is given also in Ref. [87]) and occurs on a timescale of $10^{-8}$ s or longer. Its anomalous $T$-dependence [69, 172], which is qualitatively different from the $T$-dependence of the fast quasiparticle recombination dynamics, lead the authors to a suggestion that the signal is due to the localized states near the Fermi energy. However, the processes involved have not been discussed in any detail in literature thus far.

![Figure 3.9: Photoinduced absorption due to slow component pile-up is given by the amplitude $D$ (the non-zero signal at negative time delays), whereas the contribution due to single pump pulse is given by $d_0$.](image)

In Fig. 3.9 the photoinduced transient taken on YBCO at T=80 K is shown (squares). After photoexcitation ($t = 0$) the signal relaxes within 10 ps to some non-zero value that can be represented by a constant on the 100 ps timescale. The lifetime of the slow component $\tau_L$ cannot be directly measured, since it appears to be longer than the inter-pulse separation of $t_r \simeq 10 – 12 \text{ ns}$ of our laser. This results in a signal pile-up due to accumulation of responses from many pulses. The magnitude of this pile-up $D$ [Fig. 3.9] at negative time delay $t_1$, is several times larger than a single pulse contribution $d_0$ given be the difference between photoinduced signals at times $t_3$ and $t_1$.
Figure 3.10: T-dependence of the steady-state temperature increase in the illuminated spot $\Delta T$ calculated using Eq.(2.3) and published values of thermal conductivities [95, 96, 105]. In the inset the temperature dependence of the transient temperature increase due to a single pulse excitation for YBCO single crystal is shown using Eq.(A.12).

In order to estimate the temperature dependence of the possible bolometric contribution to the slow ($\tau \gg ns$) component in time-resolved pump-probe experiments we can assume that the signal amplitude is proportional to the temperature increase

$$D \text{ (or } d_0) \approx \frac{\delta \alpha}{\delta T} \Delta T,$$

where $\alpha$ is the absorption coefficient at the probe wavelength, and $\Delta T$ is the temperature increase. If one is interested in the slow component due to a single pump pulse given by $d_0$ in Figure 3.9, one should calculate the initial temperature rise using Eq.(2.6) [more accurately Eq.(A.12)] for the transient heating. For comparison with the temperature dependence of the pile-up amplitude $D$ however, the relevant temperature increase is given by Eq.(2.3) for the steady state heating. Assuming that $\frac{\delta \alpha}{\delta T}$ is only weakly temperature dependent, the T-dependence of the bolometric contribution to $D$ or $d_0$ is determined by T-dependences of $\Delta T$ given by Eqs.(2.3) and (A.12) respectively. In Figure 3.10 temperature dependence of the steady-state $\Delta T$ is shown for YBa$_2$Cu$_3$O$_{7-\delta}$, SrTiO and K$_{0.3}$MoO$_3$ calculated using Eq.(2.3) and published values of thermal conductivities [95, 96, 105]; in the inset there is T-dependence of the single pulse $\Delta T$ for YBa$_2$Cu$_3$O$_{7-\delta}$ as given by Eq.(A.12).
No anomaly is observed near $T_c$ — shown by arrows — although the T-dependence of thermal conductivities $\kappa_a$, $\kappa_b$ in YBa$_2$Cu$_3$O$_{7-\delta}$ and K$_{0.3}$MoO$_3$ exhibit strong T-dependence near $T_c$. It follows that the bolometric contribution to the slow component has a mild T-dependence. The only anomaly in the slow component amplitude could be observed at very low temperatures where the bolometric signal is predicted to have a strong T-dependence as seen in Fig. 3.10.

Since thermal effects cannot account for anomalies in the slow component amplitude we examine in this section qualitatively the photoinduced absorption from localized intra-gap states using similar analysis as in the previous section. Again we consider two different temperature dependences of the gap: a BCS-like collective gap and a $T$-independent (pseudo-)gap existing also above $T_c$.

3.5.1 Theoretical model for intra-gap state relaxation.

Photoexcitation and initial relaxation mechanisms are supposed to be the same as for the fast picosecond component and are shown in Figure 3.11 a). The pump pulse excites carriers into a higher-lying band. The photoexcitation is followed by a fast initial relaxation increasing the occupation number of in-gap localized states. Their occupation is measured by the probe pulse through the photoinduced absorption. The lifetime of the slow signal $\tau_L$ could not be measured directly; it appears to be longer than the inter-pulse separation of $t_r \approx 12$ ns and the photoinduced transmittance does not relax completely between pulses [see Fig. 3.9]. As a result, it represents an accumulation of the responses from many pulses. Assuming for simplicity that the relaxation of the signal is exponential, we can write an equation for the steady state amplitude $D$:

$$D = d_0 \sum_{n=0}^{\infty} \exp(-nt_r/\tau_L) = d_0/(1 - \exp(-t_r/\tau_L)) \quad (3.27)$$

Here $d_0$ is the amplitude of the signal from a single pulse and $\tau_L$ is the relaxation time. Usually $D \gg d_0$ and we can expand the exponent in the denominator of Eq.(3.27) to obtain $\tau_L = t_r(D/d_0)$. From the experiments [69, 146] it appears that $\tau_L > 10$ ns. This is long in comparison with the phonon relaxation time and with the phonon escape time from the excitation volume into the bulk or thin film substrate, which is typically 100 ps. We can therefore ignore phonon escape effects and discuss only intrinsic electronic relaxation processes.

The process giving rise to the actual photoinduced optical signal from the intra-gap states is shown in Fig. 3.11 b). Here we do not discuss the optical probe process in detail, but make a very general assumption that the photoinduced change in transmission $\Delta T(t)/T$ or reflectivity $\Delta R(t)/R$ of the sample is proportional to the photoinduced density of localized states. The signal $D$ (or $d_0$) is then proportional to the number of photoinduced localized states and its $T$-dependence is mainly determined by the occupation of the intra-gap states.
Chapter 3. The Physics of Femtosecond Pump-Probe Spectroscopy.

Figure 3.11: a) The pump-probe optical diagram. The pump process exciting carriers into higher-lying band is represented by 1. This is followed by the fast relaxation (2) increasing the occupation number of localized states near the Fermi energy. The probe pulse (3) measures the density of the photoinduced localized carriers. b) A schematic diagram of the terms contributing to the relaxation of intra-gap states in a superconductor with the gap $2\Delta$. Solid and dashed lines correspond to occupied and unoccupied states, respectively. (In the case of a CDW gap, the $e-h$ pairs take the place of Cooper pairs, so the rate equation remains the same.)

Since the relaxation time $\tau_L$ is long in comparison with quasiparticle relaxation time $\tau_{ph}$ [Eq. (3.23)] and phonon relaxation times, we assume that phonons and quasiparticles can be described by equilibrium densities $N_{ph}$ and $N_{qp}$ respectively. For relaxation of localized carriers we apply arguments similar to those originally proposed by Rothwarf and Taylor [161]. The rate equation for the total density of localized excitations $N_L$ is then given by:

$$\frac{dN_L}{dt} = -RN_L^2 - \tilde{\gamma}N_L + \gamma N_{qp} + \beta N_{ph}. \quad (3.28)$$

A schematic diagram of the relaxation processes is given in Figure 3.11 b). The first term in Eq.(3.28) describes the recombination of two localized excitations to a Cooper pair with a recombination rate $R$. The second and the third terms describe the exchange of an electron or a hole between the localized and quasiparticle states with densities $N_L$ and $N_{qp}$ respectively and with rates $\tilde{\gamma}/\gamma \propto \exp \left( -\Delta E/k_B T \right)$, where $\Delta E$ is the energy barrier between trapped carriers and quasiparticles [173]. We assume that the energy barrier (in first approximation) does not depend on whether the localized state is occupied or not. The last term describes the spontaneous creation of localized excitations by phonons with rate $\beta$. 
3.5. Slow-component in photoinduced absorption.

Assuming the ansatz for $N_L = N_{L0} + n_L$, where $N_{L0}$ is the equilibrium density of localized carriers and $n_L$ is the photoinduced density created by the laser pulse and taking into account that $N_{ph}$ and $N_{qp}$ are given by their equilibrium values, we can rewrite Eq.(3.28) to obtain

$$\frac{dn_L}{dt} = -Rn_L^2 - (2RN_{L0} + \tilde{\gamma})n_L .$$

(3.29)

This equation is sufficiently general that it can be applied to different superconductors and different gaps. (For the case of the CDW gap, Cooper pairs are replaced by $e - h$ pairs.)

The analytic solution of Eq.(3.29) has the form

$$n_L(t) = \frac{n_L(0)}{1 + \frac{n_L(0)R}{\tau} \exp(t/\tau) - \frac{n_L(0)R}{\tau}} .$$

(3.30)

where $1/\tau = 2N_{L0}R + \tilde{\gamma}$. Since we are interested in the steady state solution (in Figure 3.11 noted as $D$) for the case of excitation by a repetitive laser pump pulse train, we use the condition that the total number of localized excitations that recombine between two laser pulses should be equal to the number of localized excitations created by each laser pulse, which is in turn proportional to the number of photogenerated quasiparticles

$$n_L(0) - n_L(t_r) = \eta n_{pe}$$

(3.31)

Here $n_{pe}(T)$ is the number of photoinduced quasiparticles at temperature $T$ created by each laser pulse [given by Eq.(3.13) for the mean-field-like gap and by Eq.(3.12) for a T-independent gap], $\eta \propto \gamma \tau_{ph}$ is the probability of trapping a photoinduced quasiparticle into a localized state, and $\tau_{ph}$ is the relaxation time of photoinduced carriers discussed in section 3.4.3. Since $\tau_{ph} \approx 1/\Delta(T)$ [see Eq.(3.23)] we approximate $\eta = \eta'/\Delta(T)$. Combining Eqs.(3.30) and (3.31) one obtains the stationary solution for $n_L(0)$ [72]

$$n_L(0) = N_{L0}(1 + \tilde{\gamma}/2RN_{L0}) \left[ \sqrt{1 + \frac{\eta n_{pe}}{N_{L0}^2(1 + \tilde{\gamma}/2RN_{L0})^2R\tau_r}} - 1 \right] .$$

(3.32)

Depending on temperature dependences of $R$, $N_{L0}$, and $\tilde{\gamma}$ one can simplify Eqs.(3.30) and (3.32) in low temperature and high temperature limits. Below, we discuss the two limits in case of a mean–field-like temperature dependent gap and a T-independent gap.

**Temperature dependent gap.**

We first consider a superconductor with a mean–field-like gap $\Delta_c(T)$ (which can also be used in the case of a gap formed by a CDW). In order to simplify the general solutions 3.30 and 3.32, we first estimate the temperature dependences of $R$, $N_{L0}$, and $\tilde{\gamma}$. 
When considering the \( T \)-dependence of a bi-particle recombination rate \( R \) of localized carriers within a gap \( 2\Delta_c(T) \) to the condensate, we use the Landau-Ginzburg approach. In the vicinity of the second-order phase transition we expand the rate \( R \) in even powers of the order parameter \[72\]

\[
R = \gamma + \alpha \Delta_c^2(T) + \beta \Delta_c^4(T) + .. \tag{3.33}
\]

Since above \( T_c \) all recombination processes disappear as \( \Delta_c(T > T_c) = 0 \) it is evident that \( \gamma = 0 \). Close to \( T_c \), when \( \Delta_c(T) \) is small, the relaxation rate is determined by the lowest power of the order parameter

\[
R \simeq \tilde{\alpha} (\Delta_c(T)/c)^2 \tag{3.34}
\]

where \( \tilde{\alpha} \) is a positive constant, and \( c \) is the phonon spectrum cut-off frequency. This means that close to the phase transition we have slowing down of the relaxation dynamics [174], whereas at low temperatures the relaxation rate is close to constant. The same expansion is usually used for describing the relaxation rates of localized carriers in ferroelectrics [175]. On the other hand, more rigorous calculation gives the same relation [Eq.(3.34)] for the bi-particle recombination of quasiparticles at energies just above the gap [176, 177].

To relax the carriers in localized intra-gap states via quasiparticle states (the term \( \tilde{\gamma} n_L \) in Eq.(3.29)) an energy of the order of \( \Delta_c \) is required, and so this process is exponentially suppressed at low temperatures. The term proportional to \( N_{L0} \) is also small at low temperatures, because the number of thermally excited localized excitations is small as \( (k_B T/\Delta_c(0))^\mu \), where \( \mu \) depends on the density distribution of localized states \[6\]. Therefore, for the analysis of relaxation of localized carriers at low temperatures \( T \ll T_c \) we can retain only the first term in Eq.(3.29) giving a solution of the form:

\[
n_L(t) = n_L(0)/(n_L(0)Rt + 1). \tag{3.35}
\]

The number of photoinduced localized carriers due to a single photoexcitation pulse, \( \eta m_{pe} \), is typically small compared to the number of accumulated overall photoinduced density of localized carriers \( n_L(0) \), which follows from the experimental observation that \( \mathcal{D} > d_0 \). By applying \( \eta m_{pe} = n_L(0) - n_L(t_r) \ll n_L(0) \) we can estimate \( n_L(0) \) as

\[
n_L(0) = \sqrt{\frac{\eta m_{pe}(T)}{Rt_r}}. \tag{3.36}
\]

As a result, combining Eqs.(3.34) and (3.36) one obtains an expression for the

\[\text{Here some energy distribution of in-gap localized states is assumed. If only one energy level is assumed the temperature dependence of occupancy is exponential. It should be noted that, when comparing the model to experimental data (see section 4.3) several different energy distributions were used. The results show only weak dependence on the assumed distribution.}\]
3.5. Slow-component in photoinduced absorption.

Temperature dependence of the photoinduced transmission (or reflectivity) amplitude $D$ at low temperatures

$$D \propto n_L(0) = \sqrt{\frac{\eta n_{pe}(T)}{t_r} \frac{c}{\Delta_c(T)}}$$ \hspace{1cm} (3.37)

where $n_{pe}(T)$ for a BCS-like case is given by Eq.(3.13) and $\eta = \eta'/\Delta_c(T)$. This result is a limit of Eq.(3.32) when $2N_{L0}R + \bar{\gamma}$ approaches zero.

Near $T_c$, when the number of thermally excited localized carriers becomes comparable or larger than the number of nonequilibrium carriers, the relaxation terms $2RN_{L0}n_L$ and $\bar{\gamma}n_L$ become dominant and the solution to Eq.(3.29) has an exponential rather than a power law time dependence of the form

$$n_L(t) = n_L(0) \exp\left(-t/\tau\right)$$ \hspace{1cm} (3.38)

with $1/\tau = 2R(T)N_{L0} + \bar{\gamma}$. For $T \to T_c$, the temperature dependence of the photoinduced signal amplitude $D$ is then given by

$$D \propto n_L(0) = \frac{\eta n_{pe}(T)}{(2N_{L0}R(T) + \bar{\gamma})t_r}.$$ \hspace{1cm} (3.39)

The predicted amplitude of the signal increases with increasing $T$ up to $T_c$ and drops to zero above $T_c$.

The two limiting temperature dependences of the numbers of photoinduced localized carriers $n_L(0)$ for the case of a BCS-like temperature dependent gap given by Eqs.(3.37) and (3.39) are plotted in Figure 3.12 a) and b) respectively. In both $n_{pe}(T)$ [Eq.(3.13)] is used $\Delta_c(0)/k_B T_c = 4$ and dimensionless constant $\frac{2\nu}{N(0) \hbar} = 50$.

Temperature independent gap.

In the case of a $T$-independent (pseudo-)gap $\Delta^p$ we assume that the gap exists at all temperatures. In this case, it is better to consider it as an energy-level splitting between paired and unpaired states (like in a Bose condensate of pre-formed pairs above $T_c$). The main difference is that the gap is $T$-independent and exists above $T_c$. Since the gap does not close at $T_c$ the recombination rate does not go to zero at $T_c$. Therefore the $T$-dependent recombination rate $R$ given by Eq.(3.34) is replaced by a constant $\Gamma$. However, below $T_c$ the presence of the condensate may also have an effect on the recombination of localized excitations. Again, the relaxation rate can be expanded in terms of even powers of order parameter magnitude $\Delta$. Near $T_c$ (when the order parameter is strongly $T$-dependent) the order parameter is small and we can keep only the lowest power in $\Delta^2$. If we assume that the order parameter exhibits mean-field behavior ($\Delta \propto \sqrt{1-T/T_c}$) then:

$$R \simeq \alpha(1-T/T_c) + \Gamma$$ \hspace{1cm} (3.40)

where $\alpha$ is the phenomenological constant in general different from 0.
Figure 3.12: A temperature dependence of the photoinduced in-gap localized states using a) the low-temperature limit represented by Eq.(3.37), and b) the high-temperature limit given by Eq.(3.39). The solid line represents the solution when $\tilde{\gamma} = 0$, whereas the broken lines are for non-zero $\tilde{\gamma}$ terms. As can be seen in inset to panel b), $\tilde{\gamma}$ term does not affect the low temperature behavior and only supresses the divergence at $T_c$.

