SIGNPOSTS TO THE MECHANISM OF SUPERCONDUCTIVITY IN THE CUPRATES Hajo Molegraaf



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Signposts to the mechanism of superconductivity in the cuprates

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SAMENVATTING

In het begin van de vorige eeuw werd het fenomeen supergeleiding ontdekt. Als bepaalde materialen worden afgekoeld tot onder een kritische temperatuur geleiden ze stroom zonder weerstand. De elektronen bewegen zich voort zonder energieverlies. Een fantastische eigenschap met veel interessante toepassingen, zoals mogelijke hoogspanningsleidingen zonder energieverlies, computerschips die geen warmte produceren en daardoor veel compacter en sneller kunnen worden en sterke magneten met al hun praktische toepassingen. Het duurde een halve eeuw voordat er een theorie kwam die het fenomeen verklaarde en het werd helaas duidelijk dat de kritische temperatuur waarschijnlijk niet veel hoger dan -240° C kon zijn.

Deze conventionele supergeleiders hebben een kritische temperatuur die een factor 20 tot 30 lager is dan kamertemperatuur. Supergeleiding bij kamertemperatuur is dan waarschijnlijk fundamenteel onmogelijk voor dit type materialen. Echter, weer bijna een halve eeuw later werden er nieuwe materialen ontdekt die supergeleidend zijn bij een veel hogere kritische temperatuur. Voor deze 'hoge temperatuur supergeleiders' is de kritische temperatuur (~ $100K = -173^{\circ}C$) nog maar een factor 2 tot 3 lager dan kamertemperatuur. De theorie voor de conventionele supergeleiders bleek niet op te gaan voor deze nieuwe supergeleiders. Misschien kunnen we, als we de juiste theorie hebben en we begrijpen hoe supergeleiding in deze nieuwe materialen werkt, een materiaal maken dat supergeleidend is bij kamertemperatuur. In dit proefschrift proberen we een klein stukje van de puzzel op te lossen.

Het mechanisme van hoge temperatuur supergeleiding, met name in de cupraten, is dus nog steeds niet gevonden. Het probleem is niet zo zeer dat er geen theorieën zijn om het fenomeen te verklaren, maar dat er te veel theorieën zijn. Verschillende (groepen van) mensen hebben zo hun eigen ideeën over waarom elektronen Cooper paren vormen, een basisingrediënt van supergeleiding. Voor supergeleiding in normale metalen (die alleen bij lage temperaturen supergeleidend zijn) is een theorie gevonden die goed werkt. Eén klasse theorieën voor de nieuwe, hoge temperatuur, supergeleiders is een modificatie van deze standaard theorie van Bardeen, Cooper en Schrieffer (BCS). In deze theorie oefenen de elektronen, die elkaar normaliter afstoten, via het kristalrooster een effectieve aantrekking op elkaar uit. Een tweede klasse theorieën maakt gebruik van een mechanisme van sterke wisselwerking tussen de elektronen, die ook resulteert in een effectieve aantrekking tussen de elektronen, maar van een geheel andere aard. Hoofdstuk 1 geeft een korte samenvatting van de belangrijkste theorieën van de tweede klasse.

Er is een manier om onderscheid te maken tussen de twee klassen van theorieën. Wanneer het systeem supergeleidend wordt moet er een verlaging van de vrije energie van het systeem optreden, anders had de overgang niet plaats gevonden. De mate waarin de vrije energie verlaagd wordt, wordt de condensatie energie genoemd. De vrije energie is de som van de kinetische energie en de interactie energie. In de BCS theorie gaat bij de overgang de kinetische energie omhoog, maar de interactie energie gaat meer omlaag, zodat de netto vrije energie omlaag gaat. De theorieën die uitgaan van sterke interacties tussen de elektronen voorspellen dat de kinetische energie *omlaag* gaat. Een meting van de verandering van de kinetische energie op het moment dat het systeem supergeleidend wordt kan dus een hint geven over welke klasse van theorieën van toepassing is op de cupraten.

Licht en lading zijn op een intieme manier met elkaar verbonden (door middel van de Maxwell vergelijkingen) en een meting van de respons van een materiaal op invallend licht kan eigenschappen van de (geladen) elektronen aan het licht brengen. Door middel van een reflectie meting kan de optische conductiviteit bepaald worden, waarbij de optische conductiviteit de respons van het materiaal is op een in de tijd variërend elektrisch veld (licht). Veel interessante eigenschappen van het materiaal kunnen aan de hand van de optische conductiviteit bestudeerd worden. In dit proefschrift wordt het gebruikt om de verandering van kinetische energie in de cuprate supergeleiders te bestuderen en om meer te weten te komen over de 'quantum kritische' eigenschappen van deze materialen in de normale toestand.

EEN MID INFRAROOD ELLIPSOMETER

De beste manier om de optische conductiviteit te meten is met behulp van een techniek genaamd ellipsometrie en voor het energiegebied van 0.74 tot 4.46 eV (wat het zichtbaar licht gedeelte van het elektromagnetische spectrum bevat) was een ellipsometer beschikbaar. Voor het infrarode deel van het spectrum van 1 meV tot 1 eV was een spectrometer aanwezig waarmee alleen normale reflectie en transmissie metingen gedaan konden worden. Het voordeel van ellipsometrie is dat zowel het reële als het imaginaire deel van de optische conductiviteit direct gemeten kunnen worden. Bij een standaard reflectiemeting kunnen beide delen alleen verkregen worden na toepassing van de Kramers-Kronig relaties, een wiskundige methode waarvoor een aantal aannames gedaan moeten worden. Infrarood ellipsometers waren niet beschikbaar en daarom werd er een in onze groep gebouwd. Hoofdstuk 2 beschrijft het ontwerp en de werking van dit instrument.

Om een ellipsometer goed te laten werken zijn twee polarisators van hoge kwaliteit nodig. De commercieel beschikbare polarisators waren echter niet goed genoeg. Daarom zijn nieuwe polarisators ontworpen en gemaakt. Deze polarisators zijn gebaseerd op het principe dat als licht een plak silicium raakt onder een hoek van 73.7°, één polarisatie geheel doorgelaten wordt en de andere maar gedeeltelijk. Vier platen silicium achter elkaar is dan voldoende om een hoge mate van polarisatie te krijgen.

Ellipsometrie is erg gevoelig voor de hoek van inval die het licht maakt met het materiaaloppervlak. Een kleine verandering van de hoek van inval geeft andere resultaten. De lichtbundel die gebruikt wordt is geen nauwe, parallelle bundel, maar een convergerende bundel met een openingshoek van 8°. Dit resulteert in een grote distributie van hoeken van inval wat de meting beïnvloedt. Om te onderzoeken wat het effect van meten met een distributie van hoeken van inval is, is een computermodel gemaakt van de gehele opstelling. Na doorrekening werd duidelijk dat de distributie van hoeken van inval niet genegeerd kon worden en een juiste callibratieprocedure gedaan moet worden, wat uitgelegd wordt in hoofdstuk 2.

De gehele ellipsometer bevindt zich in een vacuüm kamer met een druk van ongeveer $3 \cdot 10^{-9}$ mbar. Het te onderzoeken materiaal is bevestigd aan een 'flow cryostat' om metingen bij lage temperaturen (4K-300K) te kunnen doen. Verschillende onderdelen kunnen met de computer bestuurd worden en er is software ontwikkeld om automatisch metingen te kunnen doen en de voortgang van de metingen te kunnen volgen via internet.

KINETISCHE ENERGIE VERANDERINGEN IN DE CUPRATEN

Hoofdstuk 3 behandelt het probleem van kinetische energie veranderingen in de cupraten wanneer deze supergeleidend worden. De materialen die zijn onderzocht zijn verschillende Bi₂Sr₂CaCu₂O_{8+ δ} éénkristallen met verschillende kritische temperaturen T_c - de temperatuur waarbij het materiaal supergeleidend wordt. Voor deze materialen is het 'nearest neighbor tight binding' model van toepassing. Dat betekent dat men kan aannemen dat elektronen alleen van een atoom naar het naastgelegen atoom springen en niet over grotere afstanden in één keer. Er is aangetoond dat in dat geval de totale bijdrage van de geleidingselectronen aan de optische conductiviteit evenredig is met de kinetische energie (met een minteken). Door veranderingen van de geïntegreerde optische conductiviteit - het spectrale gewicht - te meten kan een schatting gemaakt worden van de veranderingen in de kinetische energie.

In principe is het spectrale gewicht een behouden grootheid die niet veranderd. Wanneer het systeem supergeleidend wordt ontstaat er een 'gap' in het optische spectrum. In dit energiegebied kunnen de elektronen geen energie absorberen. Het verwijderde spectrale gewicht komt terug in de vorm van een delta functie, resulterend in een oneindige geleiding en derhalve een weerstand die nul is. Echter, er is alleen sprake van verplaatsing van spectraal gewicht en de totale, geïntegreerde optische conductiviteit blijft gelijk.

De bijdrage van de *geleidings*elektronen aan de optische conductiviteit is slechts een deel van het totale spectrale gewicht. Een verandering van de kinetische energie van deze elektronen resulteert in een verandering van dit deel van de optische conductiviteit. Deze extra verandering is klein en gebeurt naast de verandering van spectraal gewicht tengevolge van de opening van de 'gap'. Ook temperatuur heeft een effect en de interessante kleine veranderingen in spectraal gewicht tengevolge van kinetische energie veranderingen moeten waargenomen worden naast grote variaties tengevolge van de temperatuur.

Het effect van de veranderingen van kinetische energie is dus klein en subtiel, en zeer precieze metingen zijn nodig om het te kunnen waarnemen. Wij hebben reflectie en ellipsometrie metingen gedaan in het energiegebied van 6 meV tot 4.46 eV met een hoge temperatuur resolutie. Door de temperatuur verandering in de normale toestand (boven T_c) te extrapoleren konden we de veranderingen in de optische conductiviteit meten wanneer T_c gepasseerd werd. Het gewicht van de delta piek (die het aantal supergeleidende elektronen weergeeft) kon niet gemeten worden en die is verkregen door het gehele spectrum te modelleren met een Drude-Lorentz model. Op deze manier hebben we voor iedere temperatuur het spectrale gewicht van de geleidingselectronen bepaald. We hebben gecontroleerd dat het resultaat onafhankelijk was van de details van het model. Ook hebben gecontroleerd dat andere effecten, zoals veranderingen in het rooster, de waarnemingen niet konden verklaren.

Wanneer supergeleiding optreedt hebben we waargenomen dat een kleine verandering van spectraal gewicht optreedt, overeenkomend met een kleine verandering van kinetische energie van de orde van grootte van 1 meV per koper atoom. Dit is meer dan de condensatie energie en een theorie voor supergeleiding in de cupraten moet derhalve een verlaging van kinetische energie als centraal mechanisme hebben. Een verlaging van kinetische energie is tegengesteld aan wat voorspeld wordt door de BCS theorie. Dit betekent dat deze theorie of een aanpassing daarvan niet de juiste manier is om supergeleiding in de cupraten te beschrijven. Een verlaging van kinetische energie betekent dat sterke interacties tussen de elektronen van groot belang zijn.

SPECTRAAL GEWICHT VERANDERINGEN IN BCS SUPERGELEIDERS

Het is nu interessant om te weten wat de resultaten zouden zijn voor een normale BCS supergeleider. Hoofdstuk 4 beschrijft de metingen die gedaan zijn aan Nb, V₃Si en MgB₂, waarvoor de BCS theorie een goede verklaring geeft voor supergeleiding in deze materialen. We verwachten daarom een afname van spectraal gewicht omdat de kinetische energie toeneemt. Er zijn echter twee problemen. Ten eerste worden deze systemen niet goed beschreven door het 'tight binding' model en daarom is de relatie tussen spectraal gewicht en kinetische energie niet zo vanzelfsprekend. Ten tweede zijn de te verwachten veranderingen veel kleiner omdat de kritische temperatuur veel lager ligt. Een berekening leert dat de te verwachten veranderingen in spectraal gewicht kleiner zijn dan wat we met onze instrumenten kunnen meten.

De metingen die we gedaan hebben laten inderdaad geen veranderingen zien bij T_c die duidelijk genoeg waren om conclusies te kunnen trekken. Nauwkeurigere metingen zijn derhalve in voorbereiding.

QUANTUM KRITIKALITEIT

In hoofdstuk 5 is het de normale toestand van de $Bi_2Sr_2CaCu_2O_{8+\delta}$ cupraten die bestudeerd wordt via de optische conductiviteit van het materiaal. In dit geval kijken we naar de infrarode frequentieafhankelijkheid, die tekenen vertoont van quantum kritisch gedrag.

Een systeem vertoont kritisch gedrag wanneer het dicht bij een fase overgang is. Een bekend voorbeeld van een fase overgang is het smelten van ijs, waarbij het systeem overgaat van een vast fase naar een vloeibare fase. Dit is een fase overgang bij eindige temperatuur, maar fase overgangen bij een temperatuur van nul Kelvin zijn ook mogelijk en die worden quantum fase overgangen genoemd. De fase overgang is er een tussen een geordende en een ongeordende toestand van het systeem, als een functie van druk, magnetisch veld of een andere parameter. Bij eindige temperatuur spelen thermische fluctuaties een belangrijke rol bij de fase overgang. Bij nul Kelvin zijn er geen thermische fluctuaties; in dit geval spelen de quantum fluctuaties een cruciale rol.

In het geval van de cuprate supergeleiders zijn er verschillende theorieën gebaseerd op quantum kritikaliteit die een quantum kritisch punt in het fase diagram voorspellen. Hoewel de quantum fase overgang bij nul Kelvin plaatsvindt, heeft het zeer specifieke gevolgen voor de eigenschappen van het systeem bij eindige temperatuur. In hoofdstuk 5 gaan we in op twee van die eigenschappen. Dicht bij het kritische punt wordt het systeem schaal invariant: het ziet er hetzelfde uit onafhankelijk van de lengte- of tijdschaal waarop het bekeken wordt. De responsfunctie van het systeem, zoals de optische conductiviteit, moeten dan beschreven worden door 'powerlaws', omdat deze functies precies de juiste schaalinvariante eigenschap bezitten. Een gevolg van de schaalinvariantie van het systeem is dat er geen specifieke energieschaal is waarmee we de energie van processen kunnen vergelijken. De enige energieschaal die aanwezig is, is de temperatuur zelf en dit resulteert in de tweede eigenschap, namelijk temperatuur-energie schaling: De responsfunctie moet voor alle temperaturen hetzelfde zijn wanneer ze geschreven wordt als een functie van energie gedeeld door temperatuur ($\hbar \omega / k_B T$).

Hoofdstuk 5 begint met een uitgebreidere inleiding in quantum kritikaliteit. Vervolgens presenteren we metingen van de optische conductiviteit van verschillende $Bi_2Sr_2CaCu_2O_{8+\delta}$ monsters. Beide genoemde eigenschappen blijken aanwezig te zijn in deze materialen, wat een sterke aanwijzing is dat quantum kritisch gedrag de eigenschappen van deze systemen bepalen. De functie voor de temperatuur-energie schaling is echter niet dezelfde over het hele energiegebied. Om dat te begrijpen zijn concepten nodig die verder gaan dan de standaard theorie van quantum kritikaliteit.