To obtain the photoinduced signal amplitude $D$, we substitute Eq.(3.40) into Eq.(3.36):

$$D \propto n_L(0) = \sqrt{\frac{\nu n'_{pe}}{(\alpha(1 - (T/T_c)^\beta) + \Gamma)t_r}}, \quad (3.41)$$

where $\beta$ is a constant (generally it can also be different from 1) and $n'_{pe}$ is the photoinduced quasiparticle density in case of the $T$-independent gap given by Eq.(3.12). In contrast to the case with the $T$-dependent gap expression (3.41) is non-zero above $T_c$ reducing to

$$D \propto n_L(0) = \sqrt{\frac{\nu n'_{pe}}{t_r}}, \quad (3.42)$$

It implies that the photoinduced absorption signal should remain observable well above $T_c$ and should reveal the presence of a pseudogap, if present.

Like in the case of a BCS-like gap a crossover to exponential relaxation [Eq.(3.38)] takes place when the number of thermally excited excitations becomes large, i.e. $T \sim \Delta^p$, and the second term in the Eq.(3.29) becomes dominant. It leads to a linear
3.5. Slow-component in photoinduced absorption.

intensity dependence of $\mathcal{D}$ given by a modified Eq.(3.39)

$$\mathcal{D} \propto n_L(0) = \frac{\eta n_{pe}'(T)}{(2N_{L0}\Gamma + \tilde{\gamma}) t_r}. \quad (3.43)$$

Note that this crossover may occur at very high temperatures since $T$-independent gap is typically $\Delta^p/k_B \gg 300K$.

![Graph](image-url)

Figure 3.13: The calculated temperature dependence of the photoinduced absorption from localized states in case of the $T$-independent pseudogap Eq.(3.41) with $\Delta^p/k_BT_c = 8$ and different $\alpha/\Gamma$ ratios.

In Figure 3.13 we plot calculated values of $\mathcal{D} \propto n_L(0)$ for the case of temperature independent pseudogap (which might be applicable e.g. in underdoped cuprates) as a function of temperature for different values of parameter $\alpha$ using Eq.(3.41). As it can be seen from Fig. 3.13 slow relaxation via localized states is present also above $T_c$. This effect is due to the temperature dependence of $n_{pe}'(T)$ controlled by the $T$-independent pseudogap above $T_c$ [see Eq.(3.12)].

From the photoinduced reflectivity data on YBCO (as in Figure 3.9), we find that close to $T_c$ the slow component amplitude $\mathcal{D}$ is on the same order as the amplitude of the fast component, $\mathcal{D} \approx T$. This suggests that also $n_L(0) \approx n_{pe}$ implying that the density of intra-gap states is comparable with the density of quasiparticle states.$^7$

$^7$ This statement should be taken with caution. We assumed that the transition probability is the same for localized carriers and quasiparticles. It should be noted however that, since localized state wave function can be represented as a sum through Bloch states of different symmetries [13], the selection rule for optical transition to a band of any symmetry 1.5 eV higher in energy can be accounted for. Therefore, the weight to the photoinduced absorption from localized carriers can be much higher than of the absorption from photoexcited quasiparticles. In this sense we can state that $n_L(0)$ and $n_{pe}$ are comparable to the order of magnitude.
This observation has important implications for the interpretation of frequency-domain spectroscopies, since it suggests that the spectra should show a significant intra-gap spectral density due to localized states, irrespective of the gap symmetry.

Assuming that the optical transition probability of the probe pulse is the same for the quasiparticles and the intra-gap states, from Eq. (3.39) one obtains

\[
\frac{D}{T} \sim \frac{n_L}{n_{pe}} = \eta \frac{\tau_L}{t_r}.
\]

(3.44)

From Fig. 3.9 \(D/T\) is typically 0.1 – 1 and using pulse repetition rate \(t_r = 12\ \text{ns}\) and \(\tau_L = 100\ \text{ns}\), one obtains an estimate of the trapping probability for carriers by localized states of \(\eta = 0.1 – 1\). Again, \(\eta\) can easily be overestimated by an order of magnitude, since selection rules for optical transition from localized and quasiparticle states might be substantially different.\(^7\)

### 3.5.2 Discussion.

The presented model for the slow component in the photoinduced absorption measurements on \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) [see Figure 3.5] describes qualitatively very well the temperature dependence of the slow component in this material. Recently, similar T-dependence has also been found in \(\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}\) [155], and \(\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}\) [178] giving evidence that this is an intrinsic property of HTSC. Moreover, slow component signal with similar temperature dependence was observed also in quasi-1D charge density wave semiconductor \(\text{K}_{0.3}\text{MoO}_3\) [146] [see section 5.2.2], where the nature of intra-gap excitations has been a subject of extensive study over the years (the reader is referred to Ref. [179] for a review).

In cuprate superconductors there is a spectroscopic evidence suggesting that there is a significant density of states in the gap possibly extending to the Fermi level. However, by normal spectroscopies it is difficult to determine whether the states in the gap are quasiparticle states or, for example, localized states. Time-resolved spectroscopy can answer this question rather effectively because of the different time- and temperature-dependences of the quasiparticles and localized carrier relaxations.

If we assume that the optical probe process is similar for the excited state absorption from localized states and from quasiparticles we can make a rough estimate for the density of the intra-gap states from the available data. Both optical probe processes involve the allowed transitions to the same final state – thus the assumption is reasonable. Moreover, from the probe pulse anisotropy measurements on \(\text{K}_{0.3}\text{MoO}_3\) (see section 5.2) it follows that the matrix elements for the fast and the slow component have the same symmetry, consistent with the assumption that the optical probe process is similar.\(^7\)

As far as the origin of the localized intra-gap states in the cuprates is concerned, it should be deferred until more data is available. However two of the most likely possibilities should be mentioned: (i) localized states associated with the
3.6 Summary.

In this chapter the basic physical concepts dealing with carrier relaxation dynamics in metals and semimetals are presented. In the first two sections we discussed femtosecond thermomodulation which was used to describe the fast transients in metals and displacive excitation of coherent phonons mechanism explaining the oscillatory components present in some data on semimetals and semiconductors. In section 3.3 we summarized the experimental results and theoretical ideas about the origin of anomalies near $T_c$ consistently observed in pump-probe experiments on high-$T_c$ superconductors.

In section 3.4 we presented the model [71] that describes the quasiparticle relaxation in case of a gap in the low energy excitation spectrum. We show that by measuring the change in absorption of the probe laser pulse with respect to the time after photoexcitation one measures the time evolution of the photoexcited quasiparticle density. Since the relaxation is strongly affected by the presence of a gap one can learn a lot about its nature and magnitude by measuring temperature, polarization, and intensity dependence of the photoinduced relaxation dynamics.

In section 3.5 we presented the model [72] describing the temperature dependence of the slow component, which was observed in the pump-probe experiments on YBa$_2$Cu$_3$O$_{7-\delta}$ [69, 70], K$_{0.3}$MoO$_3$ [146], Tl$_2$Ba$_2$CuO$_{6+\delta}$ [178], and HgBa$_2$Ca$_2$Cu$_3$O$_{8+x}$ [155] and is supposed to be electronic in origin. We considered the case where the photoinduced absorption is due to in-gap localized states and found good qualitative agreement with the data.
Chapter 4

Femtosecond spectroscopy of CaYBCO.

4.1 Introduction.

The femtosecond time-resolved optical spectroscopy measurements of CaYBCO (Ca$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$) system over a broad range of doping were motivated by first data on underdoped YBCO [70, 78]. Unlike the data on optimally doped samples [66, 69], where an abrupt drop in amplitude and divergence in relaxation time of the fast picosecond signal at $T_c$ were recorded [66, 69], no such anomalies were observed on underdoped samples. Absence of anomalies at $T_c$ suggested the presence of pseudogap above $T_c$.

In this chapter we present the results obtained on CaYBCO over a wide range of doping that were done to obtain deeper insight in the gap structure evolution in this material. The sample preparation and characterization was presented in section 2.2.1. The experiments on thin (underdoped) films were performed mainly in transmission configuration as given in Figure 2.4, whereas on single crystals (data on overdoped samples) the photoinduced reflectivity changes were measured. We used 70 fs pulses from Ti:sapphire laser at 1.5 eV for both the photoexcitation and the probe laser pulse. To avoid any coherent effects the pump and the probe were perpendicularly polarized. A typical average pump intensity was 5 mW and the illuminated spot diameter $\sim$ 60 $\mu$m giving the photoexcitation fluences $\sim$ 1 $\mu$J/cm$^2$. The ratio of pump and probe intensities was typically 100. The heating effects were accounted for as described in detail in section 2.1.5 giving the uncertainty in temperature $\pm$3 K.

In section 4.2 we summarize experimental results on quasiparticle dynamics (fast picosecond component) in CaYBCO over wide range of doping applying the analysis [71] from section 3.4. Some of the experimental data on strongly underdoped samples have already been presented before [see Refs. [70, 78, 85]] - we include the data in order to perform the analysis using the theoretical model presented in section 3.4. We first show the general systematics and make an estimate of the dimensionless constant $\frac{2\nu}{N(0)\Delta_e}$ used with fitting the T-dependence of the fast signal amplitude with
Eqs.(3.13) and (3.12). Than we focus on underdoped and overdoped data separately. In section 4.3 we present results of the analysis of the slow nanosecond component in the photoinduced absorption, which was attributed to localized in-gap states [72] (see section 3.5). After the discussion, where comparison with other spectroscopic methods is given we summarize the results.

4.2 Quasiparticle dynamics in CaYBCO.

In this section we discuss picosecond dynamics in $Y_{1-x}Ca_{x}Ba_{2}Cu_{3}O_{7-\delta}$ as a function of doping and temperature. We first reveal general features in amplitude and relaxation time of the fast transient.

Figure 4.1: Temperature dependences of the amplitude ($-T$ extracted from transmission data and $R$ from reflectivity data) of the ps component. The lines are the fits using Eqs.(3.12) - solid, and (3.13) - dashed (see text).

In Figure 4.1 the normalized temperature dependences of the photoinduced amplitude ($R$ and $T$ when reflectivity or transmission is measured respectively) of the fast ps transient are plotted for several samples at different doping levels. As one can see, the situation in overdoped region is quite similar to the data near optimal doping [66, 69] with the signal amplitude being susceptible to the superconducting transition. A rapid drop in the amplitude at $T_c$ is followed by a tail continuing up to 150 K in the optimally doped sample and up to about 100 K in the strongly overdoped one. At higher temperatures the signal amplitude becomes very small and it is very
4.2. Quasiparticle dynamics in CaYBCO.

difficult to distinguish it from the emerging "metallic"-like signal with approximately 0.1 ps decay time. This high temperature signal is probably due to the Allen [92] relaxation and/or some coherent artifact.

The situation is drastically changed in underdoped samples. The amplitude is constant up to temperatures high above $T_c$ and then gradually dropping at progressively higher temperatures as we go to more underdoped samples. Again, at higher temperatures the signal amplitude becomes hard to extract, since some very fast "metallic"-like signal becomes apparent. Crossover to metallic behavior is nicely demonstrated by Shi et al. [180] who measured the intensity dependence of the photoinduced reflectance at room temperature on 60K underdoped YBCO using 2eV probe energy. With increasing intensity the signal with 0.5 ps decay time evolves into metallic transient with opposite sign and decay time being pulse-width limited (< 100 fs), consistent with Allen’s model.

![Figure 4.2: Temperature dependences of the relaxation time $\tau_R$ of the picosecond component obtained by single exponential decay fit.](image)

In Figure 4.2 the temperature dependence of the relaxation time obtained from the fit [Eq.(2.2)] using a single exponential decay is shown for several samples. In overdoped samples, similar to the thin film data on the optimally doped sample [Figure 3.4], an anomaly is observed at 5-8 K below $T_c$. The relaxation time $\tau_R$ is nearly constant at low temperatures ($\sim 1.8$ ps), showing an upturn as $T_c$ is approached from below. It is followed by a drop above $T_c$ to a much smaller value of the order of 0.5 ps.

Similarly to the absence of the anomaly at $T_c$ in the photoinduced amplitude, in
strongly underdoped samples there is no anomaly in relaxation time either. Moreover, the relaxation time is of the order of 0.5 ps throughout the temperature interval. At intermediate doping, as shown by the relaxation time data on slightly underdoped sample with \( T_c \) of 84 K, the anomaly is less pronounced, with the low temperature relaxation time also being suppressed.

The doping dependence of the low-temperature and high-temperature relaxation time obtained by a single exponential decay fit is shown in Figure 4.3. Near optimum doping an anomaly is observed just below \( T_c \) with a drop to a much lower value at high temperatures [Figure 4.2]. It can be attributed to a presence of a T-dependent gap \( \Delta_c(T) \) which closes at \( T_c \) [?, 181]. With increasing \( \delta \) however, this divergence of \( \tau \) near \( T_c \) rapidly disappears. As shown in Figure 4.2 for \( \delta > 0.2 \), \( \tau \) is nearly constant with temperature above and below \( T_c \) and shows no visible anomaly at \( T_c \). A plot of the normal state relaxation time \( \tau_n \) for \( T > T_c \) (at 100 K) and \( \tau_s \) for \( T < T_c \) (at \( \sim 30 \) K) as a function of \( \delta \) in Figure 4.3 reveals a step-like change of \( \tau_s \) near optimum doping suggesting that the behavior in the two doping regimes is qualitatively different.

![Figure 4.3](image)

Figure 4.3: The relaxation time \( \tau \) in \( Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta} \) as a function of doping \( \delta \), \( x \) for \( T > T_c \) and \( T < T_c \) (at \( T = 100 \) K and 30 K respectively). The relaxation time \( \tau_s \) in superconducting state shows a cross-over near optimum doping, while \( \tau_n \) (\( T > T_c \)) is nearly doping and temperature independent.
4.2. Quasiparticle dynamics in CaYBCO.

The overdoped region is fairly well described using a given model [see section 3.4] with a temperature dependent mean-field-like gap that closes at $T_c$. The gap closure influences the photoinduced amplitude as well as the relaxation time, both showing anomalies at $T_c$. In underdoped samples, on the other hand, the absence of the anomalies at $T_c$ in both the amplitude and the relaxation time of the fast transient, and the presence of the signal at temperatures much above $T_c$ suggest the presence of the (pseudo-)gap far above $T_c$.

It should be noted that in overdoped samples the normal state relaxation time $\tau_n$ is actually the same as in underdoped samples (in underdoped samples relaxation time is constant throughout the temperature range). Since $\tau_n$ is still much longer than the thermomodulation time given by Allen [92] [see Eq.(3.24)] and since the amplitude of the photoinduced transient at temperatures above $T_c$ gradually decreases as temperature is increased - as in case of underdoped YBCO - it seems that some suppression in the density of states (i.e. pseudogap) exists also in overdoped YBCO.

Comparison of the fast component amplitudes with theoretical model for photoexcited state absorption.

Figure 4.4 a) shows the data obtained on optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ samples by three different groups [70, 66, 69], whereas in panel b) the data taken on underdoped YBa$_2$Cu$_3$O$_{6.82}$ sample with $T_c = 77$ K are presented. For near-optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ ($\delta < 0.1$) the data are scaled by $T_c$ and plotted as a function of reduced temperature $T/T_c$ [Figure 4.4 a)]. The data taken on optimally doped samples are clearly quite different from the data taken on underdoped sample, showing anomaly at $T_c$ suggestive of the gap closure which is absent in underdoped samples [see Fig. 4.1]. In the later case the amplitude is decreasing asymptotically to zero at temperatures much above $T_c$ implying the presence of a gap (or a pseudogap) also at much higher temperatures.

We fit the data using the theoretical model for photoexcited state absorption, where the amplitude of the fast transient $T$ is proportional to the photoexcited carrier density $n_{pe}$, which is given by expressions (3.12) and (3.13). We assume that

$$|T| \propto n_{pe} = \begin{cases} \varepsilon_1/\Delta^p & ; \Delta^p = \text{const.} \\ \varepsilon_1/(\Delta_c(T) + k_BT/2) & ; \Delta_c(T) = \Delta_{BCS}(T) \end{cases}$$

where $B = \frac{2\nu}{N(0)\hbar c}$ is the dimensionless parameter that can be estimated for the particular compound, $\Delta^p$ is the magnitude of the temperature independent pseudogap and $\Delta_c(T)$ the magnitude of the temperature dependent mean-field-like gap – in the fit BCS $T$-dependant gap $\Delta_{BCS}(T)$ is used. The values of constants for YBa$_2$Cu$_3$O$_{7-\delta}$ are: $\nu = 10 - 36$, $N(0) = 2.5 - 5$ eV$^{-1}$spin$^{-1}$cell$^{-1}$ [9] and $c = 0.1$ eV.$^1$ Thus we

$^1$ The number of phonon modes in YBa$_2$Cu$_3$O$_7$ is 39. We estimate that 10-36 of them have energy higher than $2\Delta(0)$ – depending on the magnitude of $\Delta(0)$. The phonon cut-off energy $\hbar \omega_c$ is estimated to be approx. 0.1 eV.
can estimate the dimensionless parameter \( B \) to be in a range of \( 10 - 100 \); thereby the temperature dependence is entirely determined by a magnitude and temperature dependence of the gap.

We fit the data on optimally doped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) sample using the model with T-dependent \((\Delta_c (T) \rightarrow 0 \text{ as } T \rightarrow T_c)\) isotropic gap [Eq.(3.13)], where for simplicity the BCS T-dependence [2] of the gap is used. The fits using different values of the dimensionless parameter \( B \) are shown in Figure 4.4 a) giving different values of the zero temperature gap magnitude \( \Delta_c (0) \) ranging from \( \Delta_c (0) / k_B T_c = 4 - 6 \). The best fit is made using \( B \approx 50 \) giving the magnitude of the gap \( \Delta_c (0) / k_B T_c \approx 5 \), in good agreement with other optical experiments [166, 170]. It should be stated that the resulting fit does not depend strongly on the specific T-dependence of the gap, as long as it vanishes at \( T_c \). Milder and sharper T-dependences were also used to analyze the T-dependence of the amplitude all giving the magnitudes of the zero temperature gap in the range of \( 3 - 7 \) \( k_B T_c \) depending on \( B \).
The temperature dependence of the fast signal amplitude taken on YBa$_2$Cu$_3$O$_{6.82}$ is fitted using the model with T-independent gap [Eq.(3.12)] in Figure 4.4 b). We use the same values of the dimensionless constant $B = \frac{2\nu}{N(0)\hbar c}$ as in the case of the T-dependent gap and again the best fit is obtained by $B \approx 50$ with the magnitude of the (pseudo-)gap $\Delta^p/k_B \approx 600K$. One could argue that higher $B$-s should be used in underdoped samples since $N(0)$ is decreased. On the other hand, the increase in the magnitude of the gap in underdoped samples (see below) also decreases the number of high energy phonons $\nu$ that take part in the relaxation processes. Therefore the two effects may cancel each other.

4.2.1 Analysis of data taken on underdoped samples.

Absence of anomalies in the photoinduced signal at $T_c$ in underdoped YBCO suggests the presence of the gap in the low-energy density of states already far above $T_c$. The signal asymptotically vanishes at progressively higher temperatures as one goes to more underdoped samples [see Fig. 4.1]. The data show [71] similar behavior to the pseudogap ”onset” temperatures $T^*$, obtained from other spectroscopic techniques like Raman [182], optical conductivity [183], specific heat [98] or NMR [184] for instance, all being susceptible to changes in the low-energy density of states.

Figure 4.5: The normalized temperature dependence of $\mathcal{T}$ taken on four underdoped YBCO samples [181] with critical temperatures from 48K to 77K. The data follow universal temperature dependence when temperature is normalized to $T^*$.

It should be noted however that this temperature is somewhat arbitrary and its value depends on subjective criterion in all the above mentioned techniques. As a
matter of fact, $T^*$ is a crossover temperature and not a phase transition temperature since no anomalies in thermodynamic quantities were observed at this temperature.

![Figure 4.6: The dependence of the energy gap $\Delta_p$ on doping $\delta$. Open squares correspond to the values of $\Delta_p$ determined from fits to the data using Eq.(3.12), while the solid squares are obtained by fitting the data on near-optimally doped samples using Eq.(3.13). Solid triangles were obtained by plotting the scaled magnitude of the inverse of the photoinduced transmission at low temperature $1/T_{T=0}$. In the latter case, the data were taken in a single experimental run on a series of samples obtained from the same original optimally doped film, with carefully controlled laser operating conditions to ensure that $\Delta_p$ can be compared quantitatively.

Since fast signal amplitude $R$ (or $-T$) actually asymptotically vanishes at high temperatures, it is more appropriate to discuss the doping dependence of the pseudogap magnitude $\Delta_p$, rather that of $T^*$. This avoids the somewhat arbitrary criterion for determining $T^*$ of an asymptotic function. In order to get a more quantitative picture on the pseudogap behavior, we analyze the data using the model [71] with the T-independent gap (see section 3.4). The model predicts temperature dependence of the amplitude $T$ being determined by a single parameter, namely the magnitude of the gap. In Figure 4.1 the fits to the data using Eq.(4.1) with $\Delta_p = const.$ are given by solid lines. Model predicts the universal temperature dependence of the photoinduced transmission amplitude. This can be verified by plotting the normalized temperature dependences of the amplitude vs. reduced
temperature $T/T^*$ [71] [see Fig. 4.5], where $T^*$ was taken to be the temperature, where the amplitude of the signal drops to 15% of its low temperature value. The scaling of the data gives additional proof of the theoretical model.

From the plot a ratio of $2\Delta^p/k_BT^* = 5 \pm 1$ was obtained. A plot of $\Delta^p$ versus doping $\delta$ is shown in Figure 4.6. The error bars include $\Delta^p$ variation, when the dimensionless constant $B$ is varied by $\pm 50\%$ from its estimate $B \approx 50$ (see section 4.2 for details). The error bars in $\delta$, however, are due to an indirect measurement of the oxygen content in underdoped films. From the plot, $\Delta^p$ appears to be inversely proportional to doping, $\Delta^p \propto 1/x$, with $x = 0.6 - \delta$ being proportional to the carrier concentration.

The doping dependence of $\Delta^p$ can be independently confirmed from the same data set by plotting the inverse of the low-temperature value of $T$ as a function of $\delta$, taken on a series of samples prepared from the same original film as described in section 2.2.1. As can be seen from Eq.(4.1), the value of $T$ at $T = 0$ is proportional to $\mathcal{E}_i/\Delta(0)$, from which the zero-temperature gap $\Delta(0)$ can be determined. The scaled plot of $1/T_{T=0}$ as a function of doping $\delta$ in Figure 4.6 is consistent with the values of $\Delta^p$ determined from fits of the T-dependence of fast signal amplitude. It is seen to follow the same type of behavior $\Delta^p \propto 1/(0.6 - \delta)$.

We note that the observation of an inverse dependence of gap on doping is in agreement with recent experiments on La$_{2-x}$Sr$_x$CuO$_4$ [185, 186], suggesting that it may be a more universal feature of cuprates.

### 4.2.2 Analysis of data taken on overdoped samples.

Temperature dependence of quasiparticle dynamics in YBa$_2$Cu$_3$O$_{7-\delta}$ shows that in the underdoped state the $T$-independent gap $\Delta^p(x)$ is dominant. The magnitude $\Delta^p(x)$ seems to be inversely proportional to doping. Near optimum doping, the same measurements show a dominant $T$-dependent gap $\Delta_c(T)$ which closes at $T_c$. In this section we discuss evolution of $\Delta^p(x)$ and $\Delta_c(x)$ near optimum doping and into the overdoped state. In particular, we are interested in the evolution of the gap above $T_c$. As already discussed, the relaxation time above $T_c$ in overdoped CaYBCO is still much longer than expected for Allen relaxation, also the $T$-dependence of the amplitude – gradual decrease with increasing temperature – shows the presence of the (pseudo)-gap at temperatures far above $T_c$.

The time-evolution of the photoinduced reflectivity $\Delta R/R$ is shown for $x = 0$ and 0.132 at selected temperatures in Figure 4.7 a) and b) respectively. Above $T_c$ a single exponential decay gives a very good fit to the data with the relaxation time of $\tau_B \sim 0.5$ ps. We note that beyond $\sim 3$ ps ($\simeq 6\tau_B$) the signal has decayed to a nearly constant value, indicating that no other relaxation process is present on this timescale.\(^2\) This is evident from logarithmic plots of $\Delta R(t)/R$ in Fig. 4.7 c) and d).

\(^2\) In addition, a much slower component is also observed, similar as in Fig. 3.5, but this will be a matter of discussion in section 4.3.
Figure 4.7: The photoinduced reflectivity $\Delta R/R$ from $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ above and below $T_c$ as a function of time a) for $x = 0$ ($T_c = 93$ K) and b) $x = 0.132$ ($T_c = 75$ K) at different temperatures. A 2-exponential decay fit is made below $T_c$ and a single exponential above $T_c$. In c) and d) the same data for $x = 0$ and $x = 0.132$ respectively are presented on a logarithmic scale together with fits. The signals (together with fits) in c) and d) are offset for clarity. In inset to panel b) the best fits with single exponential (dotted) and stretch exponential decay (dashed) are plotted for comparison - see text.

As described in section 2.1.4, we model the single exponential decay with Eq.(2.2)

$$\frac{\Delta R(t)}{R} \simeq A e^{-\frac{t}{\tau_R}} \left[ 1 - \text{erf} \left( \frac{-4t\tau_R + \sigma^2}{2\sqrt{2}\sigma\tau_R} \right) \right]$$

(4.2)

where $\tau_R$ is the relaxation time, $A$ is the amplitude of the signal and the part in square brackets accounts for the finite risetime. In inset to Fig. 4.7 b) we plot with dotted line the best fit to the data using single exponential decay. It can be seen that the fit cannot describe the relaxation successfully. On the other hand, the two component fit (the sum of two components with exponential decay, each given by Eq.(4.2)) presented with solid lines in Fig. 4.7 shows almost perfect match with the data. Alternatively, we tried to fit the relaxation with a stretch exponential decay,
4.2. Quasiparticle dynamics in CaYBCO.

\[ A \exp[-(t/\tau)^\mu], \] which is usually used in case of spread of relaxation times. The fit (given by dashed line in inset to Fig. 4.7 b)) is slightly better than single exponential decay, however the discrepancy is still substantial - especially at short times.

The above observation suggests that a two-component fit to the data is necessary for an accurate description. What is also particularly interesting is that in some experiments on near optimally doped YBCO [153] as well as in Tl compounds [68, 178] two picosecond components of the opposite sign were observed below \( T_c \) - one of them vanishing at \( T_c \). This suggests that two component relaxation is more general feature in near-optimally doped HTSC and puts additional weight to the two component analysis of the fast signal data. To discard the possibility that the two component behavior may arise due to surface effects and/or macroscopic inhomogeneity of the samples, we performed the same measurements on freshly polished samples finding the same behavior. Moreover, we re-analyzed the thin film transmissivity data from Ref. [85], and found the same two-component behavior there as well. Also, if the observed signal above \( T_c \) was due to inhomogeneity of the sample, its contribution to the signal on optimally doped (nearly stoichiometric) samples should be smaller than on strongly overdoped ones — as can be seen in Figure 4.1 the behavior is quite opposite.

We therefore model the response as a sum of two components, each given by Eq.(4.2), and extract the temperature dependence of the relaxation times \( \tau_A, \tau_B \) and amplitudes \( A(T) \) and \( B(T) \), where both amplitudes \( A(T) \) and \( B(T) \) are \( T \)-dependent and \( A(T) = 0 \) for \( T > T_c \).

In Figure 4.8 we plot the relaxation times \( \tau_A \) and \( \tau_B \) as functions of temperature for different dopings. The common feature for all samples is the divergence of \( \tau_A \) just below \( T_c \) similar to that reported previously for the samples near optimum doping [66, 68] as discussed in section 3.4.3. Note that Eesley et al. [68] also used two component fit when analyzing the T-dependence of the relaxation times. In contrast, \( \tau_B \) is found to be \( T \)-independent, similar as observed in underdoped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) (\( \delta > 0.15 \)). The divergence of \( \tau_A \) is far more pronounced as in the case when the single exponential fit is used [see Figure 4.2], and shifted towards \( T_c \). This can easily be understood, since when the single exponential fit is used close to \( T_c \), where signal \( B(T) \) is dominant, the effective relaxation time is closer to \( \tau_B \).

Below \( T_c \) the quasiparticle recombination time of a superconductor with a gap \( \Delta_c(T) \) is given by Eq.(3.23) - see section 3.4.3:

\[
\tau = \frac{\hbar \omega^2 \ln \left\{ 1/(\epsilon_1/2N(0)\Delta_c(0)^2 + \exp(-\Delta_c(T)/k_B T)) \right\}}{12\Gamma_{\nu}[\Delta_c(T)]^2}.
\] (4.3)

The important feature of Eq.(4.3) is that near \( T_c \) the relaxation time diverges as \( \tau \propto 1/\Delta_c(T) \), since \( \Delta_c(T) \to 0 \) as \( T \to T_c \). On the other hand, if \( \tau \) is constant, this implies that \( \Delta \) is \( T \)-independent. To model the \( T \)-dependence of the relaxation time of the divergent component \( A \) below \( T_c \), we use \( N(0) = 5 \text{ eV}^{-1}\text{cell}^{-1}\text{spin}^{-1} \),

\[^{3}\] It depends on the probe photon energy as discussed in section 3.3.3.
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Figure 4.8: The relaxation times $\tau_A$ (squares) and $\tau_B$ (open circles) as a function of temperature for $Y_{1-x}Ca_xBa_2Cu_3O_{7-}\delta$ with a) $x=0$, b) $x=0.016$, c) $x=0.101$ and d) $x=0.132$. The solid line is the relaxation time below $T_c$ given by Eq.(3.23).

$\Gamma_\omega = 10$ cm$^{-1}$ and $\omega = 500$ cm$^{-1}$, with - for simplicity - the BCS functional form for $\Delta_c(T) = \Delta_{BCS}(T)$ and $\Delta_c(0) = 4kT_c$. The results are shown by solid curves in Figure 4.8. The existence of a divergence of $\tau_A$ at $T_c$ in all the overdoped samples is evidence for the existence of a mean-field-like gap in the entire overdoped region. A simultaneous presence of the signal, whose amplitude is temperature dependent and relaxation time $\tau_B$ temperature independent (and large in comparison to metallic Allen relaxation) indicates a co-existing presence of a $T$-independent gap $\Delta^p$ and a $T$-dependent gap $\Delta_c(T)$ over the whole overdoped region.

To obtain quantitative information on $\Delta_c(T)$ and $\Delta^p$ we analyze the temperature dependence of the photoinduced reflectivity amplitude $R (= A + B)$ plotted in Figure 4.9 as a function of $T$. Qualitatively similar behavior is observed for all dopings in the overdoped region. At low temperatures $R$ is nearly $T$-independent exhibiting a slight upturn near $0.7 T_c$ and then a rapid drop to approximately 30% of its maximum amplitude just below $T_c$. Close to $T_c$, there is a clear break in the response and $R$ reverts to a much slower asymptotic temperature dependence above $T_c$ extending to 150 K or more.

To fit the data we use a sum of two components $R(T) = A(T) + B(T)$, where $A(T)$ is given by Eq.(4.1) with $\Delta_c(T) = \Delta_{BCS}(T)$, whereas $B(T)$ is given by Eq.(4.1)
4.2. Quasiparticle dynamics in CaYBCO.

Figure 4.9: The photoinduced reflectivity amplitude $\mathcal{R}$ as a function of $T$ for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with a) $x=0$, b) $x=0.016$, c) $x=0.101$ and d) $x=0.132$. The fits are made using the sum of Eqs.(3.13) and (3.12). The values of $\Delta_c(0)$ and $\Delta_p$ used in the fit are shown in the panels. Separate $A(T)$ and $B(T)$ are also shown with dotted and dashed lines respectively.

with $\Delta^p = \text{const}$. In both $B = \frac{2\nu}{N(0)h} \approx 50$ is a dimensionless constant estimated in section 4.2. Fits to the temperature dependence of $\mathcal{R}$ with the sum $A(T) + B(T)$ are plotted in Fig. 4.9. The values of $\Delta_c(0)$ and $\Delta^p$ are shown in each case. It is evident from the plots that the total amplitude $\mathcal{R}$ can only be described accurately by the two component fit and cannot be described by either $A(T)$ or $B(T)$ separately. The gap ratio obtained from the fits at different $x$ are $\Delta_c(0)/k_BT_c \approx 5 \pm 0.5$, depending only slightly on $x$. The obtained values of $\Delta^p$ and $\Delta_c(0)$ from the fits of the $T$-dependences of $\mathcal{R}$ as a function of doping are shown in Fig. 4.10. The $T$-independent gap magnitudes $\Delta^p$ obtained from underdoped YBCO data [Figure 4.6] are also included for completeness. In the overdoped region the two gaps converge $\Delta^p \rightarrow \Delta_c(0)$, but they remain clearly distinct, as indicated by the 2-component decay in Figs. 4.7 c) and d), as well as in Fig. 4.8 and in the $T$-dependence analysis of $\mathcal{R}$ [Fig. 4.9].