SUMMARY

The mechanism of high temperature superconductivity, especially in the cuprates, is still an open issue. The problem is not that there aren't any theories to explain the phenomena, but actually that there are too many. Several (groups of) people have their own ideas about the origin of the pairing of electrons into Cooper pairs, a basic ingredient of superconductivity. One class of theories is a modification to the standard theory by Bardeen, Cooper and Schrieffer (BCS), which describes superconductivity in normal metals. In this theory the electrons (which normally repel each other) exhibit an effective attraction via the lattice. A second class uses some mechanism of strong interactions between the electrons which also results in an effective attraction between the electrons, but of a completely different nature. Chapter 1 gives a very short summary of the main theories of the second class.

There is a way to distinguish between the two classes of theories. As the system becomes superconducting, the internal energy of the system becomes lower, otherwise the transition would not take place. The amount by which the internal energy lowers is called the condensation energy. The internal energy is the sum of the kinetic energy and the interaction energy of the electrons. In the BCS theory the kinetic energy is increased, but the interaction is decreased by a larger amount, resulting in the net lowering of internal energy. On the other hand, the theories that use strong interactions between the electrons predict a *decrease* of kinetic energy. Therefore, measuring the change in kinetic energy as the system becomes superconducting can give a hint about which class of theories is applicable for the cuprates.

Light and charge are intimately connected (by the Maxwell equations) and measuring the response of a material to incident light can reveal properties of the (charged) electrons. A reflection measurement results in the determination of the optical conductivity of a material, which is the linear response of the material to a time varying electric field (light). Many interesting properties of the material can be learned from studying the optical conductivity. In this thesis it is used to study the changes in kinetic energy of cuprate superconductors and to learn about the 'quantum critical' properties of the normal state of these materials.

A MID INFRARED ELLIPSOMETER

The best way to measure the optical conductivity is a technique called ellipsometry. For the energy region of 0.74 eV to 4.46 eV (covering the visible part of the spectrum) an ellipsometer was available. For the infrared region of the spectrum of 1meV to 1 eV a spectrometer used for normal incidence reflection and transmission was available. The advantage of ellipsometry is that it gives both the real and imaginary part of the optical conductivity directly. From reflection measurements one can get both parts only after applying the Kramers-Kronig relations, a mathematical method for which certain assumptions have to be made. Infrared ellipsometers were not commercially available and therefore one was build in this group. Chapter 2 describes the design and the operation of this instrument.

For proper operation of the ellipsometer two high quality polarizers are needed. The commercially available polarizers were not satisfactory. Therefore new polarizers were designed and constructed. The operation of these polarizers is based on the fact that if light hits a pure silicon wafer at an angle of incidence of 73.7°, then one polarization is transmitted fully, while the other is only transmitted partially. A stack of four silicon plates is then enough to obtain a very high degree of polarization.

Ellipsometry is very sensitive to the angle of incidence of the infrared light beam on the sample. A slightly different angle of incidence gives different results. Unfortunately, the beam that is used is not a narrow, parallel beam, but a convergent beam with an opening angle of 8°. This results in a large distribution of angles of incidence which affects the result. To investigate the effect of measuring with a distribution of angles of incidence a model was developed that simulated the entire setup, including a full distribution of angles of incidence. It became clear that the distribution of angles of incidence can not be neglected. Another type of calibration needs to be done, which are explained in chapter 2.

The entire ellipsometry system is inside a vacuum chamber with a pressure of around $3 \cdot 10^{-9}$ mbar. The sample is mounted on a flow cryostat to be able to work at low temperatures (4K-350K). Several components can be controlled by computer and software was developed to have the system perform measurements at several temperatures and monitor the progress of the measurement via internet.

KINETIC ENERGY CHANGES IN THE CUPRATES

Chapter 3 addresses the issue of kinetic energy changes in the cuprates as they become superconducting. The materials under investigation were several single crystals of Bi₂Sr₂CaCu₂O_{8+ δ} with different critical temperatures *T_c* - the temperature at which the material becomes superconducting. For these materials the nearest neighbor tight-binding model is applicable, that is, to a good approximation the electrons only move from one atom to the next and do not hop over larger distances at once. It can than be shown that the total contribution of conduction the electrons to the optical conductivity is proportional to the kinetic energy (with a minus sign). By measuring changes in the integrated optical conductivity - the spectral weight - we can therefore estimate the changes in the kinetic energy.

In principle the integrated spectral weight is a conserved quantity and does not change. When the system becomes superconducting a gap appears in the optical spectrum. In this energy range the electrons can not absorb energy. The removed optical conductivity reappears at zero energy in the form of a delta peak, giving infinite conductivity (and zero resistance). Still, the value of the total, integrated optical conductivity remains the same.

However, the contribution of the conduction electrons to the optical conductivity is only part of the total optical conductivity. A change in kinetic energy of these electrons results in a change in this part of the optical conductivity. This extra change is small and appears on top of the redistribution of spectral weight due to the opening of the gap. Also temperature has its effect and the interesting spectral weight changes must be observed on top of large changes due to the temperature variation.

The effect of a change of kinetic energy is subtle and small, and accurate measurements are needed. We performed reflection and ellipsometry measurements in the energy range from 6 meV to 4.46 eV with a high temperature resolution. By extrapolating the normal state (above T_c) temperature dependence we could estimate the changes in the optical conductivity when T_c was crossed. The weight of the delta peak at zero energy (reflecting the density of superconducting electrons) can not be measured and must be obtained by modeling the entire spectrum with a standard Drude-Lorentz model. This way we extracted for every temperature the spectral weight of the conducting electrons. We checked that the result was independent on the details of the model and that other effects, like changes in the lattice, could not explain the observed changes.

At the onset of superconductivity a small increase in spectral weight was observed, corresponding to a small decrease of kinetic energy of the order of 1 meV per copper atom. This is larger than the condensation energy and a mechanism for superconductivity in the cuprates must have a lowering of kinetic energy as a central feature. A decrease in kinetic energy is opposite to what is predicted by the BCS theory, indicating that this is not the correct way to describe superconductivity in the cuprates and that strong correlations between the electrons are important.

SPECTRAL WEIGHT CHANGES IN BCS SUPERCONDUCTORS

It is now interesting to know what the results would be for a conventional BCS superconductor. Chapter 4 describes measurements done on Nb, V_3Si and MgB₂, for which the BCS theory provides a good explanation of superconductivity in these materials. We expect therefore to see a decrease of spectral weight, because the kinetic energy increases. There are two problems though. First of all, these system are not well described by the tight-binding model and therefore the relation between spectral weight and kinetic energy is not straight forward. Second, because the critical temperature is much lower, the changes in spectral weight are expected to be smaller than can be observed with our instruments.

Indeed, the measurements did not show any changes at T_c that were clear enough to draw conclusions. More accurate measurements are in preparation.

QUANTUM CRITICALITY

In chapter 5 the normal state of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductors is studied via the optical conductivity of the material. In this case we have a close look at the infrared frequency dependence, which shows signs of quantum critical behavior.

A system shows critical behavior when it is close to a phase transition. A well known example of a phase transition is the melting of ice, where the system changes from a solid phase to a liquid phase. This is a phase transition at finite temperature, but phase transitions at zero temperature are also possible and they are called quantum phase transitions. The transition is one between an ordered and a disordered state of the system, as a function of pressure, magnetic field or an other parameter. At finite temperature thermal fluctuations play an important role in the phase transition, but at zero temperature there are no thermal fluctuations; in this case the quantum fluctuations are of crucial importance.

In the case of cuprate superconductors several theories of quantum criticality exist that predict a critical point in the phase diagram of the system. Although the quantum phase transition occurs at zero temperature, it results in specific properties of the material at finite temperature. We focus in chapter 5 on two of them. Close to the critical point the system becomes scale invariant: it looks the same regardless on what scale it is observed. Response functions of the system, like the optical conductivity, must then be powerlaws, because powerlaws have precisely this scale invariant property. A consequence of the scale invariance of the system is that there is no specific energy scale to which we can compare the energy of processes. The only energy scale that is available is temperature itself and this results in the second property, namely energy-temperature scaling: The response function must be the same for all temperatures if it is written as a function of energy dived by temperature $(\hbar \omega/k_BT)$.

Chapter 5 starts with a more detailed introduction of quantum criticality. Then we present measurements of the optical conductivity of several samples of $Bi_2Sr_2CaCu_2O_{8+\delta}$. Both properties mentioned above are found in these materials, which is a strong indication that quantum critical behavior is determining the properties of the system. The energy-temperature scaling function though is not the same over the entire energy range and its understanding may require concepts that go beyond the standard model of quantum criticality. The measurements are compared to theories of superconductivity that use quantum criticality as a driving mechanism.

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CHAPTER 1

INTRODUCTION

1.1 SOME THEORIES OF SUPERCONDUCTIVITY IN THE CUPRATES

There are many theories of superconductivity in the cuprates. One class of theories tries to modify the theory of Bardeen, Cooper and Schrieffer (BCS) for superconductivity in normal metals and apply it to the cuprates. The basic interaction that pairs the electrons into Cooper pairs is still the electron-phonon interaction. Another class uses the typical two dimensional structure of the cuprates which allows them to be described by spin 1/2 electrons on Cu-O plaquettes. Strong interactions between the electrons play a crucial role and the pairing interaction is based on an electron-electron mechanism. Here we give a short overview of the main theories (apart from BCS) that are relevant for the work in this thesis [1, 2, 3].

1.1.1 RVB

One of the first theories of superconductivity in the cuprates after its discovery came from Anderson [4, 5]. He proposed that pairs of spins on the copper atoms would form singlet pairs in a dynamic way [6], that is, by continuously changing partner, where double occupancy of the sites are not allowed. This results in a so called "resonating valence bond" state. The corresponding wave function is very similar to a BCS wave function and this forms Anderson's Ansatz for the wave function in the cuprates [7]. The Hamiltonian that works on this wave function is the t - J Hamiltonian. The excitations of the RVB state are peculiar [8, 9]. When a singlet pair with total spin zero is broken (which costs an energy J) the system is left in an exited spin state. With respect to the ground state there



Figure 1.1: *Phase diagrams for the cuprates as obtained from the RVB picture (left) of from a quantum critical picture (right).*

is no change in charge, but there is a change in the spin, giving one object with spin up and one with spin down. Another excitation can be made by taking out an electron which changes the total charge of the system and leaves one single spin from a broken pair. The quasiparticles are therefore objects with spin but no charge (spinons) and objects with charge but no spin (holons). For zero doping the mean field temperature T_{MF} at which the singlets form is highest, but the pairs are not mobile and superconductivity is suppressed. As the doping is increased T_{MF} lowers, but the phase coherence temperature of the doped holes increases because it is proportional to doping. This results in the phase diagram shown in figure 1.1. In the right quadrant the system is a normal metal. In the lower quadrant the system is a superconductor, where T_c is limited on the left side of optimal doping by the hole concentration and on the right side by T_{MF} . In the left quadrant the system has a spin gap caused by the antiferromagnetic superexchange. The extra kinetic energy required to open the spin gap is released at the superconducting temperature T_c by making the charge fluctuations coherent [10]. In the upper quadrant the system is a 'strange metal'.

For zero doping the groundstate of the t - J Hamiltonian turns out to be not the RVB state, but the antiferromagnetic state, due to 3 dimensional antiferromagnetic coupling. At finite doping and finite (low) temperature it is possible [7] that the RVB state is indeed the ground state of the Hamiltonian, which results in superconductivity.



Figure 1.2: *Kinetic energy per bond,* $\langle k_x \rangle$ *, as a function of temperature for the noninteracting tight-binding electrons (TB), the BCS solution (BCS), and the phase-fluctuation (PP) model. The large vertical arrows indicate the increase in kinetic energy upon pairing, relative to the free tight-binding model, and the small arrows indicate the additional increase due to phase fluctuations. This additional phase-fluctuation energy rapidly vanishes near T_c. Figure from [11].*

1.1.2 PHASE FLUCTUATION SCENARIO

Cuprates should be thought of as doped Mott insulators, which means that, for low doping, the number of carriers is small. As the superconducting phase is conjugate to the number operator, this implies that phase fluctuations can play an important role on the underdoped side of the phase diagram, destroying superconductivity if they are too strong. The key idea of the phase fluctuation scenario in the high- T_c superconductors is the notion that the pseudogap arises from phase fluctuations of the superconducting order parameter [11]. In this scenario, below the mean-field temperature scale T_{MF} , a $d_{x^2-y^2}$ -wave gap amplitude is assumed to develop. However, the superconducting transition is suppressed to a considerably lower transition temperature by phase fluctuations. In the intermediate temperature regime phase fluctuations of the superconducting order parameter give rise to the pseudogap phenomena. In order to have condensation into the superconducting state one needs, in addition to the binding of charge carriers into Cooper pairs, long-range phase coherence among the pairs. When coherence is lost due to thermal fluctuations of the phase at and above the transition temperature T_c , pairing remains, together with short-range phase correlations. Phase fluctuations contribute to a significant reduction of the in-plane kinetic energy upon entering the superconducting phase below T_c . The physical reason for this kinetic energy lowering is that due to phase fluctuations and the associated incoherent motion of the Cooper pairs, the pseudogap region has an higher kinetic energy (figure 1.2). When long range phase coherence finally develops at T_c , the Cooper-pair motion becomes phase coherent and the kinetic energy decreases. This effect is independent of the particular mechanism leading to pair formation [12].

1.1.3 HOLE SUPERCONDUCTIVITY

Also quite early after the discovery of superconductivity in the cuprates Hirsch proposed the theory of hole superconductivity [13, 14, 15, 16]. An important aspect of the model is a fundamental asymmetry between electrons and holes [17]. Hirsch proposes that holes are the key component of superconductivity, and in particular that in high- T_c oxides superconductivity originates from conduction of holes through O^{2-} anions. A hole causes a large disruption of its background, the filled shell anion. This deformation, which leads to considerable modification in outer-shell electron wave functions, facilitates hopping of a hole of spin σ to a neighboring site which has already been occupied by a hole of spin $-\sigma$ [18]. This results in a term in the Hamiltonian describing an enhanced hopping rate for a hole if other holes are in the vicinity. This term explicitly breaks electron-hole symmetry and, together with an attractive interaction between holes, causes considerable effective-mass enhancement for nearly filled electron bands.

The kinetic energy part of the Hamiltonian is given by:

$$T = -\sum_{\langle ij \rangle \sigma} t_{ij\sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + h.c. \right)$$
(1.1)

with

$$t_{ij\sigma} = t + \Delta t \left(n_{i,-\sigma} + n_{j,-\sigma} \right)$$

where *i*, *j* are nearest neighbor sites on a two dimensional square lattice and c_i^{\dagger} creates a hole on site *i*. It describes the hopping of holes from an O^{2–} to the next O^{2–} anion in a CuO₂ plane. The hopping term for hopping from site *i* to *j* is

larger by Δt if a hole with opposite spin is already present on the oxygen atoms [19].

At low carrier density, carriers are heavily dressed in the normal state, due to coupling to a bosonic degree of freedom. When carriers pair and the system becomes superconducting, carriers partially undress. Similarly, when the system is doped in the normal state, carriers increasingly undress [20]. This will occur if the coupling to the boson degree of freedom is a function of the local carrier concentration, and becomes weaker as the local carrier concentration increases. This feature is what makes the material a high-temperature superconductor: carriers will pair in order to undress, i.e., in order to reduce the coupling to this bosonic degree of freedom. At high concentrations, carriers are already undressed in the normal state, and hence superconductivity does not occur. The undressing will result in a lowering of the system's free energy, and hence to the condensation energy of the superconductor. Because it is an undressing transition, the kinetic energy is lowered as the system becomes superconducting; as the carriers undress, their effective mass decreases, and this higher mobility in the superconducting state is what provides the "glue" for the collective order.