At the end we should mention recent data on the untwinned YBCO single crystals [187]. There the two relaxation components with similar $T$-dependences of relaxation times $\tau_A$, $\tau_B$ and amplitudes $A(T)$ and $B(T)$, have been separately observed by
Figure 4.10: The energy gaps $\Delta_p$ and $\Delta_c(0)$ as a function of doping in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ obtained from fits to the data in Figs. 4.1 and 4.9. Open squares represent $\Delta_p$, while solid symbols are for $\Delta_c(0)$. Open and filled diamonds represent the $\Delta_p$ and $\Delta_c(0)$ respectively from Fig. 4.6. The upper dashed line represents $\Delta_p \propto 1/x$, where $x$ is the carrier concentration. The lower dashed line is a guide to the eye emphasizing the behaviour of $\Delta_c(0)$. Circles are from tunneling data [195].

measuring photoinduced reflectivity with probe polarization parallel to the a- and b-axis [187] - supporting our two-component analysis.

4.3 Absorption from in-gap localized states.

In this section we present results from analysis of the slow component amplitude at different doping levels. As we have shown in section 3.5, this slow component cannot be attributed to bolometric effects. Moreover, since it is sensitive to the superconducting transition and has extremely slow dynamics it was attributed to the photoinduced absorption from photoexcited localized carriers in the vicinity of the Fermi energy. The relaxation dynamics of in-gap states is supposed to be strongly dependent on the magnitude and T-dependence of the gap. Therefore by measuring the T-dependence of the slow component amplitude as a function of doping one can obtain additional information about the energy excitation spectrum.
4.3. Absorption from in-gap localized states.

We first apply the theoretical model [72] (see section 3.5) to analyze the temperature dependence of slow component amplitude $D$ on near-optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ [70, 69] in order to estimate the applicability of the model to analyzing the data. In sections 4.3.1 and 4.3.1 we analyze the data taken on single crystals and thin films respectively.

4.3.1 Analysis of the data using theoretical model for intra-gap state relaxation.

The temperature dependence of the slow component amplitude $D$ on near-optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ [70, 69] is plotted in Fig. 4.11. The signal amplitude increases with increasing temperature followed by an abrupt drop above $T_c$ similar to the model prediction when the gap has BCS-like temperature dependence [see Fig. 3.12]. We compare the data with the predicted $T$-dependences of $D$ using Eqs.(3.37) and (3.32), Eq.(3.37) being the low temperature limiting case of Eq.(3.32). The parameters used in the fits are the same as used in the analysis of the fast relaxation component with values of dimensionless constant $B = \frac{2\nu}{N(0)\hbar} \approx 50$ for YBa$_2$Cu$_3$O$_{7-\delta}$ [see section 4.2]. Since the magnitude of the gap is of the order of $\Delta_c(0) \sim 5kT_c$ we expect that Eq.(3.37) is valid up to temperatures close to $T_c$. We need to stress that Eq.(3.37) is independent of the shape of DOS of localized states within the gap and shows a universal temperature dependence. It can be seen from Fig. 4.11 that at low

![Figure 4.11: The temperature dependence of the (negative) photoinduced transmission amplitude $D$ in YBa$_2$Cu$_3$O$_{7}$ from [69] (open circles) and [70] (solid circles). The solid line is a plot of expression (3.37) with $\Delta_c(0)/k_BT_c = 5$ whereas the dashed line represents general solution [Eq.(3.32)] with non-zero $\tilde{\gamma}$ term and additional fourth order term in the expansion $R$ in powers of $\Delta_c(T)$.](image-url)
Figure 4.12: In panels a), c) and e) the single pulse contribution to the slow component amplitudes ($d_0$ in Figure 3.11) is shown for the optimally doped and two overdoped samples with $T_c$-s 93, 83 and 75 K respectively. In panels b), d) and f) the temperature dependences of the photoinduced pile-up amplitude (given by $D$ in Figure 3.11) is shown for the same samples.
4.3. Absorption from in-gap localized states.

Temperature there is a deviation of the calculated curve from the experimental points. To explain this effect we should remember that Eq.(3.34) for constant $R$ is valid near $T_c$ where $\Delta_e(T)$ is small. If we add the next - fourth order - term in the expansion of $R$ in powers of $\Delta_e(T)$ we can account for this discrepancy.

Near $T_c$ Eq.(3.37) fails and Eq.(3.39) should be used. It leads to a crossover from square root intensity dependence of $D$ at low temperatures described by Eq.(3.37) to linear intensity dependence near $T_c$ predicted by Eq.(3.39). Fit to the data using general solution [Eq.(3.32)] is also shown (dashed) in Fig. 4.11. In this fit we have added the fourth order term in the expansion of $R$ in powers of $\Delta_e(T)$. As already shown in Fig. 3.12 b) the effect of $\gamma$ becomes important near $T_c$ by cutting the divergence of $D$ as $T \to T_c$.

Analysis of the reflectivity data on overdoped single crystals.

In Figure 4.12 we present the temperature dependences of the slow component amplitude taken on three $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ single crystals with $T_c$-s 93, 83 and 75 K respectively. The single pulse and the ”pile-up” contribution to the slow component amplitudes (given schematically by $d_0$ and $D$ in Figure 3.11) are shown in left and right panels respectively.

One can see that the behavior is very similar in all three samples - the amplitude ($d_0$ or $D$) is slightly negative (decrease in absorption) at very low temperatures, showing an increase in absorption as temperature is raised to $T_c$ followed by a drop to some nearly constant value. As already discussed in section 3.5 the ”pile-up” amplitude $D$ reflects the behavior of the single pulse contribution $d_0$, however the exact one-to-one relationship is valid only in the case when the relaxation time does not depend on temperature. By analyzing the ratio $D/d_0$ one could in principle estimate the T-dependence of the slow component relaxation time $\tau_L$. However, due to scatter of the data (especially in $d_0$) this seems to be impossible at this stage. Nonetheless, by comparing the peaks (at $T_c$) in T-dependence of $d_0$ and $D$ in the three samples and assuming that $\tau_L$ is proportional to $D/d_0$ (see section 3.5.1), the data suggest that $\tau_L$ increases with doping. This is consistent with the decrease in the bi-particle recombination rate $R$ (see Eqs.(3.29) and (3.34) in section 3.5.1) through the decrease in the gap magnitude as one goes to more overdoped samples. Again, the assumption that relaxation of photoinduced localized carriers is determined by a bi-particle recombination in most of the temperature region seems to be valid.

Analysis of the transmission data on underdoped thin films.

Let us now focus on the data taken on underdoped YBCO thin films. T-dependences of $d_0$ for near-optimally doped and two underdoped YBCO thin films on SrTiO$_3$ substrates with $T_c$-s 89, 77 and 62 K respectively is shown in panels a), c) and e) of the Fig. 4.13. In panels b), d) and f) the T-dependences of the photoinduced pile-up amplitude $D$ is shown for the same samples.
Figure 4.13: In panels a), c) and e) the single pulse contribution to the slow component amplitudes (\(d_0\) in Figure 3.11) is shown for the near-optimally doped and two underdoped YBCO thin films on SrTiO\(_3\) substrates with \(T_c\)'s 89, 77 and 62 K respectively. In panels b), d) and f) the temperature dependences of the photoinduced pile-up amplitude (given by \(D\) in Figure 3.11) is shown for the same samples. Inset to b) T-dependence of the lock-in’s "out-of-phase" time-independent signal taken on near-optimally doped YBCO with \(T_c=89\) K (solid squares) and on insulating YBa\(_2\)Cu\(_3\)O\(_6\) (open circles).
4.3. Absorption from in-gap localized states.

Comparing the data on the near optimally doped thin film [Fig. 4.13 a) and b)] and the single crystal [Fig. 4.12 a) and b)], one can see that the single pulse contributions show very similar behavior. The pile-up signals on the other hand are substantially different at low temperatures. The photoinduced transmission data on the thin film show an upturn when temperature is decreased below ~ 50 K. The feature was observed only in the data taken on YBCO films on SrTiO substrates, where most of our experiments on underdoped samples were performed, whereas no such effect was observed on films deposited on MgO.

It should be noted that also a strong increase in the "out-of-phase" signal amplitude is observed at low temperatures in the data taken on films deposited on SrTiO [see inset to Fig. 4.13 b)]. It was found on all samples, regardless of doping. The strong increase in the "out-of-phase" signal was observed also on insulating YBaCuO film deposited on SrTiO [open circles in inset to Fig. 4.13 b)], affecting the low temperature behavior of "pile-up" amplitude \( D \) (see Ref. [70]) – otherwise no anomalies in either fast component or \( d_0 \) were observed in YBaCuO [70]. As discussed in section 2.1.2, the "out-of-phase" signal consists of all contributions to the change in absorption on time-scale longer than \( 1/\omega_M \), where \( \omega_M \) is the pump modulation frequency. The increase of the "out-of-phase" signal at low temperatures was observed only on thin films deposited on SrTiO. Since the thermal conductivity in SrTiO is much higher than that of the YBCO, implying much lower temperature increases due to photoexcitation, this anomaly cannot be attributed to the bolometric contribution to the photoinduced transmission in YBCO. Taking all together, this implies the presence of an additional long lived signal at low temperatures due to photoinduced effects in the substrate.

In the underdoped samples, the temperature dependence of the slow component amplitude is substantially different to the one in the overdoped samples. At low temperatures photoexcitation again results in a decreased absorption. As temperature is raised a sharp increase in absorption close to \( T_c \) can be observed followed by a gradual decrease. The \( d_0 \) data show very similar temperature dependence to the one given by the theoretical model for the case of T-independent gap [see Fig. 3.13].

The pile-up amplitude \( D \), similar to the data on near-optimally doped YBCO on SrTiO, shows a strong increase in amplitude also at low temperatures - presumably due to photoinduced effects in SrTiO. At higher temperatures \( D \) follows the behavior of \( d_0 \).

The notable feature in \( d_0 \) and \( D \) data sets is that at low temperatures the photoinduced absorption (both \( d_0 \) and \( D \)) is negative and then increases as temperature is increased, subsequently changing sign. This seems to be in contradiction to the theoretical model, which at low temperatures predicts monotonic increase in amplitude with no sign change. However we need to stress that taking into consideration all the possible probe transitions from occupied to unoccupied states
weighed with their matrix elements, this can easily be accounted for (For example the probability for the photon absorption, when the initial states lie 1.5 eV below $E_F$ and localized states in gap are final states for the photon absorption, is decreased.). We should mention also that some bolometric contribution to the signal might be (and probably is) superimposed on the photoinduced long-lived signal. Since the bolometric contribution is expected to be weakly T-dependent in the temperature range under study [see Fig. 3.10], we can assume it to be constant in first approximation.\footnote{Since we do not know neither the magnitude nor the sign of the bolometric component we assume it as a fitting parameter in Fig. 4.14.}

Another important feature of the data taken on overdoped samples is that the signal magnitude above $T_c$ is higher than the amplitude at temperatures far below $T_c$ in contrast to the predicted behavior by the model using a BCS-like gap [Eq.(3.37) - see Fig. 3.12]. Also, the amplitude above $T_c$ shows some weak temperature dependence. Again we should consider some T-dependence of the bolometric contribution to the long-lived signal that might give rise to the observed behavior. On the other hand, as we go to more overdoped samples the height of this "high temperature plateau" gradually decreases and the data on strongly overdoped sample can already be well fitted by Eq.(3.37). From the systematics of the data it seems likely that the signal consists of a sum of two contributions (similar to the data on fast transients, where two distinct components to the signal were observed) – one being associated with the T-independent pseudogap and the other with the T-dependent mean-field-like gap.

In Fig. 4.14 we model the data taken on overdoped and underdoped YBCO. Similar to the analysis of the fast component (see section 4.2.2) we use the two component fit in Ca$_{0.101}$Y$_{0.899}$Ba$_2$Cu$_3$O$_{6.943}$ [Fig. 4.14 a]), assuming that the signal consists of two contributions - one associated with the carrier rich regions with the mean-field-like gap and the other associated with the carrier poor regions, whose dynamics is governed by the T-independent gap. From the above analysis it is clear that no information on the magnitude of the gap(-s) can be obtained from the analysis of the slow component only. First the scatter of the data is quite high and more importantly there may be some bolometric contribution to the signal that masks the effect. Nonetheless, the agreement between the data and the model curve (solid line) is very good considering that besides the offset only two parameters were used: the relative weights to the two signals, and the ratio $\alpha/\Gamma$. The magnitudes of the low-T values of the two gaps were taken from fast component analysis [204], together with the value of the dimensionless constant $B = \frac{2\nu}{N(0)\hbar c} \sim 50$ (see section 4.2). The solid line is the sum of the two components, the dashed line represents the contribution from carrier rich regions with the BCS-like T-dependent gap, and the

\footnote{For the sake of simplicity we fit the data with the low-T solution. As has been shown in section 3.5.1, the effect of including terms corresponding to single particle relaxation ($\tilde{\gamma}$) is only in smearing out the divergence at $T_c$.}
4.3. Absorption from in-gap localized states.

Figure 4.14: a) Modelling of the temperature dependence of the slow component amplitude in Ca$_{0.101}$Y$_{0.899}$Ba$_2$Cu$_3$O$_{6.943}$ using the two component fit with the same magnitudes of the gap as determined by the analysis of the fast transient. The solid line is the sum of two components: dashed line represents the contribution from carrier rich regions with the BCS-like T-dependent gap, and dotted line representing the component describing the carrier poor regions with the T-independent gap. The ratio $\alpha/\Gamma = 100$ was used. At $T > T_c$ the dotted and the solid lines overlap. b) The slow component amplitude in YBa$_2$Cu$_3$O$_{6.82}$ fitted by Eqs.(3.41) and (3.42) with T-independent gap and again $\alpha/\Gamma = 100$. Both datasets have been shifted vertically to zero signal at $T\to 0$.

dotted line representing the component describing the carrier poor regions with the T-independent gap. The ratio $\alpha/\Gamma = 100$ was used.

In Fig. 4.14 b) the slow component amplitude in YBa$_2$Cu$_3$O$_{6.82}$ is fitted by Eqs.(3.41) and (3.42) representing the photoinduced absorption from localized states in the case of the T-independent gap. Again, we have used the value of the gap from the analysis of the fast component and $\alpha/\Gamma = 100$. The fit is quite reasonable although we must stress that in this case the scatter in the data is much higher.

Looking at the overall picture emerging from the T-dependence of the slow component amplitude data, similar conclusions can be made as from the analysis of the fast picosecond transients. In underdoped samples the T-dependence seems to be determined by the T-independent pseudogap, whereas near the optimal doping and in overdoped region the two gaps seem to coexist below $T_c$. 
4.4 Discussion.

Let us now discuss the possible origin of the observed doping dependence of carrier relaxation dynamics. As shown in the previous sections, the relaxation dynamics in underdoped and overdoped region of the phase diagram is substantially different.

In underdoped samples the relaxation time of the picosecond transient is (to a first approximation) temperature independent. The amplitude of this transient, on the other hand, is constant at low temperatures, showing no anomalies at $T_c$ and asymptotically decrease at temperatures well above $T_c$. The temperature $T^*$ (defined as the temperature where the amplitude drops to $\sim 15\%$ of its low temperature value) increases with decrease in doping in a similar way as the temperature where the anomalies in other physical quantities appear $[4, 5, 183]$ — associated with the opening of the pseudogap in the density of states. Since there are no anomalies at $T_c$ in either relaxation time $\tau$ or amplitude of the picosecond transient the results suggest, together with the relation $\tau \propto 1/\Delta$ [Eq.(3.23)], that the quasiparticle relaxation is determined by some relaxation bottleneck present in all the temperature range under investigation. We fit the data with the theoretical model for quasiparticle relaxation in the presence of a small energy gap in the density of states $[71]$ and find good agreement with the model prediction for the case of temperature independent energy gap. The behavior seems to be universal in the entire underdoped regime, since the $T$-dependences of the fast component amplitude scale to a universal curve [see Fig. 4.5] with the ratio $2\Delta^p/k_B T^* = 5 \pm 1$. It follows from the analysis that the pseudogap magnitude is inversely proportional to doping as $\Delta^p \propto 1/x$, with $x$ being the carrier concentration (doping) — see Fig. 4.6.

The temperature dependence of the slow, nanosecond timescale component in underdoped YBCO seems to be well described by the theoretical model for photoinduced absorption from in-gap localized states. Though quantitative analysis of the data is not yet possible, the measured $T$-dependence of the slow component amplitude can be well accounted for with the model assuming a $T$-independent gap, just as for the fast component.

The data from femtosecond time-resolved spectroscopy in underdoped YBCO imply there is no change in the single particle density of states at $T_c$, as there are no anomalies in quasiparticle relaxation at superconducting transition temperature. Since pairing must involve changes in the quasiparticle density of states these results suggest that pairing takes place at temperatures far above $T_c$. In this way our results support the so called pre-formed pairing models discussed in the introductory chapter. Of course, this is the simplest explanation of the data, based on the assumption that momentum scattering is fast compared to the energy relaxation. The momentum relaxation time $\tau_k$ can be inferred from infrared conductivity data $[166]$ giving $\tau_k \sim 10$.