1.1.4 INTERLAYER TUNNELING THEORY

In the interlayer tunneling theory by Anderson [21, 22, 23] the interlayer pairing energy is the mechanism for superconductivity in the cuprates. The twodimensional state of the electrons in the copper oxide planes has separation of charge and spin into excitations which are meaningful only within their twodimensional substrate; to hop coherently as an electron to another plane is not possible, since the electron is a composite object, not an elementary excitation [24]. Absence of coherent c-axis electron motion in the cuprate layer compounds implies excess of kinetic energy in this direction. Josephson-type, two-electron transport is not blocked because the spinon fluid is a pair condensate, so that singlet pairs tunnel freely. This makes the superconducting transition a 2 to 3 dimensional crossover. The actual nature of the pairing wave function is determined not by the basic interlayer mechanism which raises T_c but by the "residual interactions", be they caused by phonons, spin-fluctuations or another source.

The pairing mechanism is thus amplified within a given layer by allowing the Cooper pairs to tunnel to an adjacent layer by the Josephson mechanism. The electrons are paired at a higher temperature because the interlayer mechanism allows them to lower their c-axis kinetic energy. The ILT model predicts that the superconducting condensation energy is approximately equal to the gain in kinetic energy of the electron pairs due to tunneling. Both these quantities can be determined independently. In a series of papers by a team in Princeton and Groningen [25, 26, 27, 28, 29] it was shown that for $Tl_2Ba_2CuO_6$ the prediction based on the ILT model was two orders of magnitude different from the measured value. This ruled out ILT as a mechanism for superconductivity in the cuprates.

1.1.5 SO(5)

In the SO(5) theory of superconductivity the antiferromagnetic phase and the superconducting phase are two projections of one and the same 5-dimensional 'superspin' order parameter [30]. Three components of this order parameter are the three degrees of freedom of the Néel order and two components are the real and imaginary part of the superconducting order parameter. The superspin order parameter can, for example, point entirely in the 'antiferromagnetic' direction, giving antiferromagnetism, and then be rotated to the 'superconducting' direction. Such a rotation corresponds to applying a new operator, resulting from the SO(5) theory, to the state of the system. The order parameter of the antiferromagnetic state is the sublattice magnetization, a real 3D vector; if this vector is different from zero, there is antiferromagnetic order. Consider two fixed neighboring sites in the 2D antiferromagnet, for example in the $(\uparrow\downarrow)$ configuration. This fixed spin configuration may be viewed as a superposition of the singlet $(\uparrow\downarrow - \downarrow\uparrow)$ and the $(S_z = 0)$ triplet $(\uparrow\downarrow + \downarrow\uparrow)$. To create the macroscopic 2D antiferromagnet in the CuO_2 plane, therefore, we have to mix triplet excitations already at high temperatures into the possible singlet configurations of the spin liquid [31]. The antiferromagnetic state then results as a kind of 'condensation' of the triplet excitations into the lowest possible energy state. The density of the 'condensed triplets' corresponds to the magnitude of the sublattice magnetization. If, in the antiferromagnetic state the triplet excitation operator is replaced by a hole pair creation operator, we obtain a state which creates a macroscopic number of Cooper pairs, i.e., a superconducting state. The antiferromagnetic to superconductor 'rotation', therefore, is described by an operator, the π -operator, which replaces triplets by hole pairs.

1.1.6 QUANTUM CRITICALITY

In three dimensions fluctuations are usually weak and in one dimension they are too strong for long range order. However, In two dimensions there is a delicate balance between order and fluctuations with many interesting properties. The phase diagram of the cuprates as a function of doping and temperature is rich with all kinds of (competing) orders and transitions between these orders, even at zero temperature. Because the dominating physics of the cuprates is believed to be 2-dimensional, the theory of quantum criticality might give some insight in the phase diagram [32] (A somewhat longer introduction into quantum criticality is given in chapter 5). One phase diagram for the cuprates with a quantum critical point is shown in figure 1.1. The proposed theory is that on the right hand of the critical point there is normal superconductivity, while on the left hand side there is a coexistence of charge ordering and superconductivity [33, 34, 35, 36]. Above the critical temperature the charge ordering leads to the pseudogap phase. In another theory of quantum criticality in the cuprates the ordered phase consists of stripe ordering [37]. In fact, there are more critical points in the phase diagram: one where the Néel order vanishes, one where superconductivity emerges, and one where superconductivity vanishes, but the main focus is on the evasive and enigmatic critical point close to optimal doping.

1.1.7 MARGINAL FERMI LIQUID

The temperature dependence of the in-plane normal state resistivity of the cuprates is surprisingly linear, unlike the T^2 temperature dependence expected for a Fermiliquid. Varma and co-workers proposed a theory to explain this property [38, 39]. The momentum distribution function no longer has a jump at k_F , but the derivative does diverge at his point, like in a usual Fermi-liquid distribution function. Hence the name marginal Fermi-liquid.

Translated into a frequency dependent scattering rate this results in

$$1/\tau(\omega) \sim max(\omega, T) \tag{1.2}$$

In the marginal Fermi-liquid theory there is no energy scale other than temperature and therefore shows quantum critical scaling.

1.2 OUTLINE

A general property many of the theories that use strong electron-electron interaction to form Cooper pairs is the lowering of kinetic energy when the system goes superconducting. In such theories, above T_c , the interaction keeps the electrons confined and in a higher kinetic energy state with less possibilities to move around. When the electrons are paired and condensed, this energy is released and the kinetic energy of the system is lowered. This is the main source for the internal energy to be lowered, which results in the transition to the superconducting state. This is to be contrasted with the usual BCS theory where the kinetic energy is increased when the system becomes superconducting and the main internal energy lowering comes from the lowering of potential energy.

This is a clear difference between the two classes of theories about superconductivity in the cuprates and a measurement of the kinetic energy is needed. This turns out to be possible when the optical conductivity of the material is measured, since this is related to the kinetic energy in certain cases. Careful measurements of the temperature dependence of the optical conductivity can give insight into the changes in kinetic energy that occur as T_c is crossed.

Also the quantum critical scenario has clear consequences for the optical conductivity of the system, this time in the frequency dependence for the infrared region.

In chapter 2 we describe the characterization of a new infrared ellipsometer build in our group. In chapter 3 measurements of spectral weight changes in several cuprate superconductors are presented and carefully analyzed. In chapter 4 ellipsometry measurements of conventional superconductors are presented. In chapter 5 the phase of the optical conductivity in the normal state of $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$ is shown to be consistent with a quantum critical scenario for the cuprates around optimal doping.

CHAPTER 2

ELLIPSOMETRY

2.1 A MID INFRARED ELLIPSOMETER

There are several ways to obtain the optical properties of a sample. One is using reflection measurements over an energy range as broad as possible and obtaining the dielectric function by performing a Kramers-Kronig transformation. The advantage is that the technique is quite simple and the signal to noise ratio of the intensities can be relatively good. The disadvantage is that one needs a reference measurement, usually done by evaporating gold on the sample and repeating the measurement under the same conditions. An additional calibration must be made to take into account the non-ideal reflection of gold. Another disadvantage is that for doing the Kramers-Kronig transformation one needs the reflection spectrum over the entire frequency range, from zero to infinity. For the low frequency part this is done by extrapolating the low frequency part numerically to zero. For the high frequency part one tries to find data in the literature, or one models the known spectrum with Lorentz oscillators. For the highest frequencies it is then assumed that the reflectivity decays as $\frac{1}{\omega^4}$. This extrapolation to infinity can be done analytically. The final result can depend quite strongly on the models used for the data outside the measured frequency range.

Ellipsometry is an alternative technique [40, 41]. With this technique one can measure the real and imaginary part of the dielectric function directly, without the use of a reference or extrapolations. For the region from 0.75 eV to around 5 eV good commercial ellipsometers are available and one is used in our group. For the far-infrared region (0.01 eV to 0.1 eV) there are ellipsometers which use the radiation coming from a synchrotron, but for the mid infrared region (0.1 eV

to 0.75 eV) few ellipsometers are available, especially if one also wants to work at liquid helium temperatures in high vacuum. Since there was a need for such an instrument it was built in our group.

This mid infrared ellipsometer (MIR ellipsometer) is a combination of a home build parts and a Bruker Interferometer. The interferometer is a commercial system that is used for reflection and transmission measurements. Used as part of the ellipsometer it serves as a spectrometer of the frequency dependences. A Globar infrared source inside the ellipsometer chamber gives a spectrum with reasonable intensity from 25 meV up to around 0.8 eV. An aperture acts as the effective source of light. After that comes the first polarizer (called 'polarizer'), the sample holder with the sample and a second polarizer (called 'analyzer'). At the point where the light enters the interferometer there is a window, separating the two systems because they work in different pressure environments (the ellipsometer being an ultra high vacuum (UHV) system). The light then passes through the interferometer, which is used in bare transmission mode, and detected by a DTGS detector working at room temperature or a liquid nitrogen cooled MCT detector. The spectrum is stored by the computer which is connected to the system and controls the entire instrument.

The part inside the ellipsometer chamber from the Globar up to the rotating polarizer is situated on a rotating plate making it possible to have an angle of incidence on the sample from 45° to 90°. The sampleholder can make a compensating rotation to have the outgoing light always in the same direction.

A set of different apertures is placed on a motorized rotating wheel, making it possible to choose from different sizes and shapes. One position blocks the light completely, resulting in a closed aperture.

Between the polarizer and the analyzer is only the sample with no intervening windows. As a result the real properties of the sample are measured and no correction for windows is needed. Everything before the polarizer and after the analyzer only reduces the overall intensity of the signal and therefore has no influence on the determination of the optical properties.

The sampleholder is connected to the cold finger of a flow cryostat. Cooling with liquid helium enables us to reach a temperature of around 4K. Since there is quite a distance from the sample to the point where the copper cold finger is in contact with the liquid helium, the whole cold finger can shrink 1 to 2 mm when cooling down from 300K to 4K which changes the position of the sample. To prevent this, the sampleholder is mounted from the bottom on three steel balls, keeping the sampleholder fixed in position while minimizing heat leakage. Just above the sample the cold finger is made from a flexible copper braid. This way



Figure 2.1: Top: The setup with the source, aperture, polarizers and sample. Bottom: Closer view of the polarizers. The left polarizer is the rotating one.



the cryostat can shrink when the entire cryostat is cooled while the movement of the sample is minimal. Two temperature sensors have been mounted on the cold finger, one close to the point where the cold finger gets into contact with the liquid helium and one close to the sampleholder.

The window separating the ellipsometer chamber from the interferometer is made of several plates of silicon glued together, which makes one thick plate. It is mounted such that the light passing this window hits the silicon at the Brewster angle, giving 100% transmission for p-polarized light. Normally the analyzer is not rotated but kept at a fixed position parallel to the window, giving full transmission for the light passing the analyzer.

The sample can be cooled to 4K and to prevent gasses from freezing on its surface, the chamber has to be in high vacuum. To achieve this a turbo pump, an ion pump and a cryo pump are connected to the chamber, resulting in a pressure of $7 \cdot 10^{-10}$ mbar. A system was designed to change samples without breaking the vacuum. The sample is first inserted into a load-lock which is then pumped to $1 \cdot 10^{-7}$ mbar before being further transported into the main chamber and mounted.

Many components of the instrument can be controlled by computer and even the cryo pump can be turned on and off to reduce the vibrations during actual data acquisition. Software was developed to control the polarizers, heaters, cryo pump and other components as well as to allow the user to monitor the system via internet.

2.2 SILICON POLARIZERS

For a proper working of the instrument it is crucial to have good polarizers. For the visible region it is easy to obtain efficient polarizers with a high degree of polarization, but for the infrared it is more difficult. Commercially available KRS5 polarizers are, especially above 0.5 eV, not satisfactory (figure 2.3). Therefore new silicon plate polarizers were designed. Pure, undoped silicon wafers were cut and mounted in a holder such that the incident angle of the light corresponds to the Brewster angle of silicon (73.7°). The light with p-polarization with respect to the plates is 100% transmitted, while s-polarized light is only 40% transmitted. A sequence of 4 silicon plates gives a good degree of polarization (around 1% leakage). The design of such a polarizer is given in figure 2.2. Figure 2.3 shows the degree of polarization for a KRS5 polarizer and a silicon Brewster angle polarizer. It is clear that these new polarizers have a higher degree of polarization which is almost frequency independent. The disadvantage is their



Figure 2.2: The design of the silicon polarizers. The angle of incidence of the light on the silicon plates is the Brewster angle of silicon, 73.7°. The design has four silicon plates in a crosswise manner to compensate for a deflected beam when the light passes through the silicon plates.



Figure 2.3: The average polarizer leakage (percentage of unwanted polarization) of a commercial KRS5 grid polarizer and the silicon Brewster angle polarizer. Especially in the near infrared the leakage of the silicon polarizers is much less.

large size.

The same principle has later been adopted by the group of Kroesen [42]. The design is slightly different as the light passes six plates of silicon, resulting in an even higher degree of polarization.

2.3 MATRICES OF OPTICAL COMPONENTS

Several books are available on polarized light, ellipsometry and instrumental implementation [40, 41]. Two closely related matrix formalisms can be used in ellipsometry to describe polarized light. The Jones matrix formalism is intuitively the easiest. However here the Müller matrix formalism is used, because it allows for partially polarized light and the first component of the state vector (the Stokes vector) gives directly the intensity of the light after passing all the optical components.

A source that gives a combination of polarized and unpolarized light can be

represented by the following Stokes vector:

$$\mathbf{I_0}(s_0) = \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix}$$
(2.1)

where S_0 represents the total intensity of the light. S_1 is the difference between horizontal and vertical polarized light, S_2 is the difference between +45° and -45° polarization and S_3 is the difference between right and left polarized light. The intensity of the polarized part of the light is given by $S_1^2 + S_2^2 + S_3^2$. For completely unpolarized light these components are zero.

A source that gives partially linearly polarized light can be represented by:

$$\mathbf{I}_{\mathbf{1}}(s_0, s_1, \alpha_s) = \begin{pmatrix} s_0 \\ s_0 s_1 \cos 2\alpha_s \\ s_0 s_1 \sin 2\alpha_s \\ 0 \end{pmatrix}$$
(2.2)

where s_1 is the intensity of the polarized part of the light (relative to s_0) and α_s is the angle of polarization. The unpolarized part is given by $s_0(1 - s_1)$.