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$^6$ Here we intentionally use the term single particle instead of quasiparticle, to emphasize a more general statement that holds also in case the carriers cannot be described as quasiparticles (when the uncertainty in the particle energy exceeds its energy).
4.4. Discussion.

fs at $\omega \sim \Delta^p$, which is fast compared to energy relaxation time $\tau_R \sim 0.5$ ps in underdoped YBCO [see Figure 4.3]. Therefore, the relaxation of photoexcited quasiparticles for all momenta is determined by the same processes. There could be, in principle, some kinematic constraints [171, 191] suppressing the momentum relaxation — resulting in dependence of the quasiparticle relaxation on momentum $\vec{k}$. In this case one could, through the probe process, measure the relaxation of quasiparticles with some particular momentum, where the gap would be finite and in the first approximation $T$-independent. However, in this case the relaxation time should be (through the probe process matrix element) strongly dependent on probe wavelength and polarization, which was not experimentally observed.

Near **optimum doping** and in **overdoped** anomalies in amplitude and relaxation time at $T_c$ imply that the gap has mean-field-like $T$-dependence closing at $T_c$. With such a mean-field-like gap we can explain the divergence of $\tau_s$ at $T_c$ [see Figure 4.2] together with the fact that the signal amplitude $T$ exhibits a strong decrease at $T_c$ near optimum doping. However, the fact that the photoinduced signal with essentially the same relaxation time as in underdoped samples persists up to more than 60 K above $T_c$ implies the continuing presence of the pseudogap also near optimal doping. The analysis of the relaxation times and amplitudes of the fast ps timescale components is the basis for our observation of the co-existence of the $T$-dependent mean-field-like gap $\Delta_s(T)$ closing at $T_c$, and the $T$-independent gap $\Delta^p$ persisting to temperatures far above $T_c$ in overdoped CaYBCO. Since two distinct picosecond relaxation components are observed also at temperatures below $T_c$ data suggest that the superconducting gap $\Delta_s(T)$ does not evolve from the $T$-independent pseudogap $\Delta^p$. More likely the two components correspond to two different microscopically separated regions in the sample. Speculating on the origin of the two-gap behavior in the spatially inhomogeneous phase picture [34], it is natural to associate the behavior of $\Delta_s(T)$ with areas having high carrier density, where the gap in the quasiparticle spectrum is formed by a collective effect. Here pairing occurs simultaneously with the macroscopic phase coherence at $T_c$. In the low-density regions, where no collective effects are present, $\Delta^p$ signifies the individual pair binding energy. At $T_c$ the macroscopic phase coherence is established across both regions into a common superconducting state.

The association of the component with the longer relaxation time to the carrier rich regions of the sample and the component with the shorter relaxation time to the carrier poor regions is also physically plausible, since in the low-carrier density regions screening of the electron-phonon coupling is much weaker and therefore the relaxation rate should be larger. Also, there is a possibility of an additional relaxation mechanism in low-carrier density regions (or underdoped samples) due to spin relaxation, as discussed in section 3.4.4.

An important question arising from this analysis is, how do the two gaps (determined from femtosecond time-resolved optical data analysis) evolve in the underdoped region. The data on underdoped samples suggest the presence of only the $T$-independent pseudogap, $\Delta^p$. However, a two component picture might hold
also in underdoped YBCO, with the photoinduced absorption signal from the carrier rich regions being much weaker than the signal corresponding to carrier poor regions. This can be either due to different matrix elements of the probe process, or due to decreased effective size of the carrier rich areas. In order to answer this question systematic T-dependent measurements of photoinduced transient as a function of probe photon energy need to be performed.

Indeed, the band structure (assuming that the size of the domain is big enough that we can discuss energy bands) may be significantly different in the two phases. In that case, relative amplitudes of photoinduced absorption - corresponding to different transitions - may also be significantly different (can also be of the opposite sign). In this case, one could expect that the signs of the two components would vary with changing the probe pulse wavelength. This can actually be seen for the case of YBCO when comparing the data from Refs. [66] and [153]. In the latter case [153], the two components of the opposite sign were observed on optimally doped YBCO and underdoped Pr$_{0.25}$Y$_{0.75}$Ba$_2$Cu$_3$O$_{7-\delta}$ at the probe photon energy of 2 eV. One with the longer relaxation time was vanishing at $T_c$, whereas the other with the sub-picosecond relaxation time remained also at higher temperatures. Unfortunately the high temperature data were not available for the analysis and comparison with our results. Similarly, two components can be observed on near optimally doped Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$, electron doped Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-y}$, near-optimally doped HgBa$_2$Ca$_2$Cu$_3$O$_{8+y}$ and Bi$_2$Sr$_2$Ca$_1-y$Y$_y$Cu$_2$O$_8$, and from the anisotropy data on untwinned YBCO. Therefore it seems that the two-component behavior in time-resolved data on near optimally doped samples is quite general in HTSC.

Again, the data on slow nanosecond component seem to support the adopted picture, with a substantial density of in-gap localized states. However, as already discussed in section 4.3 quantitative analysis of the data cannot be made at this stage.

In order to put these results into perspective of other experiments probing the gap magnitude, there are several issues that need to be discussed. First we should discuss the symmetry of the order parameter. As already discussed in the introductory chapter, there is an ongoing discussion whether the order parameter has a d-wave symmetry (gapless, with nodes on the Fermi surface), or an s-wave character with an isotropic gap. There are groups (among the groups performing phase sensitive measurements) supporting evidence for d-wave [41], s-wave [43] or mixed [192, 193] order parameter. From the adopted theoretical model for photoexcited quasiparticle relaxation (see section 3.4.2) it follows that the difference between isotropic and anisotropic gap should be observed at low temperatures, where different intensity dependences of the picosecond transient are expected for an isotropic and anisotropic (d-wave) gap. The results show linear intensity dependence [see Figure 2.8] over wide range of intensities, contrary to the sub-linear dependence predicted for the gapless case. Secondly, the temperature dependence of the photoinduced signal amplitude
cannot be fitted using the solution of the model for the case of anisotropic gap. Moreover, in case of an anisotropic gap some spread in relaxation times is expected, which is also not experimentally observed. Therefore our results, based on the above arguments, support an isotropic gap (since we are indirectly probing only changes in the quasiparticle density of states we cannot say anything on the phase of the order parameter). However, we should state again, that in case of some kinematic constraints [171, 191] limiting the momentum relaxation there is a possibility that we are probing only the quasiparticles residing in lobes, where the gap magnitude is highest. At temperatures close to $T_c$, when inelastic scattering processes smear out the anisotropy of the gap, the difference between d-wave case and s-wave case is anyway questionable. Therefore we expect that the theoretical model (using isotropic gap) should be applicable also in the case the order parameter has d-wave symmetry. This could only affect the absolute gap magnitudes deduced from the analysis of the $T$-dependence of the picosecond component amplitude — which is already in case of an isotropic gap (used in the analysis of the data) accurate within $\sim 30\%$ — however the qualitative doping dependence of gap magnitudes and the two-component analysis should be unaffected.

When comparing our results with other techniques we should be aware that in case the order parameter has mixed symmetry, the bulk and surface sensitive measurements could give different results [194]. The main advocates for the d-wave order parameter symmetry are flux quantization measurements in superconducting rings with grain-boundary Josephson junctions [41] and ARPES (Angle Resolved Photoemission Spectroscopy) [44, 45] which are surface sensitive techniques, which might show different order parameter symmetry than the bulk data (in our experiments we are probing in the optical skin depth which is $\sim 100$ nm in our case).

Now, let us compare the results on the gap evolution with the data obtained by other experimental techniques. The most direct measurement of the quasiparticle density of states in HTSC seems to be tunneling. In underdoped HTSC temperature independent gap was observed by several groups in different HTSC [54, 55, 188, 189], where no shift in the gap magnitude was observed upon lowering the temperature through the superconducting transition temperature. The pseudogap magnitude was shown to decrease with increasing doping [54].

The simultaneous presence of two gaps was reported in tunneling spectra [195] over the whole doping region in HTSC. Comparing our $\Delta^p(x)$ with the gap from the Giaver (single-particle) tunneling on YBCO [195], we find very good agreement [see Fig. 4.10]. Andreev reflection [195], on the other hand, probes the phase-coherent state. It thus cannot be directly compared with the $\Delta_c(0)$ in our measurements. The coherence gap magnitude scales with $T_c$; in underdoped regime its value is much lower than the ”excitation” gap from the Giaver tunneling, whereas in overdoped the two gaps have similar magnitudes, both scaling with $T_c$.

The co-existence of $\Delta^p$ and $\Delta_c(T)$ is also consistent with the $T$-dependence of the photoemission lineshapes in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [198, 199], and follows also from
electronic Raman experiments [196, 197], although the data available at present from these two techniques are only for one or two underdoped samples. The values of the superconducting gap and the pseudogap from photoemission and Raman data are in close agreement with the data obtained from femtosecond time-resolved optical spectroscopy. However, in these two experiments the temperature dependence of the gap strongly depends on the momentum $\mathbf{k}$. In overdoped samples the gap has significant $T$-dependence in all $\mathbf{k}$ points, vanishing at $T_c$, whereas in underdoped samples the $T$-dependence of the gap is found only in the direction of the diagonal to the two principal direction $k_x$ and $k_y$; near $(\pi,0)$ points (in the $k_x$ and $k_y$ direction) the gap is essentially $T$-independent [198, 200]. However, it has been pointed out recently that these features may not be so much due to changes in electronic structure, but due to matrix elements effects [201]. As far as doping dependence of the gaps is concerned, it follows from the analysis of the electronic Raman data that the magnitude of the $T$-independent pseudogap is more or less constant with respect to doping [196], whereas superconducting gap follows $T_c$. Based on the data analysis Opel et al. argue [196] that the pseudogap is unrelated to the superconductivity.

When discussing different probes of the gap magnitude, we should mention the results from thermodynamic measurements, e.g. electronic specific heat, which played an important role in determining the gap magnitude in conventional superconductors [2]. The determination of the gap magnitude in this case [98, 190] (determined from the $T$-dependence of the electronic specific heat coefficient $\gamma(T)$ - below and above $T_c$ for $\Delta_c(0)$ and $\Delta^p$ respectively) is less straightforward than for example in tunneling or optical measurements, since it is model dependent. Nonetheless, it follows from the analysis [190] that in underdoped samples the (T-independent) pseudogap magnitude increases with decreasing doping in similar fashion and with similar values of the pseudogap magnitude as extracted from our data [see Figure 4.6]. Close to optimal doping Loram et al. argue [190] that $\Delta^p$ drops to almost zero. At this point we should mention the measurements of magnetic fields dependence of electronic specific heat [27]. The data [27] consistently with our observations show that the behavior in overdoped YBCO is closer to the BCS-like mean-field behavior, whereas in strongly underdoped samples the data show no shift in temperature of the peak in electronic specific heat with increasing magnetic field [27] as expected in the case of a weakly interacting Bose gas [27] - supporting the preformed pairing scenario in underdoped HTSC.

The femtosecond pump-probe data in optimally doped and overdoped regime imply phase separation in cuprates which should be briefly debated and compared to the experimental evidences for the phenomenon coming from other experimental probes. In general, there is a vast amount of papers supporting the spatially inhomogeneous picture in cuprates [33]. However, apart from La$_{2-x-y}$Nd$_y$Sr$_x$CuO$_4$, where static charge modulation was determined [37], in the rest of cuprates the charge inhomogeneities are assumed to be dynamic. The existence of dynamic charge inhomogeneities (usually addressed as stripes) in HTSC is deduced from EXAFS
Summary and conclusions.

In this chapter we presented experimental results using femtosecond time-resolved optical spectroscopy on HTSC system Ca$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ (CaYBCO). We analyzed [35], neutron scattering data [36, 202], or Raman [111], where the local structural distortions are associated with the presence of atomic scale charge inhomogeneities. Here we should stress the advantage of the femtosecond time-resolved spectroscopy, to separate the different components due to their different time, polarization and temperature dependences on the femtosecond time-scale, which should be faster than the timescale of stripe motion.

At the end of the discussion we should address the important issue based on the analysis of the slow nanosecond component suggesting there is a significant in-gap density of localized states in the whole doping region. The presence of localized carriers in HTSC is also one of the widely discussed topics in HTSC in recent years. Their presence was observed both in strongly underdoped region as well as near optimal doping in photoconductivity measurements [17], picosecond Raman [39, 203], and others [38]. The time-resolved optical experiments suggest that the localized states lie in the vicinity of the Fermi energy and have the lifetime on the order of 100 ns. The microscopic origin of the in-gap states is unclear. The preliminary data on electron-irradiated samples [205] show that the slow component dynamics is weakly affected by electron bombardment known for creating additional defects [206]. This implies that the localized in-gap states are not simply intra-gap defects and suggests that the origin of the in-gap states is intrinsic. The presence of a similar response in the quasi 1D Peierls charge-density wave semiconductor K$_{0.3}$MoO$_3$ [146] suggests that photoinduced vortex-antivortex excitations cannot account for the observed effect. Direct comparison with spectroscopic techniques like ARPES or tunneling can be merely speculative, since these techniques probing the density of states cannot resolve between states being itinerant or localized.

To conclude, the time-domain spectroscopy experiments of time and temperature dependence of the photoinduced quasiparticle response give a self-consistent and systematic picture of the low-energy charge excitation spectrum of CaYBCO. The results suggest that the cross-over from the underdoped to the overdoped region of the phase diagram occurs via a two-component inhomogeneous state with two coexisting gaps; one $T$-independent and one with the mean-field-like $T$-dependence. According to present time-domain spectroscopy experiments the mixed gap region is present over most of the overdoped and optimally doped phase. In order to see to what extent the two gap behavior persists in the underdoped state in cuprates additional measurements need to be done with different probe wavelengths. The situation seems very similar in other HTSC, however, further systematic temperature and doping dependent measurements have to be done.
the data using the theoretical model describing the relaxation of the photoexcited quasiparticles and localized in-gap carriers in materials with a small gap in the excitation spectrum. The data consistently show that in underdoped samples the carrier relaxation is determined by the presence of a T-independent (or weakly T-dependent) pseudogap $\Delta^p$. From the absence of the anomalies in the relaxation time and the amplitude of the picosecond component we argue that the pseudogap behavior arises due to the presence of pairing above $T_c$. In this scenario, as temperature is decreased more and more carriers are in the paired state and at $T_c$, when the density of pairs is high enough, macroscopic phase coherence is established.

Near optimal doping a crossover to a two component behavior is observed in $T$-dependences of the relaxation time and the amplitude of the fast transients, which consistently explains also $T$-dependences of the slow component data. From the relaxation time analysis of fast transients it follows that two energy gaps determine the relaxation dynamics, corresponding to two phases present in a superconductor. One shows mean field-like behavior closing at $T_c$ — manifesting itself through the divergence of the relaxation time and corresponding decrease in the photoinduced amplitude. The other T-independent pseudo-gap is present also above $T_c$. From the analysis of the fast component amplitude data we find that the magnitudes of the two gaps $\Delta^p$ and $\Delta_c (T = 0)$ decrease as we go to more overdoped samples. The two values gradually converge as we go to strongly overdoped samples. To what extent the two component picture holds also in underdoped samples remains to be seen, but there is already significant evidence that it does not. Measurements with different probe wavelengths that might be more susceptible to the carrier rich areas through the probe process matrix element, can shed some light on these issues.

At the end we should stress that a significant density of localized states in the vicinity of Fermi energy follows from the analysis of the slow nanosecond component in photoinduced absorption. The microscopic origin of the in-gap states is still unclear.
Chapter 5

Femtosecond spectroscopy of low dimensional CDW systems.

Presently, the main motivation for studying charge density wave (CDW) materials was to test the validity of the theoretical models describing the photoinduced absorption in materials exhibiting a small energy gap in the density of states and to compare the results to the ones obtained on high-Tc superconductors. Therefore we have chosen the material that has been by far the most extensively studied among low dimensional charge density waves – a quasi one-dimensional (1D) charge density wave semiconductor $K_{0.3}MoO_3$. In this material the temperature evolution of the low energy excitation spectra is more or less generally accepted [179].

We first make a general introduction to the charge density wave phenomenon, focusing on the effect of CDW formation on low energy excitation spectra in a quasi 1D material. In the sections to follow we present results obtained on $K_{0.3}MoO_3$ using the femtosecond pump-probe technique [146], while at the end we summarize the results and compare them with data obtained on HTSC.

Femtosecond time-resolved studies of $K_{0.3}MoO_3$ gave us conformation and additional proofs of the theoretical models discussed in sections 3.4 and 3.5 with several new features shedding additional light on the field of the femtosecond time-resolved spectroscopy.

5.1 Introduction to quasi 1D CDW’s.

In this section we present in a schematic way some of the most relevant aspects of quasi 1D CDW systems. For detailed description of the phenomenon the reader is referred to the recent book by Grüner [179]. Usually $K_{0.3}MoO_3$ is used as an example. Due to availability of large single crystals it is the most intensively studied quasi 1D CDW material.
5.1.1 The structure of K$_{0.3}$MoO$_3$.