Equation 2.3 shows the Müller matrices representing a polarizer, a reflecting surface and rotation over an angle α :

$$\mathbf{P}(\theta) = \begin{pmatrix} 1 & \cos 2\theta & 0 & 0 \\ \cos 2\theta & 1 & 0 & 0 \\ 0 & 0 & \sin 2\theta & 0 \\ 0 & 0 & 0 & \sin 2\theta \end{pmatrix}$$
(2.3)

$$\mathbf{S}(\psi, \Delta) = \begin{pmatrix} 1 & -\cos 2\psi & 0 & 0 \\ -\cos 2\psi & 1 & 0 & 0 \\ 0 & 0 & \cos \Delta \sin 2\psi & -\sin \Delta \sin 2\psi \\ 0 & 0 & \sin \Delta \sin 2\psi & \cos \Delta \sin 2\psi \end{pmatrix}$$
(2.4)

$$\mathbf{R}(\alpha) = \begin{pmatrix} 1 & 0 & 0 & 0\\ 0 & \cos 2\alpha & -\sin 2\alpha & 0\\ 0 & \sin 2\alpha & \cos 2\alpha & 0\\ 0 & 0 & 0 & 1 \end{pmatrix}$$
(2.5)

A polarizer rotated over an angle α is represented by $\mathbf{P}(\theta, \alpha) = \mathbf{R}(\alpha)\mathbf{P}(\theta)\mathbf{R}(-\alpha)$. In these equations $\cos 2\theta = \frac{1-\tau^2}{1+\tau^2}$ where τ is the (amplitude) transmission of the
unwanted polarization relative to the correct polarization. Therefore the intensity $T_l = \tau^2$ of the unwanted polarization with respect to the wanted polarization is given by

$$T_l = \frac{1 - \cos 2\theta}{1 + \cos 2\theta} \tag{2.6}$$

In the representation of the matrices **P** and **S** we ignored prefactors which depend on the sample and polarizer properties. These prefactors only reduce the overall intensity and do not affect the ratio of the minimum and maximum intensity, nor do they introduce a change in the relative phase shift of the light. Therefore these prefactors are absorbed in the source intensity s_0 . This does mean that every new setup has a different s_0 and the value of s_0 obtained from one setup can not be used for another setup.

In the ideal case, with perfect polarizers and no other instrumental imperfections the intensity measured by the detector is given by the first component of $\mathbf{P}(0, \pi/4)\mathbf{S}(\psi, \Delta)\mathbf{P}(0, \alpha)\mathbf{I}_0$. This evaluates to

$$I(\alpha) = s_0(1 - \cos 2\psi \cos 2\alpha + \sin 2\psi \cos \Delta \sin 2\alpha)$$
(2.7)

Using the ellipsometric parameters ψ and Δ one can calculate the dielectric function:

$$\rho = \tan \psi \, \mathrm{e}^{\mathrm{i}\Delta} \tag{2.8}$$

$$\epsilon = \tan^2 \phi \left(\frac{1 + \rho^2 + 2\rho \cos 2\phi}{(1 + \rho)^2} \right)$$
(2.9)

where ϕ is the angle of incidence of the light on the sample.

2.4 DATA

Figure 2.4 shows a typical measured spectrum with the polarizer rotated to the angle of maximum intensity and one with the polarizer rotated to the angle of minimum intensity. With the aperture closed, the background signal is black body radiation (modified by the beamsplitter and the detector response) coming from the ellipsometer chamber. Black body radiation after the interferometer in the Bruker IFS 113 is also added to the signal. However, this is a constant intensity as a function of the path difference of the interferometer, which therefore does not contribute to the spectrum at finite wavelength. The sample is situated before the interferometer. As a thermal black body radiation, emitted by the sample surface, is added to signal. This is also modulated by the interferometer and



Figure 2.4: Spectra with and without background contribution

thus observed in the final spectrum. The spectra therefore have a background which has to be subtracted (figure 2.4). The background is measured by closing the aperture and taking a spectrum. Afterwards it is subtracted from the spectrum with open aperture to obtain the spectrum of light reflected by the sample.

These spectra are taken for a number of polarizer angles α and figure 2.5 shows the intensity as a function of polarizer angle for a typical measurement at 0.25 eV. One expects the background to be independent of the rotation angle of the polarizer, but there turns out to be a slight sine dependence on the signal, which runs 180° out of phase with the actual measurement. We speculate two possible explanations, which might both be at work.

When the polarizer is rotated to an angle that gives minimum intensity, the light (with open aperture) is absorbed by the two polarizers which are warmed up. When the aperture is closed to measure the background, the detector sees a slightly warmer environment with a slightly higher response. When the polarizer is rotated to an angle that gives maximum intensity, the polarizers cool down again and the radiation with closed aperture is lower.

Alternatively it may be related to the warming of the detector due to the change in intensity during rotation of the polarizer. When the polarizer is rotated to an angle that gives minimum signal, the heat load (of infrared radiation) on the detector is also minimal and the detector (which is a liquid nitrogen cooled MCT detector) has optimal response. When the aperture is closed it measures a certain value for the background intensity. When the polarizer is rotated to



Figure 2.5: Polarizer angle dependence of spectrum and background measured with the MCT detector. The right vertical axis is an expanded scale to show the dependence of the background signal on the polarizer angle α .



Figure 2.6: Fourier components of the measured intensity.

an angle for which the signal is maximal (with open aperture), the heat load on the detector is also maximal. The detector warms up slightly and has a lower response. Therefore, the measurement of the background (closed aperture) is lower.

The signal (after subtraction of the background) can be described by a sine function and in the ideal case we expect a perfect sine with an intensity as a function of polarizer angle α of $I(\alpha) = s_0(1 + p_2 \sin(2\alpha + 2\phi_2))$, where p_2 and ϕ_2 are determined by the sample properties. However, experimental imperfections can change the coefficients and introduce other Fourier components. In general we can write the intensity as:

$$I(\alpha) = s_0 \left(1 + \sum_{n=1}^{\infty} p_n \sin n(\alpha + \phi_n) \right)$$
(2.10)

Figure 2.6 shows the p_n components of a measurement up to n = 4 as a function of frequency. The p_2 component has a clear frequency dependence because it is mainly determined by the dielectric function $\epsilon(\omega)$ which has a frequency dependence. The other components are much smaller.

Ideally we expect the system to be 180° symmetric, because rotating the polarizer 180° results in the same polarization. Therefore we expect all odd terms $(p_1 \text{ and } p_3)$ to be zero. However, a slight asymmetry in the polarizer rotation can introduce odd terms. The beam might be deflected and the spot can wander around slightly over the detector element, giving an intensity variation that is only 360° symmetric. However, for the analysis this is not important: The intensity can now be described by $I(\alpha) = s_0(1 + p_1 \sin(\alpha + \phi_1))(1 + p_2 \sin(2\alpha + 2\phi_2))$. This leaves the 2α coefficient unaffected, and since the Fourier components are orthogonal to each other the 2α component alone can be used to determine the sample properties.

2.5 DISTRIBUTION OF ANGLES OF INCIDENCE

Close to grazing angle of incidence the ellipsometric parameters ψ and Δ depend strongly on the angle of incidence. The beam is a convergent beam and has a spread of angles of 8° around the central ray. Every ray in the cone of rays that converges to the focal point on the sample has therefore a different local angle of incidence. Moreover, each ray has it's own local *s* and *p* direction on the sample. Figure 2.7a shows the local angle of incidence ϕ and local *s* and *p* direction for a particular ray. The silicon plates in the polarizers have an angle of incidence



Figure 2.7: Figure showing the parameters involved in the calculation of the distribution of angles of incidence. a) The beam as it hits the sample. The *x*, *y* and *z* axes define the frame of reference. The sample is mounted in the *x*, *y*-plane with it's normal *n* coinciding with the *z* axis. The central ray (gray) has an angle of incidence ϕ_0 with the sample normal *n*. A particular ray has an angle β which runs from 0 to the maximal spread in angles (in the simulation 8°) and γ runs from 0 to 2π . At this point the *s* and *p* polarization directions are as indicated. The ray and the sample normal *n* define a plane of incidence and the angle between them is the angle of incidence ϕ . The local *p'* direction lies in the plane of incidence and the local *s'* direction is perpendicular to it. b) The beam as it hits the silicon plates in the polarizer. The plate is rotated over an angle α and the plate normal *n* is rotated away from the *z*-axis.

of 73.7° with the central ray. Because the plates are rotated over an angle α , the local angle of incidence ϕ and local *s* and *p* directions also change (figure 2.7b).

We modeled a system with a fully unpolarized source, a rotating polarizer with 4 silicon plates, mounted crosswise (figure 2.2), a sample with known dielectric function and a second, non rotating polarizer. With a distribution of angles of incidence of 8° around the central ray we calculated for each ray the intensity at the detector. The beam is divided into small segments and for each segment the angle of incidence is calculated (figure 2.8). The path trough polarizers and sample is calculated and in the end all intensities are added. Interference between the rays and multiple reflections inside the silicon plates was ignored. Figure 2.8 shows the result of a typical calculation. The central ray has a pure



Figure 2.8: Intensity as a function of polarizer angle α from the simulation of the distribution of angles of incidence. 'central' is the intensity from the central ray. 'outside' is the intensity from a ray with $\beta = 8^{\circ}$ and $\gamma = 90^{\circ}$. 'full' is the (normalized) intensity from all rays. Note that the 'outside' ray has a kink at $\alpha = 90^{\circ}$ and $\alpha = 270^{\circ}$ as explained in the text. These kinks are averaged out in the full beam.

sine dependence, as expected, with no other Fourier components. The 'outside' ray has $\beta = 8^{\circ}$ and $\gamma = 90^{\circ}$ (figure 2.7). Note the kink at polarizer angle $\alpha = 90^{\circ}$ and $\alpha = 270^{\circ}$. These are the angles for which the first silicon plate that this particular ray meets switches to the opposite one in the polarizer holder (figure 2.2). This results in a sudden change in the local angle of incidence when the ray is not the central one. Each ray has a different angle α for which it switches the first silicon plate and as a result in the intensity from the full beam the kinks are averaged. It results in a curve with higher Fourier components. From the simulation we found that the 4α component is 0.1% of the 2α component, a factor 10 smaller than observed in the real measurement (figure 2.6). Therefore other effects must be the main cause of the higher Fourier components.

Figure 2.9 shows $\cos 2\psi$ and $\cos \Delta$ of a model dielectric function. $\cos 2\psi$ was chosen to be 0.5, an average value of a typical sample. It turns out that the effect of the distribution of angles of incidence on ψ is minimal. The effect is larger



Figure 2.9: The effect on $\cos 2\psi$ and $\cos \Delta$ of different methods for including the distribution of angles of incidence. The 'central' curve for the central ray, with no distribution. The 'full' curve gives the effect using the full simulation of angles of incidence and the 'approximated' curve is the effect using the approximated method as explained in the text.

on Δ and therefore we varied $\cos \Delta$ from -1 to 0, covering the range of values that occurs with the samples that we will measure in the infrared. From these values of ψ and Δ the dielectric constant is calculated using equation 2.8. This value of ϵ is then used in the distribution of angles of incidence algorithm to calculate an intensity as a function of polarizer angle as described above. From this sine function the parameters $< \cos 2\psi >$ and $< \cos \Delta >$ were calculated using equation 2.7, where the <> indicates an average over a distribution of angles of incidence. The original and average ellipsometric parameters are shown in figure 2.9. As already noted, the distribution of angles of incidence has negligible effect on ψ , but the effect on Δ can not be ignored. ψ is mainly determined by the angle α for which the measured intensity is at a minimum and this is clearly not affected by the distribution of angles of incidence (figure 2.8, compare 'full' and 'central' curve). Δ on the other hand is mainly determined by the ratio of the minimum intensity over the maximum intensity and this *is* affected by the distribution of angles of incidence, as can be seen by comparing the 'full' curve with the 'central' curve in figure 2.8.

The calculation using the distribution of angles of incidence is very time consuming. It's inversion (obtaining the dielectric constant that corresponds to a certain measured intensity as a function of polarizer angle α) takes even longer. A direct analytical inversion is of course not possible and the correct dielectric constant has to be found by a non linear fitting procedure, which involves performing the calculation procedure many times, including a calculation for derivatives. Moreover, the final result is not very stable and the obtained value of ϵ can be far off from the correct one.

Therefore we used an approximation, where only β (figure 2.7) is varied and γ is kept at zero. This captures the largest variation in angles of incidence while keeping the number of calculations limited. With an angle of incidence of the central ray of 60°, varying β from -8° to $+8^{\circ}$ while $\gamma = 0$ gives an angle of incidence variation from 52° to 68°. Varying β in the same way while $\gamma = 90^{\circ}$ gives an angle of incidence variation from 60° to 60.3°, clearly a smaller range.

Every value of β results in a angle of incidence ϕ and a $\psi(\phi)$ and $\Delta(\phi)$. Using equation 2.7 this gives an intensity variation $I(\alpha, \phi)$ on the detector. The total intensity is the sum of all these intensities and the coefficients in front of the $\cos 2\alpha$ and $\sin 2\alpha$ just add up:

$$I(\alpha) = 1 - \left(\frac{1}{N}\sum_{i}^{N}\cos 2\psi_{i}\right)\cos 2\alpha + \left(\frac{1}{N}\sum_{i}^{N}\sin 2\psi_{i}\cos\Delta_{i}\right)\sin 2\alpha \qquad (2.11)$$

where $\psi_i = \psi(\phi_i)$ and $\Delta_i = \Delta(\phi_i)$.

This $I(\alpha)$ can again be used to obtain a average $\langle \psi \rangle$ and $\langle \Delta \rangle$, using equation 2.7, and it is also shown in figure 2.9. It is clear that this approximated distribution of angles of incidence has some effect, but it is smaller than the full calculation. An analysis of the data based on the full distribution of angles of incidence would therefore be useful, but in this thesis we limit ourselves to the approximated method.

An experimental method to circumvent the problems related to a distribution of angles of incidence is to collimate the beam, that is, to limit the beam to a narrow region around the central ray. To reduce the effect of the distribution of angles of incidence to a level that one can safely ignore it, the spread in angles must not be larger than 2°. This can be achieved by putting apertures in the beam path that cut the outer rays. The needed cut of the beam though leads to a large reduction in intensity, which itself leads to a signal to noise increase that is larger than the systematic error introduced by using the full beam.

2.6 CALIBRATION

An ellipsometric measurement is performed by choosing an angle of incidence, setting the polarizer and analyzer at a certain angle and measuring the spectrum. The polarizer is than rotated to another angle (the analyzer is kept fixed) and a new spectrum is taken. This is repeated until the polarizer has been rotated over 360° . For each frequency of the spectra that were taken, the intensity as a function of the angle α of the polarizer can be fitted with a sine function.

The basic equation that describes the measured intensity as a function of polarizer angle α is given by equation 2.7 and assumes an ideal setup. Of course in reality the optical components are not perfect: The polarizers can have a leakage and the source can in principle be polarized. Moreover, the polarizers are mounted in motor blocks which have their own definition (by use of opto couplers) of zero rotation. This zero does not coincide with horizontal polarization and a polarizer offset angle α_0 has to be determined. The same holds for the analyzer: It is mounted such that the polarization of the analyzer polarization angle α_2 is close to 45°, but an accurate value has to be determined.

With these extra parameters the Stokes vector describing the system is given by

$$\mathbf{I} = \mathbf{P}(\theta_2, \alpha_2) \, \mathbf{S}(\psi, \Delta) \, \mathbf{P}(\theta_1, \alpha + \alpha_0) \, \mathbf{I}_1(s_0, s_1, \alpha_s) \tag{2.12}$$

and the first component gives the intensity as a function of polarizer angle α . The main Fourier components in this expression are the $\cos 2\alpha$ and $\sin 2\alpha$ terms, but the polarized source leads to small 4α terms. To be able to determine the calibration parameters independently a measurement with a sample with known optical properties and a measurement with the polarizers parallel with no sample need to be combined. The sample in this case is a thick piece of silicon which was measured with another ellipsometer (see section 2.7) in the 0.75 eV to 4.5 eV energy range. The obtained dielectric function was fitted with a Drude-Lorentz model which was then used to extrapolate the data to the needed infrared energy range.

This way there is for every frequency a dataset of intensities versus polarizer angle α like figure 2.5. A set of parameters needs to be found that gives the best fit for all datasets, which is done by performing a non linear fit of equation 2.12 to all the datasets simultaneously. The polarizer offset α_0 and analyzer angle α_2 were determined frequency independently, while the polarizer leakage parameter $\cos 2\theta_1$, analyzer leakage parameter $\cos 2\theta_2$ and source polarization parameters s_1 and α_s were determined with a frequency dependence. Figure 2.10 shows the obtained calibration parameters. The polarizer and analyzer leakage is 1 to



Figure 2.10: The calibration parameters: polarizer and analyzer leakage and source polarization. The polarizer offset angle α_0 is 94.9° and the analyzer angle is 45.4°.

2 percent, with the polarizer being the better one. The source polarization is significant and needs to be included to have a good fit of the measured intensity as a function of polarizer angle α . With this set of parameters determined a new measurement of a sample with unknown properties can be done. The intensity versus polarizer angle can be fitted with the same technique, but now with ψ and Δ as the unknown parameters.

2.7 WOOLLAM ELLIPSOMETER

An ellipsometer produced by J.A. Woollam Co. was used to determine the dielectric function from 0.74 eV to 4.46 eV. The optical components for ellipsometry in this energy range are much better than those for the infrared range. Therefore the accuracy of this instrument is much better than that of the infrared ellipsometer. In contrast to the infrared ellipsometer, which measures a entire frequency range in one scan, this instrument uses a monochromator and does ellipsometric measurements for each frequency separately. This allows for a measuring mode where one fixes the frequency and measures the ellipsometric parameters as a function of time.

The beam of this ellipsometer is a parallel beam of only 2 mm diameter and problems with a divergent beam are negligible. Given the better accuracy of this instrument it is considered to give more reliable results then the infrared ellipsometer in the region of overlap (0.74 eV to 1 eV).

2.8 OTHER CORRECTIONS

To do low temperature measurements on the Woollam ellipsometer a cryostat is situated between the two polarizers. This cryostat has windows and the measured ellipsometric parameters are the combination of the transmission through the windows and reflection on the sample. In Jones matrices the part between the polarizers can be modeled as:

$$\begin{pmatrix} w_p & 0 \\ 0 & w_s \end{pmatrix} \begin{pmatrix} r_p & 0 \\ 0 & r_s \end{pmatrix} \begin{pmatrix} w_p & 0 \\ 0 & w_s \end{pmatrix}$$
(2.13)

The relevant value to determine is the (complex) ratio $\frac{r_p}{r_s}$ in the case without windows, or $\frac{w_p^2 r_p}{w_s^2 r_s}$ in the case with windows. Measuring once with windows and once without windows one can calculate $\frac{w_p^2}{w_s^2}$, which can be used at all temperature for a window correction.

Ideally the window is isotropic and the light hits the windows normal to the surface of the window, which would mean that $w_p = w_s$ and a window correction is not necessary. In practice a slight deviation from normal angle of incidence and stress inside the window makes a correction important.

The measurements were usually done at large angle of incidence $(60^\circ - 80^\circ)$ and the measured ellipsometric response is a combination of all three axes of the crystal:

$$\rho^{ps} = \frac{\sqrt{\epsilon_x \epsilon_z} \cos \theta + \sqrt{\epsilon_z - \sin^2 \theta}}{\sqrt{\epsilon_x \epsilon_z} \cos \theta - \sqrt{\epsilon_z - \sin^2 \theta}} \cdot \frac{\cos \theta - \sqrt{\epsilon_y - \sin^2 \theta}}{\cos \theta + \sqrt{\epsilon_y - \sin^2 \theta}}$$
(2.14)

where ρ^{ps} is the pseudo ellipsometric response and $\epsilon_{x,y,z}$ are the dielectric functions in the *x*, *y* and *z* directions (figure 2.7). When it is assumed that $\epsilon_x = \epsilon_y$ and ϵ_z is known, equation 2.14 can be solved for ϵ_x and gives four solutions. Two of them are clearly unphysical, but the other two could both be right. One of the possible good solutions can be excluded because it is not Kramers-Kronig consistent: The Kramers-Kronig transform of the imaginary part does not give the real part. Actual measurements provide the dielectric function only on a limited frequency range and therefore this check can not be done. However, simulations show that if the imaginary part of the c-axis response is almost zero and the real part is small (as is the case for cuprate superconductors), the correct solution is the one closest to the pseudo dielectric function.

2.9 RESULTS AND CONCLUSIONS

Figure 2.11 shows the obtained ellipsometric parameters of $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$, Si and FeSi using the infrared ellipsometer, where in the analysis the distribution of angles of incidence was taken into account using the approximate method. Also shown are the ellipsometric parameter obtained with the Woollam ellipsometer. The match between the two instruments is acceptable.

The instrument can be improved on several points. An main improvement would be the avoidence of the convergent beam and reducing the spread of angles of incidence to a maximum of 2° . To an acceptable error the beam can then be assumed to have no distribution at all, which simplifies the analysis and increases the reliability of the measurements. However, with the present Globar source such a narrowing of the beam leads to 50 times lower signal and a considerable reduction of the signal-to-noise ratio.



Figure 2.11: Measurements of Si, FeSi and $Bi_2Sr_2CaCu_2O_{8+\delta}$ with the MIR ellipsometer (points) and the Woollam ellipsometer (lines). Around 0.8 eV the intensity is almost zero, leading to unphysical results.

Another improvement would be the use of a detector working at room temperature. Such a detector would not detect the background radiation, because it operates at the same temperature. When the polarizer is rotated to an angle that gives maximum intensity, the background signal around 0.1 eV is almost 50% of the main signal from the reflection of the sample. When the polarizer is rotated to an angle that gives minimum intensity, the background signal around 0.1 eV is 10 to 100 times larger than the main signal from the reflection of the sample. Without the need to measure and subtract a background signal the measurement would improve considerably in the region upto 0.3 eV. However, the reason the use a cooled detector is the much improved signal-to-noise ratio of the detector respons and this advantage would be lost.

A known disadvantage of the MCT detector that was used is the non linear response of this detector. The use of a more linear detector could be an improvement. Also the use of a beamsplitter that gives higher throughput around 0.8 eV would allow a better comparison with the (Woollam) visible light ellipsometer discussed in section 2.7.

For an accurate determination of ψ and Δ measurements at many polarizer angles α have to be taken. A typical measurement last around 15 minutes. This is not much slower than an measurement of an entire spectrum on the visible light ellipsometer. However, the latter instrument has the advantage that it uses a monochromator and the measurement of one single frequency is much faster. The MIR ellipsometer always measures an entire spectrum and the minimal operation time is 15 minutes. Therefore accurate temperature dependent measurements, as are conducted in chapter 3, can not be done, because a single run from 4K to 300K would take too long. There would be too many instabilities in the system which makes the temperature scan unreliable.

CHAPTER 3

SPECTRAL WEIGHT TRANSFER IN CUPRATE SUPERCONDUCTORS

We present optical data¹ of several cuprates measured with a temperature resolution of 1K in order to be able to detect small changes in the optical conductivity at the critical temperature. We fitted the spectra for every temperature with a Drude-Lorentz model and extracted the intraband spectral weight as a function of temperature. The bismuth based samples show an increase of the intraband spectral weight when the system crosses the superconducting transition temperature, equivalent to a lowering of kinetic energy of the order of 1 meV per copper atom.

3.1 INTRODUCTION

When the temperature drops below the critical temperature some materials can lower their free energy by entering the superconducting state. The energy difference between the normal state and the superconducting state is called the condensation energy. For a BCS superconductor the kinetic energy increases while the interaction energy decreases slightly more, resulting in the needed net lowering of free energy [43].

The cuprate superconductors have a number of important differences with respect to BCS superconductors. The most apparent one is the height of the critical temperature, which is of the order of 100K. Within the standard BCS model

¹This work was done in close collaboration with Cristian Presura, who helped with measuring the $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $YBa_2Cu_3O_{7-\delta}$ samples.

this can only be explained by an unrealistically large electron-phonon interaction. Another important difference is the symmetry of the gap, which is in the case of conventional BCS superconductors fully symmetric, or *s*-wave, and has the same value for all directions in *k*-space. In the case of cuprate superconductors the gap is believed to have a *d*-wave symmetry, which means that the gap is zero in certain directions in *k*-space [1]. Also the normal state turns out to be unconventional, with for example a linear temperature dependence of the resistance and the appearance of a pseudogap in the underdoped side of the phase diagram. These and other differences can not easily be explained within the standard BCS model. Therefore other models have been proposed with a different mechanism to pair the electrons in the superconducting state.

Several of these models use a mechanism that results in a lowering of kinetic energy when the system becomes superconducting. In the model by Hirsh [13, 15, 20] two holes can move more easily when they hop together. Various other models predict that in the cuprates, the normal state is not a Fermi liquid and that superconductivity is driven by recovering frustrated kinetic energy of single charge carriers when pairs are formed [44, 10, 11], by lowering the ab-plane zero-point kinetic energy [45], or by Bose-Einstein condensing Cooper pairs that are already present in the normal state [46].

To capture the essential physics that describes superconductivity one uses an effective low energy Hamiltionian, since the full Hamiltonian is to complicated to solve. When the full Hamiltonian is considered, the transition to the superconducting state must be driven by a lowering of the potential energy, as is shown by Chester using the virial theorem [47]. However, for an effective low energy model the kinetic energy terms can incorporate effects of the potential energy terms of the full Hamiltonian. There is no virial theorem restriction on the expectation values of the kinetic and potential energy terms of the effective Hamiltonian. Therefor, the effective low energy Hamiltonian can have a superconducting transition driven by a lowering of the (effective) kinetic energy [48].

The kinetic energy E_{kin} of the effective low energy Hamiltonian is given by

$$E_{kin} = \frac{2}{N} \sum_{k} \epsilon_k n_k \tag{3.1}$$

where ϵ_k is the dispersion of the band, n_k the momentum distribution function and *N* the number of *k* vectors. Apparently there are two ways to change the kinetic energy: changing the band dispersion or changing the distribution function. The model by Hirsch changes the dispersion because the hopping term changes when two holes pair, which affects the band they are moving in. In general, though, we expect ϵ_k to be invariant and therefore the change should



Figure 3.1: The momentum distribution functions for the Fermi liquid (FL), the superconductor (SC) and a non-Fermi liquid (NFL).

come from n_k [1, 49]. Figure 3.1 shows the momentum distribution for a Fermi liquid, the superconducting state and hypothetical non Fermi liquid. For a BCS superconductor the normal state is a Fermi liquid and the distribution function broadens when the system enters the superconducting state: electrons are moved to higher kinetic energy and the kinetic energy increases. If, though, the normal state is not a Fermi liquid, with a distribution function even broader than that of the superconducting state, then the kinetic energy lowers when the system becomes superconducting.

From the Kubo formula [50] we can derive a relation between the optical conductivity of a band and its dispersion [49]:

$$\int_0^\infty \sigma_{1,\delta}^{LB}(\omega) \,\mathrm{d}\omega = \frac{\pi e^2 a_\delta^2}{2\hbar^2 V} E_K \tag{3.2}$$

where $\sigma_{1,\delta}^{LB}(\omega)$ is the real part of the optical conductivity of the single band in the lattice direction δ , a_{δ} is the lattice constant in direction δ , V is the volume of the unit cell and

$$E_K = \frac{2}{a_\delta^2 N} \sum_k \frac{\partial^2 \epsilon_k}{\partial k^2} n_k \tag{3.3}$$

When the effective low energy Hamiltonian is given by the Hubbard model, then the optical conductivity splits into intraband transitions in the lower Hubbard band and interband transitions in the upper Hubbard band [51]. Of largest



Figure 3.2: Calculation of the intraband spectral weight A_{LB} for a BCS superconductor with a *d*-wave gap. The critical temperature is 80K and the hole doping is 0.15. The dispersion is given by $\epsilon_k = t(\cos k_x + \cos k_y) + 2t' \cos k_x \cos k_y$ with t = -297.6 meV and t' = 81.8 meV.

interest is the optical response of lower Hubbard band around the Fermi energy, for which, due to the nearest neighbor tight-binding character of the band, $E_K = -\frac{2}{N} \sum_k \epsilon_k n_k = -E_{kin}$. Therefore the spectral weight of the low energy band is related to the kinetic energy [52, 19, 1]:

$$A_{LB} = \int_0^\infty \sigma_{1,\delta}^{LB}(\omega) \, \mathrm{d}\omega = -\frac{\pi e^2 a_\delta^2}{2\hbar^2 V} E_{kin} \tag{3.4}$$

where A_{LB} is the spectral weight of the low energy band, including a delta peak in the superconducting state.

This relation between the intraband spectral weight and the kinetic energy of the charge carriers is valid for a system described by the nearest neighbor tight binding model, with only a hopping parameter t. For the cuprates also a next nearest neighbor hopping term t' is needed for a good description of the system. The simple relation between the intraband spectral weight A_{LB} and the kinetic energy is in this case not evident. Figure 3.2 shows a calculation of the intraband spectral weight as a function of temperature for Bi2212 assuming a dispersion ϵ_k based on the tight binding model with a nearest neighbor (t) and a next nearest neighbor (t') hopping term [54, 55], a Fermi liquid for the normal state and a BCS superconductor for the superconducting state. Also shown is the kinetic energy as a function of temperature, using the same parameters for the dispersion. The kinetic energy is still proportional to the intraband spectral weight, although not exactly. A measurement of the spectral weight can therefore be used as an estimate of the kinetic energy changes, even when a correct description of the



Figure 3.3: *Kinetic (top) and potential (bottom) energies of the repulsive Hubbard model in the normal (NS) and superconducting (SC) states as a function of temperature for low doping (\delta = 0.05, left) and high doping (\delta = 0.20, right). The vertical dotted lines represent the value of T_c. Pairing is mediated by a reduction of the kinetic energy. Figure from [53].*

system needs higher order terms in the tight binding expansion.

The calculated increase of kinetic energy is a result of the use of the BCS theory for describing the superconducting state of Bi2212. Another approach is to calculate the kinetic energy for the two-dimensional Hubbard model [53], using a dynamic cluster calculation. The results are shown in figure 3.3 and indicate a lowering of kinetic energy as the system becomes superconducting.

The approach to measure the optical conductivity has been used by several groups to estimate the changes in kinetic energy along the c-axis [56] as well as along the copper-oxide planes [57, 58, 59]. Spectral weight changes have been measured for the *ab*-plane optical conductivity of Bi₂Sr₂CaCu₂O_{8+ δ} and other high-*T_c* cuprates [60, 61], with an experimental accuracy of ~ 0.04 eV². Optical thin film absorption [62, 63], thermal difference reflectance [64], femtosecond spectroscopy [65, 66] and ellipsometry [67] have indicated that, for light polarized along the *ab* plane, an influence exists at energies exceeding 1 eV.

The expected changes in the spectral weight are small. Especially for the

in-plane measurements the changes are also small relative to the total spectral weight, which demands very careful measurements. Moreover, there is a relatively large overall temperature dependence of the spectral weight on top of which the changes at the critical temperature have to be observed. A measurement of the spectral weight at a temperature just above the critical temperature and one well below would result in a too large change, or even a change of the wrong sign. Also when the temperature resolution is too poor one would not be able to observe the changes.

Here we present a detailed and extended analysis of measurements that were published before [57], together with the same analysis of measurements on new materials. The samples and measuring methods are described in section 3.2. The measured spectra and analyzing methods are described in section 3.3. The results of the analysis of spectral weight changes are described in section 3.4 and are discussed in section 3.5. In section 3.6 we draw some conclusions.