Molybdenum oxides A$_{0.3}$MoO$_3$, where A is a monovalent metal like K, Rb, or Tl - also called blue bronzes due to their shiny blue appearance - are well known for their interesting electronic properties arising from their one-dimensional (1D) chain structures [179, 208, 209, 210]. The schematic structure of K$_{0.3}$MoO$_3$ is shown in Fig. 5.1. K$_{0.3}$MoO$_3$ crystallizes in a monoclinic unit cell (lattice parameters are given in caption to Fig. 5.1). The structure contains rigid units comprised of clusters of ten distorted MoO$_6$ octahedra, sharing corners along monoclinic $b$-axis. This corner sharing provides an easy path for the conduction electrons along the chain direction. The chains also share corners along the [102] direction and form infinite slabs separated by the potassium cations. The [102] direction together with [010] direction form a cleavage plane. At room temperature K$_{0.3}$MoO$_3$ is a highly anisotropic one-dimensional metal with conductivity ratios $\sigma_b : \sigma_{2a-c} : \sigma_{2a+c} = 30 : 1 : 0.05$. This enables one to treat it as a quasi 1D metal.

![Schematic structure of K$_{0.3}$MoO$_3$.](image)

Figure 5.1: Schematic structure of the monoclinic K$_{0.3}$MoO$_3$. Unit cell parameters at room temperature from Ref. [207]: $a = 18.249 \pm 0.01\text{Å}$, $b = 7.56 \pm 0.005\text{Å}$, $c = 9.855 \pm 0.006\text{Å}$, $\beta = 117^\circ 32^\prime \pm 5^\prime$.

5.1.2 CDW ordering in quasi 1D materials.

The main reason for occurrence of various instabilities (spin density waves, charge density waves, superconductivity) in quasi 1D materials is the reduction of phase space from three-dimensions (3D) to one-dimension. This can best be seen by considering the response function of the 1D electron gas. In this case the Fermi surface consists of only two points: one at $k_F$ and the other at $-k_F$. The Lindhard response function
5.1. Introduction to quasi 1D CDW’s.

[211] in 1D for T=0 is given by

\[ \chi(q) = \int \frac{d^2k}{2\pi^2} \frac{f_k - f_{k+q}}{\epsilon_k - \epsilon_{k+q}} = \frac{e^2}{\pi \hbar v_F} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \quad (T = 0), \]  

(5.1)

exhibiting a divergence at \( q = 2k_F \) [212]. This implies that any small external perturbation leads to a divergent charge redistribution suggesting that at T=0 the electron gas itself is unstable with respect to the formation of a periodically varying electron charge (or spin) density with the period \( \frac{\pi}{k_F} \). This divergent response function caused by the topology of the Fermi surface — usually referred to as a perfect nesting — leads to various instabilities at low temperatures, depending on the particular interaction of the electronic system. The CDW ground state develops in low dimensional metals as a consequence of the electron-phonon interaction. As the name implies the ground state is described by a charge density redistribution accompanied by periodic lattice distortions.

Mean field results for the system of 1D electron gas and lattice.

The system of coupled 1D electron gas and lattice can be treated using the mean field approach [see section 3.1 in Ref. [179]], giving a finite transition temperature

\[ k_B T_c^{MF} = 1.14\epsilon_0 e^{-1/\lambda}, \]

(5.2)

where \( \epsilon_0 \) stands for the cut-off energy usually taken to be equal the Fermi energy \( \epsilon_F \), and \( \lambda \) is the dimensionless electron-phonon coupling constant. The critical temperature \( T_c^{MF} \) is determined as the temperature when one of the phonon frequencies, renormalized due to the electron-phonon interaction, goes to zero at wave vector \( q = 2k_F \). The softening of the phonon frequency as temperature is decreased towards the transition temperature is the so called Kohn anomaly [211]. Below the Peierls transition, the renormalized frequency of this mode is zero - indicating a "frozen-in" lattice distortion [179]. That is a macroscopically occupied phonon mode with non-vanishing expectation values \( \langle b_{2k_F} \rangle = \langle b_{-2k_F}^\dagger \rangle \), where \( b \) and \( b^\dagger \) are the phonon annihilation and creation operators respectively. One can define the complex order parameter as an average expectation value of the "frozen-in" mode population [179]

\[ |\Delta| e^{i\phi} = g \left( \langle b_{2k_F} \rangle + \langle b_{-2k_F}^\dagger \rangle \right), \]

(5.3)

where \( g \) is the electron-phonon coupling constant. Using this mean field approximation one obtains the same equation that describes temperature dependence of the superconducting gap in the framework of weak coupling BCS theory

\[ \frac{1}{\lambda} = \int_0^{\epsilon_0} \frac{d\epsilon_k}{2k_B T} \frac{d\epsilon_k}{\sqrt{\epsilon_k^2 + \Delta_{CDW}^2}}. \]

(5.4)
Here $\Delta_{CDW} = |\Delta|$ is the magnitude of the order parameter. The only difference between Eq. (5.4) and its equivalent from BCS theory is that the cut-off energy in the case of CDW is the Fermi energy $\epsilon_F$ in contrast to the Debye frequency $\omega_D$ in a BCS superconductor. This is due to the fact that for the charge density wave the energy gap develops in response to a static distortion of the underlying lattice and the relaxation effects (retardation) do not play a role. Therefore, the entire electron spectrum is effected by the electron-phonon interaction and the relevant cutoff energy is $\epsilon_F$. From Eq. (5.4) it follows that

$$\Delta_{CDW} (T = 0) = 2\epsilon_0 e^{-1/\lambda}$$

(5.5)

giving together with Eq. (5.2) the BCS relation between the critical temperature and the magnitude of the low energy gap

$$2\Delta_{CDW} (T = 0) = 3.52k_B T_{c}^{MF}.$$  

(5.6)

Since from Eq. (5.5) it follows that $\Delta_{CDW}$ is determined by $\epsilon_F$ instead of $\omega_D$, critical temperatures in 1D CDW’s are substantially higher than in BCS superconductors. For example, in K$_{0.3}$MoO$_3$ the low-T gap magnitude deduced from optical experiments is $2\Delta_{CDW} (T = 0) \approx 1400\, K$, giving $T_{c}^{MF} \approx 330\, K$.

Since Eq. (5.4) describing the T-dependence of the single-particle gap in CDW’s equals the BCS expression, the formulas worked out for superconductors can be applied to describe temperature dependencies of various quantities in the charge density wave state. The appearance of the single particle (SP) gap, for example, also leads to a finite coherence length which corresponds to the spatial dimension of the electron-hole pairs. At zero temperature it is given by a BCS expression

$$\xi_0 = \frac{\hbar v_F}{\pi \Delta_{CDW}}$$

(5.7)

where $v_F$ is the Fermi velocity. In these materials, similar to HTSC, coherence lengths are very short - of the order of several unit cells.

**Fluctuations and interchain coupling.**

From the mean field analysis given above one obtains a non-zero transition temperature $T_{c}^{MF}$ where the long range order develops. This is an artifact of the mean field analysis since the effects of fluctuations of the order parameter in 1D have thus far been neglected. In strongly anisotropic materials, due to reduction of the phase space, fluctuations become important and in a strictly 1D system there is no long range order [174]. The argument is essentially the same as the argument for the absence of the long range order in a Heisenberg antiferromagnet; the existence of gapless collective excitations prevents long range order and only short range correlations occur at low temperatures. In the CDW system this gapless excitation is the so called phase mode (see next section).
5.1. Introduction to quasi 1D CDW’s.

The long range order also leads to a well defined single particle gap, which is also not realized in a strictly 1D system. Instead, the short range correlations lead to a pseudogap due to a suppressed density of states near $E_F$. As the temperature is decreased the suppression becomes more and more pronounced [213] and the correlation length increases.

Going to a quasi 1D system, the coupling between adjacent chains should be taken into consideration. Due to interchain interactions charge density wave fluctuations become correlated, leading to a transition at finite temperature $T^{3D}_c$ [179] into a ground state with a 3D long-range order. Since Coulomb interactions seem to be dominant, the two neighboring chains tend to align themselves with a phase difference of $\pi$ [see Fig. 5.2 a)].

![Figure 5.2: a) Charge density wave modulations on the neighbouring chains. Coulomb interactions lead to the out of phase charge density modulation on the neighbouring chains. b) The temperature evolution of fluctuations in a system of coupled chains leading to long range order below $T^{3D}$.](image)

In Fig. 5.2 b) we plot the temperature evolution of fluctuations in a system of coupled chains leading to long range order below $T^{3D}_c$. At $T^{MF}_c$ the system of coupled chains does not undergo a phase transition; instead correlations build up along the chains with the correlation length $\xi_{\parallel} \propto 1/T$ [179]. Upon cooling, as fluctuations are reduced, the interchain correlations become important and the correlation length...
perpendicular to the chain direction $\xi_\perp$ at temperature $T^*$ exceeds the distance between two adjacent chains $d_\perp$. Below this temperature the fluctuations have a 3D character with fluctuations on neighboring chains strongly coupled. Upon further temperature decrease the correlation lengths $\xi_\perp$ and $\xi_q$ diverge as $\propto (T - T_{c}^{3D})^{-1/2}$ [179] and the system eventually undergoes a second-order phase transition to a 3D ordered state below $T_{c}^{3D}$ [179]. The formation of a 3D CDW ordered state is concurrent with the appearance of a gap $\Delta_{\text{CDW}}$ in the SP excitation spectrum.

If one neglects additional fluctuations near $T_{c}^{3D}$ the behavior of the transition to the ordered ground state is a mean-field-like. However, short coherence lengths in these materials suggest that the critical Ginzburg-Landau fluctuations may be important in the vicinity of $T_{c}^{3D}$.

Also, it should be stated that the above model is oversimplified since it considers that the interchain coupling is isotropic. Nonetheless, x-ray data on K$_{0.3}$MoO$_3$ [214] seem to follow the general scheme. From the analysis of the Bragg pattern it follows a crossover at $\sim 200$ K from 3D fluctuation region that exists up to approximately 20 K above $T_{c}^{3D}$, to a region where quasi 2D fluctuations exist [214].

### 5.1.3 Collective excitations in CDW materials.

Below $T_{c}^{3D}$ there is a long range three dimensional ordered state with a well established single particle gap. As expected for a complex order parameter [Eq.(5.5)], besides the single particle excitations both the phase and amplitude excitations occur. In the first approximation the modes are decoupled and represent independent oscillations of the amplitude and phase of the order parameter [179]. Both modes are plotted in Fig. 5.3 in the $q = 0$ limit.

In the $q = 0$ limit the phase excitation corresponds to the translational motion of the undistorted condensate. Such a translational motion does not change the condensation energy and consequently the excitation for $q = 0$ is gapless. In reality, one has to take into account also the commensurability effects (thus far we have considered incommensurate CDW modulation with the lattice period) and long range Coulomb forces [179] which modify the phason dispersion relation ($\omega_\phi \propto q$) and bring also strong temperature dependence in the dispersion relation [see chapter 6 in Ref. [179] for details]. Also, one finds that the frequency of the mode remains finite at $q = 0$ due to pinning of the phason by impurities. Namely, pinning acts as a restoring force shifting the phason frequency to some finite value also at $q = 0$. From frequency-dependent conductivity measurements [215] it follows that the dynamics of the pinned CDW in K$_{0.3}$MoO$_3$ is quite complex. The data at temperatures below $T_{c}^{3D}$ show a well defined high frequency pinning mode ($q = 0$) at $\sim 0.1$ THz and a distribution of the low-frequency pinning modes. The neutron data [216], on the other hand, show the same value of $\sim 0.1$ THz also for the frequency of phase mode at critical wavevector $q = 2k_F$.

On the other hand, the modulation of the amplitude changes the condensation
5.1. Introduction to quasi 1D CDW’s.

Figure 5.3: A schematic of the collective excitations in 1D CDW: phason and amplitudon. Changes in the charge density and ionic displacements are indicated. The charge density and the atomic positions in the metallic state are shown in the upper part.

energy and has therefore a finite frequency. In spin density wave materials the amplitude mode frequency would be the same as the gap frequency. In charge density waves, however, fluctuations of the single particle gap also lead to fluctuations of the ionic positions and the amplitude mode oscillation frequency is substantially lower than the gap frequency [179]. Since with amplitude mode oscillations there is no net displacement of the electronic charge with respect to the ionic positions the mode is expected to be Raman active. Its temperature dependence can be calculated within the Ginzburg-Landau theory [179] and was found to drop to zero at the Peierls transition temperature.

Experimentally temperature dependences of amplitude mode frequencies and damping were studied by Raman [217] and neutron [216] spectroscopy. At temperatures close to zero amplitudon frequency is $\omega_A \sim 1.7$ THz. The frequency softens as $T^{3D}_c$ is approached, but no drop to zero occurs. From its temperature dependence it follows that it should drop to zero close to the mean-field Peierls transition temperature $T^{MF}_c$ deduced from Eq.(5.6) [216]. This seems to indicate that the amplitude excitations are controlled by the mean-field behavior of the distorted Peierls chain. Neutron data show continuous behavior at $T^{3D}_c$, meaning that the amplitude mode frequency does not drop abruptly at $T^{3D}_c$. From neutron data [216] it follows that at $q = 2k_F$ there is an overdamped structure in the vicinity of $T^{3D}_c$ that evolved from underdamped Kohn anomaly and separates into amplitude and phase modes at temperatures below $T^{3D}_c$ [see Fig. 5.4 b)]. Theoretical studies of the dynamics of the Peierls chain [218] indeed show coupling between phason and amplitudon in some temperature interval below $T^{3D}_c$ and show that the dynamics of the collective modes is not strongly affected by
Figure 5.4: a) The mean-field behavior of the frequency of the Kohn anomaly $\nu_K$, amplitude mode $\nu_A$, and phase mode $\nu_p$ for the critical $2k_F$ wave vector. b) A schematic of the $T$-dependence of the collective modes frequencies ($\nu_{i}$) and damping ($\Gamma_{i}$) calculated for the Peierls chain (Refs. [218] and [216]). Damping constant $\Gamma_{i}$, is experimentally obtained from the damped oscillator fit to the dynamical structure factor: $S(\nu) \propto \frac{\nu \Gamma_{i}}{(\nu^2 - \nu_{0}^2)^2 + \nu^2 \Gamma_{i}^2}$. Interchain coupling. This is supported by neutron [216] and Raman [217] data. A schematic picture of the collective mode frequencies and damping near critical wave vector $q = 2k_F$ from Tutiš and Barišić [218] compared to the mean field result are shown in Fig. 5.4.

5.2 Femtosecond spectroscopy of quasi 1D CDW $K_{0.3}MoO_3$.

In this section we present femtosecond transient reflectivity measurements on $K_{0.3}MoO_3$ enabling for the first time a real-time observation of the reflectivity modulations caused by the collective CDW excitations. We report temperature dependence of the amplitude $A(T)$, frequency $\omega_A(T)$, and the damping constant $\Gamma_A(T)$ of the amplitude mode, and the $T$-dependence of the phase damping constant $\tau_p(T)$. We also report $T$-dependence of the electron-hole recombination lifetime $\tau_s$ across the CDW gap below, as well as above $T_c^{3D}$.

5.2.1 Experimental Set-Up.

In experiments presented here the set-up given in section 2.1.3 was used in the reflectivity configuration. The pump laser power was kept below 5 mW, exciting approximately $10^{18} - 10^{19}$ carriers per cm$^3$ [219]. The pump/probe intensity ratio was $\sim 100$. Steady-state heating effects were accounted for as described in section 2.1.5. Experiments were performed on $K_{0.3}MoO_3$ single crystals with the laser polarization in the $a$-$b$ plane; $a$ being the [102] direction and $b$ being the chain direction [207] [see Fig. 5.5 a)]. Since the signal amplitudes were found to be strongly polarization dependent,
we also performed the probe polarization dependence measurements. The crystal orientation was determined using an atomic force microscope, where the direction of the chains can be clearly resolved if the sample is freshly cleaved [Fig. 5.5].

Figure 5.5: a) Surface structure of $K_{0.3}MoO_3$ as expected from the bulk crystal data. The lattice constants and the crystallographic orientation are indicated. b) The direction of chains [010] determined by atomic force microscope (AFM). The picture present an AFM image over the area of 30nm$\times$30nm.