3.2 SAMPLES AND EXPERIMENTS

Different groups provided us with high quality single crystals. The details of growth and characterizations are described in various papers. The Bi₂Sr₂CaCu₂O_{8+ δ} single crystals [68] consisted of pieces of 1mm by 3mm with a thickness of 0.1 mm, which were mounted together in a mosaic. We measured two different dopings of Bi₂Sr₂CaCu₂O_{8+ δ} : underdoped (T_c =66K) and optimally doped (T_c =88K). The optical response in the visible region changed slightly after cleaving, but there was no effect on the temperature dependence. Also a rotation of the crystal by 90° had an effect on the frequency dependence of the optical response, since Bi₂Sr₂CaCu₂O_{8+ δ} has a slight anisotropy, but again the temperature dependence was the same. The Bi₂Sr₂Ca_{0.92}Y_{0.08}Cu₂O_{8+ δ} single crystal was an optimally doped sample of 1mm by 3mm and had an critical temperature of 95.11K [69]. The YBa₂Cu₃O_{7- δ} sample was a twinned film of 10mm by 10mm with a critical temperature of 91K [70].

The samples were measured optically using normal incidence reflection in the energy range from 6.2 meV to 0.68 eV, called here the infrared (IR) range. They were also measured using ellipsometry in the range from 0.74 eV to 4.46 eV, called the 'visible' range (VIS). Ellipsometry directly provides the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where ω is the angular frequency of the light. For large angles of incidence there is a slight admixture of c-axis response to the measured dielectric function for which we corrected using c-axis dielectric data from literature [71]. The dielectric function in the infrared range was obtained using the Kramers-Kronig transformation, where the knowledge of the full dielectric function in the visible range was used to obtain a very accurate result, with little dependence on the extrapolations to zero and infinite frequency.

In the infrared region a Fourier transform spectrometer was used with a flow cryostat for the low temperature measurements. The pressure inside the cryostat was typically $1 \cdot 10^{-7}$ mbar. The measurements were done in the following way: First the sample was measured at several temperatures, stabilizing the temperature before each measurement. Then measurements were taken continuously, while the temperature was lowered and raised very slowly, going from 300K to 4K in 3.5 hours and back in another 3.5 hours, repeating this 2 or 3 times. Then gold was evaporated on the sample (in situ) and all the measurements were repeated to obtain the reference measurement. In this way measurements of the reflectivity ($R(\omega)$) at discrete temperatures were obtained and continuous runs with a temperature resolution of typically 1K. In the case of YBCO no infrared reflection measurements were done, because it would not have been possible to remove the evaporated gold, needed for the reference, from the film.

In the visible region an ellipsometer with a monochromator was used, again with a flow cryostat for the measurements at low temperatures. The pressure in this cryostat was typically $3 \cdot 10^{-9}$ mbar. First, measurements at discrete temperatures were done, measuring the full spectrum from 0.74 eV to 4.46 eV. Then measurements at single frequencies were done, going up in temperature from 4K to 300K in 3 hours, one frequency at a time, or continuously cycling a few frequencies in a short period, going up in temperature in 3 hours. In this way measurements were obtained with a temperature resolution of 0.5K and a frequency resolution of 25 meV to 60 meV in the range from 0.74 eV to 2.5 eV (sometimes up to 3.7 eV).

3.3 MEASUREMENTS AND ANALYZING METHODS

The results are spectra of the dielectric function over a large temperature interval as well as spectra with a temperature interval of 1K. Figure 3.15-figure 3.18 show for each sample the measured reflection, the dielectric function and optical conductivity as a function of frequency for selected temperatures and as a function of temperature for selected frequencies. For those samples where we have infrared data one can see the reduction of the optical conductivity in the far-infrared region as a result of the opening of the superconducting gap, also observable as the upward turn of the reflection for low frequencies ($\sim 60 \text{ meV}$). Around 120 meV the reflection has the opposite trend and bends down at T_c , also as a result of the opening of the gap. What is unexpected is that for even higher energies (well above the gap) the reflection again shows an upward turn, observable for energies as high as 0.5 eV before the noise is to large for the infrared spectrometer. And even for very high energies, around the plasma frequency of around 1 eV and up to 2.5 eV, the dielectric function shows a kink at the critical temperature.

Also note that there is, relative to the change at T_c , a large overall temperature dependence in the curves. To obtain the extra changes due to the onset of superconductivity it would not be correct to take the difference between a spectrum just above T_c and one at low temperatures (4K). It would estimate a too large change or even a wrong sign for the change at T_c . Also note that the changes at the critical temperature are subtle and that with a too coarse temperature resolution one would not be able to resolve these changes.

3.3.1 ANALYZING METHODS

From these measurements we want to obtain the changes in the optical conductivity when superconductivity sets in. We analyzed the spectra in two different ways, both of which enable us to determine the spectral weight changes related to superconductivity.

A real optical experiment measures not only the optical conductivity of the low energy band (intraband transitions) but also the optical transitions to all other bands (interband transitions). The most prominent interband transitions are observed around 1.5 eV and higher and are well separated from the intraband transitions. Therefore we make the distinction between the two by attributing all transitions below a certain cutoff frequency ω_c to the intraband transitions and all others to the interband transitions. We take ω_c to be 1 eV, which is close to the plasma frequency of the samples. Furthermore, in the superconducting state, spectral weight is transferred to the delta peak at zero frequency, which can not be measured directly. Therefore it has to be obtained from fitting the measured data at low frequencies with a response determined by a delta function at zero frequency with spectral weight *D*. One can fit the real part of the dielectric function in the far infrared with $\epsilon_1(\omega) = -D/\omega^2$ or extract it from fitting the reflection data. Well below T_c this can be done in quite a reliable way.

The optical conductivity contains an additional residual Drude term, which corresponds to the optical response of the thermally excited quasiparticles. This is a narrow Drude-like peak, which weakens and becomes extremely narrow when the temperature approaches zero. The corresponding optical response is almost purely dispersive for frequency well above the linewidth of this peal. As a



Figure 3.4: Decomposition of a typical optical spectrum into different Lorentz oscillators. The thick black line is the total optical conductivity. Dotted lines are the individual interband oscillators and solid lines are the individual intraband transitions, which have center frequency ω_0 smaller than ω_c . The gray area is the total spectral weight A_{LB} of the intraband transitions.

result the contributions to $\sigma(\omega)$ of the residual Drude term and of the condensate delta-function become inseperable in the limit $\omega \to \infty$, which in practice already happens for Bi2212 when $\omega > 15$ meV. A fit to the experimental data then returns the sum of the spectral weight of the delta-function and the residual Drude peak. Because this sum is the quantity of interest for the analysis of the kinetic energy, this approach has been used in the following sections of this thesis.

In the analysis we define the following spectral weights:

$$A_{l+D} = \int_{0}^{\omega_{c}} \sigma_{1}(\omega) \, \mathrm{d}\omega$$

$$A_{h} = \int_{\omega_{c}}^{\infty} \sigma_{1}(\omega) \, \mathrm{d}\omega$$

$$A_{LB} = \frac{1}{8} \sum_{i} \omega_{p,i}^{2} , \quad \omega_{0,i} < \omega_{c}$$
(3.5)

where $\sigma_1(\omega)$ is the real part of the measured optical conductivity. A_{l+D} can be obtained by directly integrating the measured data and adding *D* and is an estimate for the spectral weight of the intraband transitions. But these transitions



Figure 3.5: The real part of the dielectric function of optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ at 1.24 eV. The dotted lines are polynomial fits to the data below T_c and above T_c . The extrapolated value of the fit to the data above T_c is called the 'extrapolated normal state'.

might be broad and extend to above the cutoff frequency ω_c . Significant changes in the optical spectrum above ω_c might be a result of changes in the intraband transitions which are not taken into account in A_{l+D} . These changes *are* taken into account in A_{LB} , which is the sum of the spectral weights $(\omega_{p,i}^2)$ of all oscillators with a center frequency ω_0 below the cut-off frequency ω_c . A_{LB} can only be obtained by fitting the entire spectrum with a suitable oscillator model (figure 3.4).

3.3.2 **TEMPERATURE DEPENDENT DATA**

To obtain the changes due to superconductivity we need to compare the measured data in the superconducting state with the values as they would be if superconductivity were absent. We therefore extrapolated the temperature dependence of the normal state of the data to below T_c (figure 3.5). We did this for every frequency separately and obtained an 'extrapolated normal state' spectrum, denoted by the subscript \tilde{n} . In this way we obtained an extrapolated normal state reflection spectrum ($R_{\bar{n}}(\omega)$) in the infrared region and an extrapolated normal state dielectric function ($\epsilon_{\bar{n}}(\omega)$) in the visible region. To focus on the changes due to superconductivity we calculated the difference of the superconducting state spectra with the extrapolated normal state spectra to obtain a difference spectrum: $\Delta R(\omega) = R_s(\omega) - R_{\bar{n}}(\omega)$ and $\Delta \epsilon(\omega) = \epsilon_s(\omega) - \epsilon_{\bar{n}}(\omega)$. Figure 3.15-figure 3.18 show these difference spectra.

A second method to characterize the changes that occur at the critical temperature is to look at the derivative of the temperature dependent data. In the normal state the data roughly has a T^2 temperature dependence. Calculating $f'(T) = -\frac{1}{T} \frac{\partial f(T)}{\partial T}$ (where $f = R, \epsilon_1, \epsilon_2$) results in a constant value if the temperature dependence is indeed T^2 . We calculated for each frequency the average value of f' in the normal state and subtracted this from f'. This results in a derivative curve that is zero if a normal state T^2 behavior is followed. A positive value means an upward deviation from the T^2 behavior, when f is followed from high temperature to low temperature. A negative value means a downward deviation. Take for example the R' curve of Bi₂Sr₂CaCu₂O_{8+ δ}, T_c=88K (figure 3.16g). The reflection at 60 meV (figure 3.16d) has an upward turn at T_{c_r} resulting in an bump in the derivative curve. The reflection at 120 meV though has a downward kink and the corresponding derivative curve is negative. In the color plot of figure 3.15-figure 3.18 these derivative curves are all plotted together. A black color corresponds to f' being zero, a blue color corresponds to positive values and a red color to negative values.

We can compare the two methods of estimating the changes at the critical temperature. An upward (downward) kink in *R* results in ΔR being positive (negative): the reflectivity is higher (lower) in the superconducting state. The derivative (in the previous definition) will then, at *T*_c, show a bump (dip) and the color in the color plot will be blue (red). When the two (independent) methods are compared in figure 3.15-figure 3.18 we see a good correspondence, which make us feel comfortable about estimating the observed changes at the critical temperature.

3.3.3 FREQUENCY DEPENDENT DATA

The frequency dependent data was modeled using a Drude-Lorentz model, with the dielectric function $\epsilon(\omega)$ given by:

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_{k} \frac{\omega_{p,k}^{2}}{\omega_{0,k}^{2} - \omega^{2} - i\gamma_{k}\omega}$$
(3.6)

where $\omega_{p,k}$ is the plasma frequency of each oscillator, $\omega_{0,k}$ its center frequency, γ_k its width and ϵ_{∞} represents the contribution of the interband transistions above 5 eV to the dielectric function.

In the infrared region the reflection $R(\omega) = \left|\frac{\sqrt{\epsilon(\omega)}-1}{\sqrt{\epsilon(\omega)+1}}\right|^2$ was fitted with this model and in the visible region the dielectric function itself was fitted. The visible part of the spectrum needs three oscillators to fit the observed interband

transitions. In the infrared we used different combinations of Drude and mid infrared oscillators to fit the spectrum (figure 3.4).

This same model is used to fit the superconducting state spectrum and the extrapolated normal state spectrum. It turns out that the reflection data around 120 meV has a temperature dependence in the superconducting state that is hard to fit with a normal Drude-Lorentz model. Also the difference spectrum fails to fit in an satisfactory way in this region. This is due to the fact that a gap opens in the optical conductivity which can not be simulated with a few oscillators. Especially to obtain a nice difference spectrum one needs to add more oscillators around 120 meV, a few of them having negative weight to simulate the reduction of optical conductivity.

We therefore added a gap function to the model to solve this problem. The opening of the gap is modeled by multiplying the imaginary part of the Drude oscillator (proportional to the optical conductivity) by a broadened step function. The real part of the dielectric function is obtained by a Kramers-Kronig transform of this gapped imaginary part. To be able to find an analytical form of the gapped dielectric function we used the following form for the gap function: For $\omega \leq \omega_g(1 - \delta_g)$ it has a constant value $0 \leq y_g \leq 1$. For $\omega \geq \omega_g$ it has a constant value of 1. In between it is a third order polynomial with zero derivative at $\omega = \omega_g(1 - \delta_g)$ and $\omega = \omega_g$. This results in the following form:

$$\theta(\omega) = \begin{cases} y_g &, \quad \omega \le \omega_g - \omega_g \delta_g \\ y_g + (1 - y_g) \frac{((2 + \delta_g)\omega_g - 2\omega)((\delta_g - 1)\omega_g + \omega)^2}{(\delta_g \omega_g)^3} &, \quad \omega_g - \omega_g \delta_g < \omega < \omega_g \\ 1 &, \quad \omega \ge \omega_g \end{cases}$$
(3.7)

Using the imaginary part of the Drude oscillator $\epsilon_2(\omega) = \frac{\gamma \omega_p^2}{\omega(\omega^2 + \gamma^2)}$ we get the real part of the gapped dielectric function by:

$$\epsilon_1(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\theta(x) \, x \, \epsilon_2(x)}{x^2 - \omega^2} \, \mathrm{d}x \tag{3.8}$$

which can be done analytically. The spectral weight that is removed from the gapped region is recovered in the δ -function at zero frequency and its contribution to the real part of the dielectric function is:

$$\epsilon_1(\omega) = -\frac{2}{\pi\omega^2} \int_0^{\omega_g} (1 - \theta(x)) x \,\epsilon_2(x) \,\mathrm{d}x \tag{3.9}$$

In this way an analytical expression can be found for a gapped Drude oscillator and no numerical integration is needed. The procedure can be extended for a general Lorentz oscillator with center frequency ω_0 , but that is not used in this analysis. Also the step function $\theta(x)$ can be a polynomial of arbitrary order.



Figure 3.6: *a)* The gap function $\theta(\omega)$ for a broad gap, intermediate gap and a narrow gap. b) The ungapped optical conductivity $\sigma_1(\omega)$ and the optical conductivity multiplied with the gap function. *c)* The corresponding dielectric function $\epsilon_1(\omega)$ obtained from a Kramers-Kronig transform of the optical conductivity. *d)* The corresponding reflectivity.

3.4 SPECTRAL WEIGHT CHANGES

To find the spectral weight of the intraband transitions we need to fit the spectra and extract A_{LB} from the model parameters. We tried different models, always combined with the same set of oscillators to fit the interband transitions. For each model we fitted the 20K data (superconducting state) with all parameters free to adjust, obtaining a good fit for this temperature. We then fixed most of the parameters and allowed only a few to change for the fits at all other temperatures, as well as the extrapolated normal state spectrum. For each temperature we obtained a fitted spectrum and plotted for certain frequencies the fitted reflection or dielectric function as a function of temperature and compared this with the measured temperature dependence at the selected frequency. A_{LB} can now easily be calculated by summing the spectral weight of all oscillators that have a center frequency below ω_c . As a second method we calculated from both the fitted spectra in the superconducting state and the extrapolated normal state a difference spectrum $\Delta R(\omega)$ and $\Delta \epsilon(\omega)$ which we compared with that obtained from the measured data.

Allowing too many parameters to vary results in an over determination of the temperature dependence and noise becomes randomly distributed among different parameters. Allowing too few parameters to vary gives a bad fit of the temperature dependence. Therefore we tried different combinations of parameters that are free to vary as a function of temperature to find out which ones are relevant for the measured changes in temperature.

From both methods we can obtain the change in A_{LB} as superconductivity sets in. The first method gives A_{LB} for each temperature. We can extrapolate the normal state of $A_{LB}(T)$ to below T_c and calculate the difference of A_{LB} from the superconducting state. We will call this $\Delta A_{LB}^{(1)}$. From the difference spectra the change in A_{LB} can be calculated by taking the difference between $A_{LB,s}$ and $A_{LB,\bar{n}}$. We will call this $\Delta A_{LB}^{(2)}$.

The first model we tried has one narrow Drude oscillator and two mid infrared oscillators, together with three to five interband oscillators, depending on the sample (and within this model we allow different sets of parameters to change as a function of temperature). The second model is the same as the first, except that the Drude oscillator is gapped using the method described before.

We will now discuss the fits for all samples. The case of optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ is done in somewhat more detail. We start with a few parameters free and allow more parameters to change in order to obtain an acceptable result. For the other samples we do not discuss the results of all the different fitting models as for the optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$. Instead we present only the results of the model which provided the best fit in each case.

3.4.1 OPTIMALLY DOPED $Bi_2Sr_2CaCu_2O_{8+\delta}$, T_c =88K

The first model has three interband oscillators, 2 mid infrared oscillators and 1 Drude oscillator (figure 3.4). Figure 3.19 and figure 3.20 show the case where the width of the Drude peak and the first mid infrared oscillator were allowed to change. The width γ of the Drude peak sharpens considerably below T_c , eventually going to zero which means that the Drude peak has become a delta peak. As a result the reflectivity shows an increase at T_c , but this model clearly is not able to fit the reflectivity at around 0.1 eV. Also the temperature dependence of $\epsilon(T)$ is wrong. The wiggle in $\Delta R(\omega)$ around 0.1 eV (a result of the opening of the

gap) is not reproduced and at high energies (around 1 eV and above) $\Delta R(\omega)$ and $\Delta \epsilon_1(\omega)$ are too small. Of course ΔA_{LB} is zero.

In figure 3.21 and figure 3.22 we show the same model but with the Drude oscillator gapped. We allowed only the with of the Drude and the first mid infrared oscillator to change, as well as the gap. The reflectivity at 0.1 eV is now fitted very well, but for $\epsilon_1(T)$ the change at T_c is not well reproduced. When the temperature gets well above T_c the gap parameters lose their meaning and can show irregular behavior.

We tried many combinations of parameters that were allowed to change, except for the spectral weight of the individual oscillators. These fits always give similar results: The temperature dependence (especially at T_c) of the real part of the dielectric function at high energies (around 1 eV) is not well reproduced. Also $\Delta R(\omega)$ and $\Delta \epsilon_1(\omega)$ are often too small around 1 eV.

In figure 3.23 and figure 3.24 the strength of the Drude and MIR oscillator are allowed to change also, as well as one interband oscillator. The fit for $\epsilon_1(T)$ improves and since we allow the spectral weight to change, A_{LB} will now also change as a function of temperature. From the figure we see that it shows an increase as the critical temperature is crossed and we estimate the extra increase to give $\Delta A_{LB}^{(1)} \approx 0.02 \text{ eV}^2$. The change in $A_{LB}^{(2)}$ from comparing the extrapolated normal state with the superconducting state is $\Delta A_{LB}^{(2)} \approx 0.016 \text{ eV}^2$, which is of the same sign and order of magnitude.

In figure 3.25 and figure 3.26 we show a model where the infrared data is described by only one broad Drude oscillator. We then fitted *only* the ellipsometry data, above 0.75 eV. Of course the infrared fit is not good in this case, but allowing the strength of the Drude oscillator to change gives again an increase of A_{LB} , indicating that we obtain already a good impression of the changes in the spectral weight of the intraband transition by fitting the high energy data alone.

3.4.2 UNDERDOPED $BI_2SR_2CACU_2O_{8+\delta}$, T_c =66K

The results for the underdoped Bi₂Sr₂CaCu₂O_{8+ δ} sample are similar to the optimally doped case. Good results are only obtained if the spectral weight of some oscillators are allowed to change, which results in an increase of spectral weight (figure 3.27 and figure 3.28). The estimate for the change from $A_{LB}^{(1)}$ is 0.02 eV² while from $A_{LB}^{(2)}$ it is 0.012 eV². Again there is an increase and both methods give similar results.

3.4.3 OPTIMALLY DOPED $B_{12}SR_2CA_{0.92}Y_{0.08}CU_2O_{8+\delta}$, $T_c=95K$

Also for this sample we get bad fitting results if we allow only the width of the Drude and mid infrared oscillator to change and the fits improve if we allow for intraband spectral weight to change (figure 3.29, figure 3.30), which results in A_{LB} showing an increase as the system becomes superconducting.

3.4.4 OPTIMALLY DOPED $YBa_2Cu_3O_{7-\delta}$, $T_c=91K$

In this case we do not have infrared reflectivity data and our spectral weight analysis will be based on the visible light ellipsometry data alone. We needed a few more oscillators to fit the interband transitions, which is already clear from the optical conductivity data (figure 3.18). The infrared data was modeled with a broad Drude and a delta function. Already the plots of $\Delta\epsilon_1(\omega)$ and $\Delta\epsilon_2(\omega)$ show a different behavior when compared to the bismuth based samples: For YBa₂Cu₃O_{7- δ} the sign of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ is opposite for energies around 1 eV. The spectral weight analysis (figure 3.31 and figure 3.32) also shows different results, with $A_{LB}^{(1)}$ having no change at all at T_c , or perhaps a small decrease.

3.5 DISCUSSION

3.5.1 OBSERVATIONS & INTERPRETATION

We fitted the spectrum of each sample with different models and with different sets of free parameters. In the infrared region the best fit is obtained when we make use of the gap function. Furthermore, the fits improve considerably when we allow the spectral weight of intraband oscillators to change. When it is allowed to change, it results in an increase of intraband spectral weight at the superconducting transition for the bismuth based samples (figure 3.8) (YBa₂Cu₃O_{7- δ} is discussed later). This increase of $A_{LB}(T)$ turns out to be quite robust against details of the model. Even when the choice of the other free parameters is such that we do not have a good fit of the details of the spectrum as a function of temperature, $A_{LB}(T)$ always shows the same behavior. Figure 3.7 [57] shows the temperature dependence of the low frequency spectral weight A_{l+D} (equation 3.5) obtained with a model that did not fit the details of the infrared spectrum as well as the model used for figure 3.8, but the changes in spectral weight are the same. Because the details of the infrared spectrum are reproduced much better in figure 3.8, also the noise is reproduced in more detail.



Figure 3.7: Temperature dependence of the low frequency spectral weight A_{l+D} and high frequency spectral weight A_h (equation 3.5) as published in [57].

The two different methods of estimating changes in A_{LB} (fitting the difference spectrum or fitting the temperature dependent spectra) are consistent with each other. For each model and set of free parameters the two methods give the same sign and order of magnitude for ΔA_{LB} .

When the changes in intraband spectral weight are interpreted as kinetic energy changes per copper atom, we come to the numbers shown in table 3.9. Since the estimation of the kinetic energy lowering involves an extrapolation of the normal state, we would adapt a conservative error bar of 25%. But we feel confident about the sign of the changes, at least for the bismuth based samples. A value of around -0.7 meV is certainly large enough to account for the condensation energy: Estimates of the condensation energy of $Bi_2Sr_2CaCu_2O_{8+\delta}$ vary from 0.06 to 0.25 meV/Cu, depending on the doping [72, 73].

Recently other measurements have been done on $Bi_2Sr_2CaCu_2O_{8+\delta}$ with sim-



Figure 3.8: Intraband spectral weight $A_{LB}(T)$ versus T^2 for all measured samples. Note the upward change at T_c for the bismuth based samples.

sample	doping	T_c	ΔE_K [meV/Cu]
$Bi_2Sr_2CaCu_2O_{8+\delta}$	UD	66K	-0.6
$Bi_2Sr_2CaCu_2O_{8+\delta}$	OPD	88K	-0.7
$Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$	OPD	95K	-0.6
$YBa_2Cu_3O_{7-\delta}$	OPD	91K	no change

Figure 3.9: *The changes in kinetic energy per copper atom for each sample. UD = underdoped, OPD = optimally doped.*

ilar results. Reflection measurements on $Bi_2Sr_2CaCu_2O_{8+\delta}$ thin films [58] indicate spectral weight changes with a lowering of kinetic energy of the same order. Short-pulse interlayer tunneling spectroscopy measurements [74] also give results that may be interpreted with a kinetic energy lowering in the superconducting state. Measurements on YBa₂Cu₃O_{7- δ} [59] indicate no spectral weight changes for optimally doped samples, similar to our findings.

Several theoretical models use the concept of kinetic energy lowering as a

driving mechanism for superconductivity in the cuprates. The model of hole superconductivity [16], where pairs of holes move more easily than single holes, predicted a lowering of kinetic energy of the same order as observed in these measurements. Also a model based on phase fluctuations [11] of the superconducting order parameter, where a transition takes place from phase-incoherent Cooper-pair motion in the pseudogap regime above T_c to a phase-coherent motion at T_c , predicts a lowering of kinetic energy. A more phenomenological calculation of the spectral weight using a model for the scattering rate based on ARPES data [49] also predicts a lowering of kinetic energy for the optimally and underdoped samples, which is a result of the different momentum distribution functions of the non-Fermi-liquid normal state and the superconducting Fermi-liquid state. Dynamical cluster calculations for the two-dimensional Hubbard model [53] indicate that superconductivity is driven by a lowering of kinetic energy (figure 3.3).

The connection between spectral weight changes and kinetic energy relies on the applicability of the nearest neighbor tight-binding model, which in turn depends on the assumption that only a nearest neighbor hopping term *t* is relevant. It is possible that also a next nearest neighbor term *t'* or other terms are relevant. We have verified [55] that the next nearest neighbor hopping term of Bi₂Sr₂CaCu₂O_{8+ δ} does not change the direction of the spectral weight change predicted by the nearest neighbor tight binding model (see figure 3.2 where higher order hopping terms were included in the calculation).

3.5.2 COMPARISON WITH THERMAL-DIFFERENCE MEASUREMENTS

Thermal-difference measurements [75] already showed that at high energy changes occur in the optical response when superconductivity sets in. In figure 3.11 we show for the high energy range the ratio of the reflectivity in the superconducting state (R_s) over the extrapolated normal state reflectivity ($R_{\bar{n}}$): $R_s/R_{\bar{n}} = 1 + 1/R_n \cdot \Delta R$, with $\Delta R = R_s - R_{\bar{n}}$. The general trend is the same, with a structure below 2 eV which is a result of changes in the plasma frequency. With only reflection at high energy it becomes difficult to point out what causes this change in plasma frequency. Since we have access to both the real and imaginary part of the dielectric function in this region, we can calculate the contribution of ϵ_1 and ϵ_2 to $R_s/R_{\bar{n}}$ separately using $\Delta R = \partial R/\partial \epsilon_1 \cdot \Delta \epsilon_1 + \partial R/\partial \epsilon_2 \cdot \Delta \epsilon_2$, where $\Delta \epsilon_{1,2} = \epsilon_{1,2}^s - \epsilon_{1,2}^{\bar{n}}$. This is also show in figure 3.11 and it is clear that below 2 eV mainly the changes in the real part of the dielectric function are responsible for the changes in the reflectivity.



Figure 3.10: Thermal difference measurements as measured by Holcomb et al. Figure from [75].

3.5.3 SCATTERING RATE

At high energies the dielectric function in the normal state follows a T^2 temperature dependence (figure 3.15 - figure 3.18) while at low energies, in the far infrared around 60 meV, the temperature dependence is linear, as also seen in the temperature dependence of the resistivity in these materials. In figure 3.12 we plotted for the optimally and underdoped Bi₂Sr₂CaCu₂O_{8+ δ} crystal the temperature dependence of the frequency dependent scattering rate $1/\tau$. Shown is $1/\tau$ at low and high energies. Indeed the scattering rate has, in the normal state, a linear temperature dependence for low energies while the temperature dependence is quadratic for high energies. This indicates that the temperature dependence of the optical response at high energies is not dominated by the temperature dependence of the results from our fits, which indicate that allowing only the scattering rate to change is



Figure 3.11: The data presented as the ratio between the reflectivity in the superconducting state over the extrapolated normal state $R_s/R_{\bar{n}}$. Also shown are the partial derivatives to ϵ_1 and ϵ_2 , showing that below 2 eV mainly $\Delta \epsilon_1$ is responsible for the changes.

not enough and an increase of spectral weight is needed. This is in contrast with recent ideas [76] where it is claimed that the changes at high energies are a result of the changes in the scattering rate at low energies alone.

3.5.4 THERMAL EXPANSION

Thermal expansion measurements [77] have shown that at the critical temperature the expansion of the lattice shows a small anomaly. The screened plasma frequency of the electrons in the tight-binding band involves the density of electrons and the hopping amplitude, which both depend on the lattice parameter. This plasma frequency appears around 1 eV as the zero crossing of $\epsilon_1(\omega)$ and a change of the lattice parameter might result in a change in ϵ_1 . To investigate how large the contribution of the lattice expansion to the temperature dependence



Figure 3.12: Frequency dependent scattering rate $1/\tau$ for underdoped and optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ as a function of temperature for selected frequencies. Note that for low frequencies the normal state follows a linear temperature dependence while for high energies it follows a quadratic temperature dependence. The calculation of $1/\tau$ involves the base plasma frequency wich was found by the method described in section 5.3.2 and figure 5.2.



Figure 3.13: Thermal expansivity $\alpha(T) = \frac{1}{L} \frac{\partial L}{\partial T}$ as measured by Meingast et al. Figure from [77].


Figure 3.14: Temperature derivative of the plasma frequency ω_p of optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$, T_c =88K. The peak at T_c is much larger than the peak in thermal expansivity [77], indicating that superconductivity induced changes are not a result of lattice changes.

of the plasma frequency is, we note that the hopping parameter has a power dependence on the lattice parameter [78], typically $t \sim a^{-7/2}$. The plasma frequency is proportional to the electron density and the hopping parameter and is therefore proportional to the lattice expansion: $\omega_p \sim a^{\nu}$. When we compare $\frac{1}{\omega_p} \frac{\partial \omega_p}{\partial T} = \frac{1}{\omega_p} \frac{\partial \omega_p}{\partial a} \frac{\partial a}{\partial T} = \nu \frac{1}{a} \frac{\partial a}{\partial T}$ (figure 3.14) with measurements of the thermal expansivity (figure 3.13 [77]), we see that we need a value for $|\nu|$ of about 10-20, where one typically expects a value of order unity [78]. Moreover, the anomaly in the thermal expansivity measurements at T_c is much smaller than in $\frac{1}{\omega_p} \frac{\partial \omega_p}{\partial T}$, indicating that the change at T_c in $\omega_p(T)$ and $\epsilon_1(T)$ around 1 eV can not be the result of lattice changes. Already a direct comparison of $\epsilon_1(T)$ around the plasma frequency (around 1 eV) with the thermal expansion shows a clear difference, since a change in T_c is hardly observable in the thermal expansion, while it is clearly present in $\epsilon_1(T)$.