### 5.2.2 Experimental Results.

In Fig. 5.6 a) we show the photoinduced reflectivity $\Delta R/R$ as a function of time $t$ at different temperatures. Below $T_{c}^{3D}$ a damped oscillatory component is observed on top of a negative induced reflectivity, the latter exhibiting a fast initial decay followed by a slower $\sim 10\text{ps}$ decay [see Fig. 5.6 c)]. As $T_{c}^{3D}$ is approached from below the oscillatory signal disappears, while the fast transient signal remains observed well above $T_{c}^{3D}$, as shown by the time trace at 210K. In Fig. 5.6 b) we plotted only the oscillatory component together with its Fourier transform in the insert, showing a peak in the spectrum at $\nu_A = 1.7$ THz ($58\text{ cm}^{-1}$). The frequency corresponds to the $A_1$ symmetry amplitude mode observed in Raman [217] and neutron scattering experiments [216]. In Fig. 5.6 c) we show only the transient induced reflectivity signal at $T = 45$ and 110K, with the oscillatory component and the slow component $\mathcal{D}(T)$ subtracted. The logarithmic plot enables us to clearly identify two components with substantially different lifetimes, one with $\tau_s \simeq 0.5$ ps, and the other with $\tau_p \gtrsim 10$ ps at low $T$. For reasons which will become apparent, we attribute them to the quasiparticle relaxation $\mathcal{S}(T)$ and the phason relaxation $\mathcal{P}(T)$ respectively. We note that $\mathcal{P}(T)$ displays no sign of oscillatory response, in accordance with the expectation that the phason relaxation is overdamped in this type of experiment. In order to
Chapter 5. Femtosecond spectroscopy of low dimensional CDW systems.

Figure 5.6: a) The time-resolved photoinduced reflectivity in $K_{0.3}\text{MoO}_3$ at various temperatures below and above $T_a^{3D} = 183K$. The signals offset for clarity. b) The oscillatory transient signal $\Delta R_A/R$ after subtraction of the decay components $d_0$, $D$, $S$ and $P$ in Eq.(5.8). The fit to the data is made using the first term in Eq.(5.8). The insert shows the Fast Fourier transform (FFT) spectrum of the signal. c) The time-evolution of the transient signal with the oscillatory component subtracted shown at $T=45 K$ and $110 K$, displayed in a logarithmic scale to emphasise the difference in relaxation times $\tau_p$ and $\tau_s$. 
5.2. Femtosecond spectroscopy of quasi 1D CDW $K_{0.3}MoO_3$. enable a quantitative analysis, we separate out different components of the signal according to their temperature dependence and probe polarization anisotropies.

We performed measurements of the probe polarization anisotropy of the signal below and above $T_{c}^{3D}$. Similarly to YBCO [69] the signal amplitude does not depend on the pump pulse polarization. However, as the probe polarization is changed with respect to the crystal $a$-axis strong angular dependence is observed in Fig. 5.7. The fast transient amplitude [Fig. 5.7 c)] shows maximum for $E\|a$, whereas the magnitude of the oscillatory component has almost no polarization dependence [Fig. 5.7 b)].

![Figure 5.7: a) The dependence of the photoinduced signal on the probe polarization, with $\alpha$ being the angle between the probe polarization and the crystal [102] axis. The data was taken at 100 K. b) The amplitude of the oscillatory signal $A(T)$ as a function of probe polarization with respect to the crystal [102] direction. c) The amplitude of the fast transients as a function of probe polarization with respect to the crystal [102] direction below (solid ) and above (open circles) $T_{c}^{3D} = 183$ K.](image)

To be able to describe various contributions to the time resolved transient we should briefly consider the situation in the CDW material below $T_{c}^{3D}$ after photoexcitation. Similarly to superconductors, an ultrashort laser pump pulse first excites electron-hole pairs via an interband transition in the material [see Fig. 3.6]. In the process which is similar in most materials including metals, semiconductors and superconductors [92, 93], these hot carriers very rapidly release their energy
via electron-electron collisions reaching the states near the Fermi energy within $\tau_i = 10 \sim 100$ fs. The presence of the CDW gap in the single particle (SP) excitation spectrum inhibits the final relaxation step resulting in relaxation bottleneck. The photoexcited carriers accumulate above the gap (see section 3.4.2). This causes a transient change in reflectivity $\Delta R$ due to the transient change in dielectric constant arising from excited state absorption processes. The density of these accumulated photoinduced carriers $n_{pe}$ can thus be determined as a function of temperature and time after photoexcitation from the transient reflectivity change $\Delta R_s(t)/R \propto n_{pe}(t) = S(T)e^{-t/\tau_s}$, where $\tau_s$ is the characteristic quasiparticle recombination time (see section 3.4.2).

In addition to the transient change of reflectivity due to the single particle excitations discussed above, a transient reflectivity signal is expected also from the collective modes. The amplitude mode is of $A_1$ symmetry and involves displacements of ions about their equilibrium positions $Q_0$, which in turn depend on the instantaneous surrounding electronic density $n(t)$. Since the typical time of the perturbation of the electronic system $\tau_i$ is much shorter than the vibration period of the collective mode $h/\omega_A$, the photoexcitation can be thought of as a $\delta(t)$ -function-like perturbation of the density. Thereby the pump pulse acts as a time-dependent displacive excitation of the ionic equilibrium position $Q_0(t)$. The response of the amplitudon to this perturbation is a modulation of the reflectivity $\Delta R_A/R$ of the form $A(T)e^{-t/\tau_A} \cos(A t + \phi_0)$ by the displacive excitation of coherent phonons (DECP) mechanism [127] described in section 3.2; $A = \sqrt{\omega_A^2 - (1/\tau_A)^2}$ according to Eq.(3.6).

The $\delta-$ function-like photoexcitation also gives rise to a displacement of charges with respect to the ions, directly exciting the CDW phase mode. Since this is infrared-active, we expect the resulting change of the dielectric constant $\Delta \varepsilon/\varepsilon$ to lead to a directly observable reflectivity transient, which for small $\Delta \varepsilon$ can be approximated as $\Delta R_p/R \simeq \Delta \varepsilon/\varepsilon$. In equilibrium, the phason mode is expected to be pinned [179] and at a finite frequency $\omega_p > 0$ [215], but in non-equilibrium situation such as here, where the excess carrier kinetic energy may easily exceed the de-pinning energy, the mode may be de-pinned. In this case we may expect an overdumped reflectivity transient that can be written as $\mathcal{P}(T)e^{-t/\tau_p} \cos(\omega_p t + \phi)$, with $\omega_p \to 0$, but with the damping constant which is expected to be similar to that of the amplitudon mode $\tau_p \simeq \tau_A$, i.e. $\sim 10$ ps [218].

Summing all the contributions in $K_{0.3}$MoO$_3$ the photoinduced transient reflectivity signal is of the form:

$$\Delta R(t, T)/R(T) = A(T)e^{-t/\tau_A} \cos(A t + \phi_0) + \mathcal{P}(T)e^{-t/\tau_p}$$

$$+ S(T)e^{-t/\tau_s} + d_0(T, t) + \mathcal{D}(T).$$

(5.8)

For completeness we also include here an additional term $d_0(T, t)$ due to a single pump pulse contribution to the long-lived signal and $\mathcal{D}(T)$ - the signal at negative time delays due to pile-up of the slow component signals [see section 3.5]. Both
d_0(T,t) and \mathcal{D}(T) were observed experimentally. Fortunately - as we show above - different contributions to \Delta R/R can be effectively distinguished experimentally by their very different time-dynamics and temperature and polarization dependences.

Temperature dependences of \nu_A (= \omega_A/2\pi) and \Gamma_A = 1/(\pi\tau_A) derived from fits to the real-time oscillations are shown in Fig. 5.8 a), and \tau_A is plotted in Fig. 5.8 b). They closely follow the expected behavior for the amplitudon mode and are in good agreement with previous spectroscopic neutron \cite{216} and Raman \cite{217} data. The amplitude of the modulation \mathcal{A}(T) falls rather more rapidly with T than \nu_A and is rather isotropic in the a – b plane [see Fig. 5.7 b)].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.8.png}
\caption{a) The amplitude \mathcal{A}(T) (diamonds), frequency \nu_A (full circles) and damping constant \Gamma_A = 1/(\pi\tau_A) (squares) as functions of temperature. The data from Refs. \cite{216} (open circles) and \cite{217} (open triangles) are also included for comparison. b) \tau_p as a function of T (open circles). The amplitudon decay time \tau_A is also plotted for comparison (squares). c) \mathcal{P}(T) as a function of temperature.}
\end{figure}

In Fig. 5.8 b) and c) we plot T-dependence of \tau_p and \mathcal{P}(T) respectively. At T =50 K \tau_p = 12 \pm 2 \text{ ps} in agreement with the \Gamma = 0.05 \sim 0.1 \text{ THz linewidths of the pinned phason mode in microwave and IR experiments} \cite{208, 216, 220}. With increasing temperature \tau_p is approximately constant up to 90 K and then falls rapidly as T \rightarrow T_c. The decrease of \tau_p near T^{3D}_c is consistent with increasing damping due to the thermal phase fluctuations arising from coupling with the lattice and SP excitations. Comparing \tau_p and \tau_A [also plotted in Fig.5.8 b)], at 50K \tau_p \simeq \tau_A but the fall-off at higher temperatures appears to be faster for \tau_A than for \tau_p. The amplitude \mathcal{P}(T) exhibits somewhat different behavior. It appears to show first an increase with increasing T and then drops as T \rightarrow T^{3D}_c. Such T-dependence behavior
was previously observed - but not yet satisfactorily explained - for the threshold field \( E_t \) in some non-linear conductivity experiments \([221, 222]\).

Figure 5.9: a) Temperature dependence of \( S(T) \). The fit to the data for \( S(T) \) is shown using the Eq.(3.13) with the BCS-like gap \( \Delta_{BCS}(T) \) opening at \( T_{c}^{3D} = 183 \) K. b) The single-particle relaxation time \( \tau_s \) as a function of \( T \) and a fit using expression (3.23).

Let us now turn to the transient reflectivity signal due to photoexcited single-particle excitations. The temperature dependence of the photoinduced signal amplitude is given in Fig. 5.9 a): \( S(T) \) is nearly constant up to nearly 100 K, then increases slightly and later drops very rapidly near \( T_c \). The rapid drop in amplitude is consistent with the closure of the CDW gap at \( T_{c}^{3D} \), and shows similar behavior as overdoped YBCO. We fit the data using the model \([71]\) (see section 3.4.2) with the BCS-like gap \( \Delta_{CDW}(T) \) as given by Eq.(3.13)

\[
S(T) \propto n_{pe} = \frac{\mathcal{E}_I/(\Delta_{CDW}(T) + k_B T/2)}{1 + B \sqrt{\frac{2k_B T}{\pi \Delta(T)}} \exp\left(-\Delta_{CDW}(T)/k_B T\right)}.
\]  

(5.9)

Here \( \mathcal{E}_I \) is the pump laser intensity per unit cell and \( B = \frac{2\nu}{N(0)\hbar} \) is the constant, depending on the material parameters. Taking that \( N(0) \sim 2 - 3 \text{ eV}^{-1}\text{spin}^{-1}\text{cell}^{-1} \) (Ref.[179]), \( \nu \sim 0.1 \text{eV} \) \([223]\), and taking \( \nu \sim 1-5 \) (since the gap magnitude is also of the order of 0.1 eV \([208]\)), one obtains the value of \( B \sim 10 \). We fit the T-dependence of \( S \) with expression (5.9) in Fig. 5.9 a). We find that the amplitude \( S(T) \) obtained from the fits to the time-resolved data agrees remarkably well with the model for \( T < T_{c}^{3D} \). The value of the gap obtained from the fit of Eq.(3.13) with \( B = 10 \) was \( \Delta(0) = 850 \text{K} \pm 100 \text{K} \) in good agreement with other measurements \([208]\).

We note here that in contrast to the response of the collective modes \( A(T) \) and \( \mathcal{P}(T) \), both of which disappear within 10-20 K below \( T_c \), \( S(T) \) gradually drops to a
constant value at approximately 240 K; i.e. appears to show a pseudogap up to 60 K above $T_c$. The polarization anisotropy of the signal $S(T)$ for $T > T_c^{3D}$ is the same as for $T < T_c^{3D}$ [as shown in Fig. 5.7 c)], strongly suggesting that the origin of the signal $S(T)$ above $T_c$ is the same as below $T_c^{3D}$ i.e. photoexcited SP states above the gap.

As expected, the $T$-dependence of the relaxation time $\tau_s$ [Fig. 5.9 b)] is qualitatively different from $\tau_p$ and $\tau_A$. As $T \rightarrow T_c^{3D}$ $\tau_s$ appears to diverge and then drops to $\tau_s \sim 0.25$ ps above $T_c$. Such behavior is in agreement with the expected temperature-dependence of the SP relaxation across the gap given by the model [71] (section 3.4.3). The solid line in Fig. 5.9 b) shows the fit to the data using Eq.(3.23) with a BCS-like $T$-dependent gap $\Delta_{CDW}(T)$ with $T_c^{3D}=183$ K.

It should be noted that the behaviors of the amplitude and the relaxation time above $T_c^{3D}$ is quite different. The relaxation time shows a sharp drop to a constant value — consistent with the mean-field behavior with a narrow ($\sim 10$ K) fluctuation region. On the other hand, the amplitude of the fast transient after sharp decrease at $T_c^{3D}$ gradually drops to a constant value at about 240 K. Above this temperature both the signal amplitude and the relaxation time are constant — up to more than 350 K; the relaxation time being comparable to the Allen $e$-$ph$ relaxation time. It follows that the increase in the amplitude at $\sim 240$ K as temperature is decreased is not due to the 3D critical fluctuations, since this would affect the relaxation time above $T_c^{3D}$ as well. More likely, the increase in amplitude is due to a locally formed pseudogap due to fluctuating presence of the CDW modulation. Whether the fluctuations have a three dimensional or a quasi two-dimensional character as deduced from x-ray data [214] cannot be resolved.

To complete the data analysis we show in Fig. 5.10 a) the pile-up amplitude (see section 3.5.1) of the slowly-decaying signal $D(T)$ as a function of temperature. Similar to the analysis of the slow component amplitude on YBCO (section 4.3) one can also plot the $T$-dependence of the single pulse contribution to the slow component $d_0$ that has similar behavior to $D(T)$ [Fig. 5.10 b)]. However, at temperatures below $\sim 130$ K one should scan the signal to $>100$ ps in order to be able to differentiate between the slow component and the phason contribution with a $\sim 10$ps relaxation time, which is experimentally difficult.\footnote{When performing very long scans one has to move the retroreflector by several cm. In case the system is not optimally aligned this might result in changing the lateral position of the probe beam waist on the sample with respect to the pump beam waist. This can bring some systematic error, effecting the read-out of magnitude of the long lived signal.}

The magnitude of the pile-up is approximately 10 times higher than the single pulse contribution (similar to the data on YBCO where the ratio is 2-5 depending on doping (section 4.3), implying the typical timescale of the order of 100 ns. Moreover, its magnitude (when compared to the amplitude of the fast component) is also substantially larger than in YBCO. Its anomalous temperature dependence clearly rules out a thermal origin and strongly suggests excitations involving in-gap localized
states as discussed in section 3.5. As the gap closes excitations from intra-gap states to the quasiparticle states are no longer possible, explaining the drop of the photoinduced signal above \( T_c \). We fit the data using a model for intra-gap state relaxation [72]. The parameters used in the fit are the same as used in the analysis of the fast relaxation component with values of dimensionless constant \( B = \frac{2\nu}{N(0)\hbar c} \approx 10 \) [see section 5.2]. Since the magnitude of the gap is of the order of \( \Delta_c (0) \approx 5kT_c \) we expect that Eq.(3.37) is valid up to temperatures close to \( T_c \). The fit using Eq.(3.37) is shown by the dashed line, whereas the general solution [Eq.(3.32)] is given by the solid line.

It should be noted however that some long-lived non-bolometric signal exists also above \( T_c \) gradually dropping to a constant value at approx. 240 K – the same temperature where \( S(T) \) was found to drop to a constant value [see Fig. 5.9]. It can be attributed, similarly to the reasoning when \( T \)-dependence of \( S(T) \) was analyzed, to the presence of the pseudogap in the density of states due to a locally formed SP gap. The probe polarization data [inset to Fig. 5.10 a)] show the same angular dependence as the fast picosecond components \( S(T) \) and \( P(T) \).

### 5.3 Conclusions.

The femtosecond time-resolved spectroscopy data presents some qualitatively new information on the single-particle and collective excitations in quasi-1D materials. We
found that because of the qualitatively different time, temperature, and polarization characteristics, the responses of the different components can be very effectively separated. The real time oscillations of the amplitude mode were observed for the first time. We note however that although coherent oscillations were reported on the superconductor YBa$_2$Cu$_3$O$_{7-\delta}$, no $T$-dependence of the oscillation frequency was reported; the oscillations were not attributed to any collective electronic mode, but to the $c$-axis phonons [145, 144, 159]. Apart from directly extracting the $T$-dependences of $A(T)$, $\nu_A(T)$ and $\tau_A(T)$ in good agreement with previously published values, we also observed an overdamped mode, which we tentatively assigned to the relaxation of the phason mode. In addition to the observation of $T$-dependence of photoinduced SP population as predicted by theory [71], we find - also in agreement with calculations [71] - that the SP recombination time across the gap diverges as $\tau_s \propto 1/\Delta$ as $T \to T_c$. From the fact that the SP population appears to persist above $T_c$ the measurements shows clear evidence for the existence of a pseudogap for SP excitations above $T_c$ and suggests the presence of local CDW fluctuations, rather than critical fluctuations of the order parameter which would appear as a tail also in the SP relaxation time $\tau_s$ above $T_c$ - but does not.

At the and we should briefly discuss the implications of the presented results on the analysis of the data taken on HTSC. One of the reasons for applying this experimental method on K$_{0.3}$MoO$_3$ was to test the validity of the theoretical models (see sections 3.4 and 3.5) adopted for HTSC. We found that both the fast component $S(T)$ and the slow component $D(T)$ on K$_{0.3}$MoO$_3$ follow the predictions of the theoretical models. Not only the qualitative behavior is nicely reproduced, but also the quantitative value of the SP gap in K$_{0.3}$MoO$_3$ obtained from the fit is in good agreement with the published values. This is an important fact when comparing the magnitudes of the gap obtained from the analysis of the fast component amplitude in time-resolved pump-probe experiments with the values obtained from other techniques, tunneling for example. From the data on K$_{0.3}$MoO$_3$ it follows that though the model is quite crude, the error in the determined magnitude of the gap is of the order of 10-20 %. Secondly, since the temperature dependence of the slow component on K$_{0.3}$MoO$_3$ is almost identical as the slow component on overdoped YBCO (at least at temperatures below $T_c$), it gives some constraints regarding the nature of the in-gap states — if, of course, we assume that the nature of localized states in the two classes of materials is the same. For example, photoinduced vortex-antivortex excitations proposed for describing long lived component in HTSC cannot account for the observed effect in K$_{0.3}$MoO$_3$. Also, it seems that the origin of the localized states is non-magnetic since no magnetic excitations exist in blue bronze. However, in order to pin down the origin of intra-gap localized states, additional experiments on irradiated samples in magnetic field etc. have to be performed.
Chapter 5. Femtosecond spectroscopy of low dimensional CDW systems.
Chapter 6
Summary and conclusions.

Recent data obtained by femtosecond time-resolved spectroscopy on near-optimally doped high-$T_c$ superconductors showed that fast picosecond reflectivity transients strongly depend on temperature [66, 68, 69]. Moreover, systematics of the data showed that there is also some long lived non-bolometric component with lifetime on the nanosecond range that was attributed to photoexcited localized states near Fermi energy [69]. In both signals strong increase in amplitude was observed as temperature was lowered through $T_c$. In addition, in fast signal this is accompanied by divergence in the relaxation time [66, 68].

These observations led us to investigate quantitatively the photoexcited carrier relaxation dynamics in cuprates. We showed [71] that the photoexcited carrier relaxation is strongly affected by the presence of a small energy gap in the density of states. The gap creates a relaxation bottleneck increasing the typically 100 femtosecond relaxation time to picoseconds. By measuring changes in reflectivity or transmission of the suitably delayed probe optical pulse one probes the time evolution of the photoexcited carrier density. The amplitude and the relaxation time of the fast photoinduced transient strongly depends on temperature and the magnitude of the single particle gap. Therefore, by analyzing the T-dependences of the amplitude and relaxation time one can determine the magnitude and temperature dependence of the gap. Further, qualitative analysis of the slow component shows [72] that its temperature dependence can be well accounted for by considering absorption from photoinduced in-gap localized states [72]. According to the models [71, 72], both the fast and the slow component should drop to zero as temperature is increased above $T_c$ since there is no gap in the density of states present above $T_c$. This situation was found to be well reproduced in near-optimally doped YBa$_2$Cu$_3$O$_7$-$\delta$ [66, 69], however the data on underdoped YBa$_2$Cu$_3$O$_{7-\delta}$ [181] show strong deviation from the observed behavior in near-optimally doped samples. From the absence of the anomalies in fast component at $T_c$ the data suggested the photoexcited carrier relaxation being governed by the presence of the temperature-independent pseudogap.

In order to analyze the evolution of gap(-s) we applied the femtosecond time-resolved spectroscopy to a high temperature superconductor Ca$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$. 

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We performed measurements on a number of thin film samples on various substrates as well as on a number of single crystals over wide range of doping. We analyzed both the temperature dependence of the fast and slow component dynamics using adopted theoretical models [71, 72]. In strongly underdoped materials the absence of anomalies in amplitude and relaxation time of the fast transient at $T_c$ imply the presence of the temperature-independent pseudogap $\Delta^p$ [181] which is inversely proportional to doping [71]. Near optimum doping and in the overdoped region, on the other hand, we found that the relaxation dynamics is governed by two energy scales implying the co-existence of two distinct gaps [204]. One is a temperature-independent pseudogap $\Delta^p$ and the other is a temperature-dependent gap $\Delta_c(T)$ with the mean-field-like temperature dependence. Similar results were obtained also from the analysis of the slow component.

Since in underdoped samples there is no anomaly in either relaxation time or amplitude of the fast transient, the data support the presence of some kind of preformed pairing [58, 59, 60] above $T_c$ in underdoped regime. This is consistent with recent tunneling data [54, 195] on variety of high-$T_c$ superconductors. A crossover to overdoped region seems to proceed via a 2-component inhomogeneous state with two co-existing gaps corresponding to carrier rich and carrier poor regions. Similarly, two component behavior follows from other femtosecond time-resolved optical experiments on near-optimally doped cuprates can be observed on near optimally doped $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [68, 156, 178, 153, 155], therefore it seems that the situation regarding time-resolved data on near optimally doped samples is quite general in HTSC.

The two component behavior is reflected also in the slow component data near optimal doping and in overdoped $\text{CaYBCO}$. The observed behavior is consistent with the model [72] where the slow component is due to absorption from photoinduced in-gap localized states. The microscopic origin of the in-gap states is still unclear, however recent experiments on electron-irradiated samples [205] show that the in-gap states are intrinsic and not merely due to defects. Moreover, the same behavior was recently observed also in near-optimally doped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ [155] and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+x}$ [178] implying that the localized in-gap states in the vicinity of Fermi energy are another characteristics of HTSC.

Finally, we used femtosecond time-resolved spectroscopy to study also a quasi one-dimensional charge-density wave (CDW) semiconductor $\text{K}_0.3\text{MoO}_3$ [146]. Similar to HTSC a fast transient was found, whose amplitude and relaxation time showed anomalies at $T_c = 183$ K, concurrent with the opening of the Peierls gap. The amplitude of the fast transient shows an abrupt drop at $T_c$, whereas the relaxation time shows divergence at $T_c$ in agreement with the theoretical model [71]. Moreover, the amplitude of the single particle gap found from the fit to the data was found to be in agreement with the well established value of $2\Delta(0) \sim 1400$ K. Above $T_c$ the fast signal amplitude drops gradually to a constant at $\sim 240$ K, which was attributed to the presence of the pseudogap in the single particle excitation spectrum.
In addition, amplitude mode reflectivity oscillations were observed in real time, whose frequency \( \nu_A(T) \), amplitude \( A(T) \) and damping constant \( \tau_A(T) \) are in close agreement with frequency-domain measurements. A \( T \)-dependent overdamped response is also observed and on the basis of the \( T \)-dependence of its amplitude and damping it is tentatively attributed to relaxation of the phason mode.

A long lived nanosecond component was also observed in \( \text{K}_{0.3}\text{MoO}_3 \). Since it cannot be accounted for by a bolometric mechanism and since it follows the behavior for absorption from photoinduced localized states [72] it is attributed to the presence of the intra-gap localizes states. The nature of intra-gap excitations in \( \text{K}_{0.3}\text{MoO}_3 \) has been a subject of extensive studies over the years (see Ref.[179] for a review), however no final consensus has been made regarding their origin. Although the \( T \)-dependence of the amplitude of the long lived component is quite similar as in HTSC and one could argue that localized states in the two cases have common nature, in order to pin down the origin of localized in-gap states additional experiments need to be performed.
Chapter 6. Summary and conclusions.
Appendix A

Heating of the solid due to laser excitation.

In this appendix we present the derivation of temperature rise in the illuminated volume of the crystal under investigation in time-resolved pump-probe experiments. In the first section we describe the steady state heating, where the pulsed laser is approximated by the continuous wave (CW) laser at the same wavelength and average power $P_0$. In the low photo-excitation experiments CW heating is far more pronounced than the non-equilibrium heating due to single laser pulse which is derived in the second section.

In general, when attempting to find a solution for the temperature rise in the solid one seeks the solution of the heat-conduction equation

$$ \nabla \cdot \overrightarrow{j} (\overrightarrow{r}, t) + \rho_s c \frac{\partial T (\overrightarrow{r}, t)}{\partial t} = A (\overrightarrow{r}, t) \quad , $$  \hspace{0.5cm} (A.1)

where $T (\overrightarrow{r}, t)$ is temperature and $\overrightarrow{j} (\overrightarrow{r}, t)$ the heat flow per unit area, $\rho_s$ being the density and $c$ the specific heat of the solid. $A (\overrightarrow{r}, t)$ represents the net energy per unit volume and per unit time generated within the solid due to absorption. We can solve the equation using the Fourier’s law

$$ \overrightarrow{j} (\overrightarrow{r}, t) = -\kappa \nabla T (\overrightarrow{r}, t) \quad , $$  \hspace{0.5cm} (A.2)

where $\kappa$ is the thermal conductivity tensor. Since in these experiments the laser beam is traveling in the direction of one of the eigenvectors of the orthorhombic crystal (actually it is tilted by approx. 6 degrees), we obtain the deferential equation for conduction of heat in an anisotropic orthorhombic crystal

$$ \rho_s c \frac{\partial T (\overrightarrow{r}, t)}{\partial t} = \sum_i \kappa_i \frac{\partial^2 T (\overrightarrow{r}, t)}{\partial x_i^2} + A (\overrightarrow{r}, t) \quad , $$  \hspace{0.5cm} (A.3)

where $\kappa_i$'s are the thermal conductivities in the $a$, $b$ and $c$ direction ($c$ being the direction perpendicular to the surface). We can calculate the temperature rise in the
illuminated area by choosing the proper Green’s function\(^1\) and the generated energy per unit volume and time for the two cases, equilibrium and non-equilibrium one. In both cases we consider the TEM\(_{00}\) Gaussian beam traveling in the \(z\) direction, and hitting the crystal at \(z = 0\). Since the temperature rises are of the order of several Kelvins we can neglect the thermal radiation loss which substantially simplifies the boundary condition to
\[
\frac{\partial T(x', y', z', t)}{\partial z} \bigg|_{z=0} = 0. \tag{A.4}
\]
For semi-infinite solid the additional boundary condition is \(T(z \to \infty) = T_\infty\).

### A.1 Steady state heating.

When we are interested in the steady state heating effect we are solving the Eq.(A.3) by equaling the left side to zero, \(\frac{\partial T(x', y', z', t)}{\partial t} = 0\). Since in all the experiments TEM\(_{00}\) laser mode was used, we approximate the generated energy per unit volume and time to be
\[
A(x', y', z') = 4 \frac{(1 - R) P_0 \alpha}{\pi d^2} \exp \left( -\frac{2(x'^2 + y'^2)}{d^2} \right) \exp (-\alpha z') \tag{A.5}
\]
where \(P_0\) is the average power of the pump\(^2\) laser beam, \(d\) is the diameter of the illuminated spot, \(\alpha\) the absorption coefficient, \(R\) the reflectivity at the particular wavelength and \(x\) and \(y\) are 0 at the center of the TEM\(_{00}\) beam.

To obtain the Green’s function appropriate to a boundary condition A.4 one takes the Green’s function for the inﬁnite solid [89] and apply a method of images to obtain
\[
G(x', y', z'; r^\prime) = \frac{1}{4\pi \sqrt{\kappa_z (x-x^\prime)^2 + \kappa_y (y-y^\prime)^2 + \kappa_x (z-z^\prime)^2}} \tag{A.6}
\]
Using A.5 and A.6 one can calculate the temperature rise as
\[
\Delta T(x, y, z) = \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' G(x, y, z; x', y', z') A(x', y', z') \tag{A.7}
\]

The integral A.7 can be simplified by changing the variables to \(r_x = \frac{1}{P_0} \sqrt{\kappa_x \kappa_z} (x - x')\), \(r_y = \frac{1}{P_0} \sqrt{\kappa_y \kappa_z} (y - y')\), \(r_z = \frac{1}{P_0} \sqrt{\kappa_x \kappa_y} (z \pm z')\) and using cylindrical coordinates \(r_x = \rho \cos \phi\), \(r_y = \rho \sin \phi\) and \(\tilde{z} = r_z\) giving the expression for the temperature rise

\(^1\) We shall take the Green’s function as the temperature at \((x, y, z)\) at time \(t\) due to instantaneous point source of strength unity generated at point \(P(x', y', z')\) at time \(t'\), the solid being initially at the temperature of cold finger.

\(^2\) The intensity of the probe beam is usually more than two orders of magnitude lower than the probe, therefore can be neglected.
A.2 Transient heating.

To calculate the temperature rise due to absorption of a single laser pulse with Gaussian lateral (TEM$_{00}$) and temporal profile with pulse width $\tau$, we have to solve Eq. (A.3) with

$$A(\overrightarrow{r}, t') = \frac{4(1-R)P_0\alpha}{\pi d^2} \exp \left( -\frac{2(x'^2+y'^2)}{d^2} \right) \exp \left( -\alpha' t' \right) \exp \left( -\frac{2t'^2}{\tau^2} \right). \quad (A.9)$$

Again we obtain the Green’s function appropriate to a boundary condition A.4 by taking the Green’s function for the infinite solid[89, 203] and apply a method of images to obtain

$$G(\overrightarrow{r}, t; \overrightarrow{r'}, t') = \frac{1}{8\sqrt{d_xd_yd_z\pi^3 (t-t')^3}} \times \exp \left( -\frac{1}{4(t-t')} \left( \frac{(x-x')^2}{d_x} + \frac{(y-y')^2}{d_y} \right) \right) \times \exp \left( -\frac{(z-z')^2}{4d_z(t-t')} \right) \times \exp \left( -\frac{(z+z')^2}{4d_z(t-t')} \right). \quad (A.10)$$

where $d_i = \kappa_i/\rho_sc$ are the thermal diffusivities in the principal directions. We calculate the temperature rise by solving

$$\Delta T(\overrightarrow{r}, t) = \int_{-\infty}^{t} dt' \int \int \int d\overrightarrow{r'} G(\overrightarrow{r}, t; \overrightarrow{r'}, t') A(\overrightarrow{r'}, t') \frac{A(\overrightarrow{r'}, t')}{\rho_sc}. \quad (A.11)$$
Appendix A. Heating of the solid due to laser excitation.

We can solve the lateral part of the integral A.11 explicitly to obtain

\[
\Delta T(\vec{r}, t) = \frac{P_0 \alpha (1 - R)}{4\pi \rho_s c} e^{-\alpha z} \times \int_{-\infty}^{t} dt' \frac{\exp\left(\frac{-2t'^2}{\tau^2} + \alpha^2 d_z (t - t') - \frac{x^2}{4(t-t')d_x+d^2} - \frac{y^2}{4(t-t')d_y+d^2}\right)}{\sqrt{4(t-t') d_x+d^2} + \sqrt{4(t-t') d_y+d^2}}(A.12)
\]

\[
\times \left[1 + \text{erf}\left(\frac{2z - 4\alpha d_z (t-t')}{4\sqrt{(t-t') d_z}}\right) + e^{2\alpha z}(1 - \text{erf}\left(\frac{2z + 4\alpha d_z (t-t')}{4\sqrt{(t-t') d_z}}\right))\right],
\]

where \(\text{erf}(x) = \int_{0}^{x} \exp(-t^2) \, dt\). Detailed analysis in connection to transient heating in high-\(T_c\) superconductors is given in Refs. [203, 39].
Appendix B

List of publications.

Publications in refereed journals


14. J. Demsar, B. Podobnik, V.V. Kabanov, D. Mihailovic, Th. Wolf, "The superconducting gap $\Delta_c$, the pseudogap $\Delta'$ and pair fluctuations above $T_c$ in overdoped Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ from femtosecond time-domain spectroscopy", *Phys. Rev. Lett.* **82**, 4918 (1999).


**Conference proceedings**

1. D. Mihailovic, I. Poberaj, T. Mertelj, J. Demsar, "Localized states in photoinduced and metallic YBa$_2$Cu$_3$O$_{7-\delta}$", *Proceedings of the International workshop*


**Book chapter**

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[82] In our experiments we were using Hamamatsu Avalanche Photodiode APD C5460.

[83] In our experiments we were using EG&G digital lock-in amplifier model 7260.

[84] In our experiments we were using Optistat by Oxford Instruments.


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[219] The carrier density was estimated assuming an absorption length $l = 0.1 \mu m$ at 800 nm.