3.5.5 YBA₂**CU**₃**O**_{7- δ}

Our measurements on the YBa₂Cu₃O_{7- δ} film show surprisingly different results with respect to the bismuth based samples. The optical conductivity itself shows more structure between 1 and 2 eV and also the difference spectrum $\Delta\epsilon(\omega)$ (figure 3.18) shows more structure. More striking is the positive sign of $\Delta\epsilon_1(\omega)$ around 1 eV. The change in intraband spectral weight A_{LB} shows at T_c no change or perhaps even a decrease, in contrast with the bismuth based samples. In the case of YBa₂Cu₃O_{7- δ} it is known that the *a* and *b* directions of the crystal have different plasma frequencies, and since we did measurements on a twinned film, there is a mixing of these. Furthermore, around 1.5 eV there seems to be an interband transition with a large temperature dependence. This might blur the changes due to spectral weight transfer and since we have no infrared data it is difficult to make decisive conclusions. It has also been proposed [79] that at the superconducting transition charge is transferred between the Cu-O planes and chains. This results in spectral weight changes for a particular crystal direction and might obscure changes due to kinetic energy lowering.

3.6 SUMMARY AND CONCLUSIONS

We presented optical data of several cuprates measured with a temperature resolution of 1K in order to be able to detect small changes in the optical conductivity at the critical temperature. Normal incidence reflectivity in the region from 6.2 meV to 0.68 eV and ellipsometry in the region 0.74 eV to 4.46 eV was used. We estimated the changes at T_c by calculating a difference spectrum $\Delta R(\omega)$ in the infrared region and a difference spectrum $\Delta \epsilon(\omega)$ for the visible region. As a second method to estimate superconductivity related changes we calculated the derivative of the temperature dependent curves, which agrees qualitatively very well with the difference spectra. To observe changes in the intraband spectral weight A_{LB} we fitted the spectra for every temperature with a Drude-Lorentz model and extracted A_{LB} as a function of temperature. In the far infrared a good fit was only achieved by using a gap function applied to the Drude oscillator. The best results were obtained when we allowed the intraband spectral weight to vary as a function of temperature. The YBa₂Cu₃O_{7- δ} sample showed no observable superconductivity induced changes of the spectral weight $A_{LB}(T)$ at the critical temperature, although in the visible region there are clearly changes at T_c. The bismuth based samples showed an increase of the intraband spectral weight when the system crosses the superconducting transition temperature. Within the nearest neighbor tight-binding model this spectral weight is related to the kinetic energy and these changes indicate a lowering of kinetic energy of the order of 1 meV per copper atom for the bismuth based samples.

APPENDIX: GAP FUNCTION

In this appendix we will give the analytical form of the real part of the gapped Drude function:

$$\begin{aligned} \epsilon_1(\omega) &= \frac{2}{\pi} \int_0^\infty \left(\frac{\theta(x) \, \gamma \omega_p^2}{(x^2 + \gamma^2)(x^2 - \omega^2)} - \frac{(1 - \theta(x)) \, \gamma \omega_p^2}{\omega^2 (x^2 + \gamma^2)} \right) \, \mathrm{d}x \\ &= s \int_0^\infty \frac{\omega^2 + (\theta(x) - 1)x^2}{(x^2 + \gamma^2)(x^2 - \omega^2)} \, \mathrm{d}x \\ &= s \int_0^\infty \frac{\omega^2 + (c_0 - 1)x^2 + c_1 x^3 + c_2 x^4 + c_3 x^5}{(x^2 + \gamma^2)(x^2 - \omega^2)} \, \mathrm{d}x \end{aligned}$$

with $s = \frac{2\gamma\omega_p^2}{\pi\omega^2}$. The gap function is a third order polynomial $\theta(x) = c_0 + c_1x + c_2x^2 + c_3x^3$. The integral is splitted in three parts. Part 1 is from 0 to a_0 where the gap function has a constant value with $c_0 = y_g$ and $c_1 = c_2 = c_3 = 0$. a_0 is to be taken 0 if $\omega_g - \omega_g \delta_g \le 0$, otherwise $a_0 = \omega_g - \omega_g \delta_g$. Part 2 is from a_0 to ω_g where $c_0 = \frac{1}{\delta_g^3} \left(2 + \delta_g^3 + 3\delta_g(y_g - 1) - 2y_g\right)$, $c_1 = \frac{1}{\delta_g^3\omega_g} \left(6(y_g - 1)(1 - \delta_g)\right)$, $c_2 = \frac{1}{\delta_g^3\omega_g^2} \left(3(\delta_g - 2)(y_g - 1)\right)$, $c_3 = \frac{1}{\delta_g^3\omega_g^3} \left(2(y_g - 1)\right)$. The last part is from ω_g to infinity, where $c_0 = 1$ and $c_1 = c_2 = c_3 = 0$.

The individual parts evaluate to

$$\begin{split} I_1 &= -2\left(\omega^2 - \gamma^2(y_g - 1)\right) \arctan\left(\frac{a_0}{\gamma}\right) \\ &+ \gamma \omega \, y_g \left(\log|a_0 - \omega| - \log|a_0 + \omega|\right) \\ I_2 &= I_2(\omega_g) - I_2(a_0) \\ I_2(x) &= 2 \, c_2 \, \gamma \left(\gamma^2 + \omega^2\right) x + c_3 \, \gamma \left(\gamma^2 + \omega^2\right) x^2 \\ &- 2 \left(\gamma^2(1 - c_0) + c_2 \, \gamma^4 + \omega^2\right) \arctan\left(\frac{x}{\gamma}\right) \\ &+ \gamma \, \omega \left(c_0 + c_2 \, \omega^2\right) \left(\log|x - \omega| - \log|x + \omega|\right) \\ &+ \gamma^3 \left(c_1 - c_3 \, \gamma^2\right) \log|x^2 + \gamma^2| \\ &+ \gamma \, \omega^2 \left(c_1 + c_3 \, \omega^2\right) \log|x^2 - \omega^2| \\ I_3 &= -\pi \, \omega^2 + 2\omega^2 \arctan\left(\frac{\omega_g}{\gamma}\right) \\ &- \gamma \, \omega \left(\log|\omega_g - \omega| - \log|\omega_g + \omega|\right) \\ \end{split}$$
with $\epsilon_1 = \frac{\omega_p^2}{\pi \, \omega^2(\gamma^2 + \omega^2)} \left(I_1 + I_2 + I_3\right). \end{split}$



Figure 3.15: Spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$, $T_c=66K$. a/b/c) Frequency dependence of $R/\epsilon_1/\epsilon_2$. d/e/f) Temperature dependence $R/\epsilon_1/\epsilon_2$. g/h/i) Derivative of temperature dependence $R/\epsilon_1/\epsilon_2$. j/k/l) Difference between $R/\epsilon_1/\epsilon_2$ in the superconducting state and in the extrapolated normal state. m/n/o) Derivative of temperature dependence versus frequency and temperature. Blue (red) color indicates and increase (decrease) of the superconducting state with respect to the normal state.



Figure 3.16: Spectra of $Bi_2Sr_2CaCu_2O_{8+\delta}$, $T_c=88K$. a/b/c) Frequency dependence of $R/\epsilon_1/\epsilon_2$. d/e/f) Temperature dependence $R/\epsilon_1/\epsilon_2$. g/h/i) Derivative of temperature dependence $R/\epsilon_1/\epsilon_2$. j/k/l) Difference between $R/\epsilon_1/\epsilon_2$ in the superconducting state and in the extrapolated normal state. m/n/o) Derivative of temperature dependence versus frequency and temperature. Blue (red) color indicates and increase (decrease) of the superconducting state with respect to the normal state.



Figure 3.17: Spectra of $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$, $T_c=95K$. a/b/c) Frequency dependence of $R/\epsilon_1/\epsilon_2$. d/e/f) Temperature dependence $R/\epsilon_1/\epsilon_2$. g/h/i) Derivative of temperature dependence $R/\epsilon_1/\epsilon_2$. g/h/i) Difference between $R/\epsilon_1/\epsilon_2$ in the superconducting state and in the extrapolated normal state. m/n/o) Derivative of temperature dependence versus frequency and temperature. Blue (red) color indicates and increase (decrease) of the superconducting state with respect to the normal state.



Figure 3.18: Spectra of YBa₂Cu₃O_{7- δ}. *a/b/c*) Frequency dependence of $R/\epsilon_1/\epsilon_2$. *d/e/f*) Temperature dependence $R/\epsilon_1/\epsilon_2$. *g/h/i*) Derivative of temperature dependence $R/\epsilon_1/\epsilon_2$. *j/k/l*) Difference between $R/\epsilon_1/\epsilon_2$ in the superconducting state and in the extrapolated normal state. *m/n/o*) Derivative of temperature dependence versus frequency and temperature. Blue (red) color indicates and increase (decrease) of the superconducting state with respect to the normal state.

0 ω

0.5

1

1.5

R @ 0.06 eV R @ 0.12 eV R @ 0.25 eV 0.99 0.825 0.9 data fit data data • 0.898 • 0.98 0.82 fit fit 0.896 0.97 0.815 0.894 0.96 0.81 0.892 0.95 0.805 0.89 0.94 0.8 0.888 0.93 0.886 0.795 0.92 0.884 0.79 0 Т 100 200 0 Т 100 200 0 Т 100 200 $\epsilon_1 @ 0.87 \text{ eV}$ ε₁ @ 1.24 eV $\epsilon_1 @ \text{ 1.61 eV}$ -0.56 -0.58 -0.6 2.855 2.85 2.845 1.84 data data data 1.82 fit fit 1.8 -0.62 2.84 2.835 -0.64 1.78 -0.66 2.83 1.76 -0.68 2.825 1.74 -0.7 2.82 1.72 -0.72 2.815 -0.74 1.7 2.81 т 0 100 200 100 200 100 200 0 Т 0 ε₂ @ 0.87 eV ε₂ @ 1.24 eV ε₂ @ 1.61 eV 2.82 2.8 2.78 2.76 1.46 1.26 لمنامليا data fit data 1.44 data fit . 1.24 fit 1.42 1.22 1.4 2.74 1.38 1.2 2.72 2.7 1.36 1.18 1.34 2.68 1.16 1.32 2.66 2.64 1.3 1.14 0 т 100 200 0 т 100 200 0 100 200 $\Delta \mathsf{R}$ $\Delta \epsilon_1$ $\Delta \sigma_1$ 0.02 0.04 4 0.015 0.02 2 0.01 0 0 0.005 -0.02 -2 0 84A⁽²⁾ -0.04 = 0 eV2 -4 -0.005 0.5 ω1 2 0 ω 1 1.5 3 ω 1 2 3 Δτ 100 50 -50 -100 -150 -200 -250 -300 -350 -400

$Bi_2Sr_2CaCu_2O_{8+\delta}$, $T_c=88K$

Model with 3 interband oscillators, 2 MIR oscillators and 1 Drude oscillator. Parameters allowed to change: γ of the first MIR osc and γ of the Drude osc.

Figure 3.19: The measured temperature dependent data together with the fits.

Model with 3 interband oscillators, 2 MIR oscillators and 1 Drude oscillator. Parameters allowed to change: γ of the first MIR osc and γ of the Drude osc.



Figure 3.20: The temperature dependence of the parameters that are allowed to change.



Model with 3 interband oscillators, 2 MIR oscillators, 1 gap function and 1 gapped Drude oscillator. Parameters allowed to change: γ of the first MIR osc, ω_g , δ_g and y_g of the gap and γ of the gapped Drude osc.

Figure 3.21: The measured temperature dependent data together with the fits.

Model with 3 interband oscillators, 2 MIR oscillators, 1 gap function and 1 gapped Drude oscillator. Parameters allowed to change: γ of the first MIR osc, ω_g , δ_g and y_g of the gap and γ of the gapped Drude osc.



Figure 3.22: The temperature dependence of the parameters that are allowed to change.



Figure 3.23: The measured temperature dependent data together with the fits.

8A(1) [eV² 8A_{I+D} [eV² model parameters 4.94 4.17 eps.inf. : ε..=2.66795 4.16 4.92 third interband osc : $\omega_0=4.955$, $\omega_p=5.448$, $\gamma=2.374$ 4.15 4.9 4.14 second interband osc : ω_0 =3.829, ω_p =1.211, γ =0.541 4.88 4.13 first interband osc : ω0=2.441, ωp=1.829, γ=2.028 4.12 4.86 second MIR osc : ω₀=0.688, ω₀=0.610, γ=0.496 4.11 4.84 4.1 first MIR osc : ω0=0.206, ω0=1.552, γ=0.650 4.82 4.09 gap : ω_q =0.158, δ_q =0.776146, y_q =0.0853285 4.8 4.08 gapped Drude osc : ωn=1.464, γ=0.042 0 Т 100 200 0 Т 100 200 eps.inf. : ε, [eV²] first interband $osc : \gamma$ [eV] first interband osc : ω_p^2 2.3 2.67 4.1 2.665 4 2.25 2.66 3.9 2.655 2.2 3.8 2.65 2.15 3.7 2.645 3.6 2.64 2.1 3.5 2.635 2.05 3.4 2.63 2.625 3.3 2 т 100 0 Т 100 200 200 0 200 0 Т 100 [eV²] first MIR osc : y [eV] first MIR osc : ω_n^2 gap:ω_g [eV] 2.52 0.655 0.4 4 2.5 0.65 0.35 0.645 2.48 0.3 0.64 2.46 0.635 0.25 2.44 0.63 0.625 0.2 2.42 0.62 0.15 2.4 0.615 0.1 2.38 0.61 0 100 200 0 т 100 200 0 т 100 200 gap : δ gap : y [eV2 gapped Drude osc 2.2 2.5 0.9 0.8 2.15 2 0.6 2.1 1.5 0.5 2.05 0.4 1 0.3 2 0.2 0.5 1.95 0.1 0 0 1.9 100 0 Т 0 т 100 200 0 T 200 100 200 gapped Drude osc : y [eV] 0.065 0.06 0.055 0.05 0.045 0.04 0 т 100 200

$Bi_2Sr_2CaCu_2O_{8+\delta}$, $T_c=88K$

Figure 3.24: The temperature dependence of the parameters that are allowed to change.

0 ω

0.5

1

1.5

R @ 0.06 eV R @ 0.12 eV R @ 0.25 eV 0.84 1 0.9 data fit 0.98 0.96 data data • 0.88 0.82 fit 0.86 0.8 0.94 0.84 0.78 0.92 0.9 0.82 0.76 0.88 0.8 0.74 0.86 0.78 0.72 0.84 0.82 0.76 0.7 0 Т 100 200 0 Т 100 200 0 Т 100 200 $\epsilon_1 @ 1.61 \text{ eV}$ $\epsilon_1 @ 0.87 \text{ eV}$ ε₁ @ 1.24 eV 2.86 2.855 2.85 2.845 -0.56 -0.58 -0.62 -0.64 -0.66 -0.68 -0.7 1.84 data data data 1.82 fit fit 1.8 2.84 2.835 2.83 2.825 1.78 1.76 -0.72 -0.74 -0.76 2.82 1.74 2.815 1.72 т 0 Т 100 200 100 200 100 200 0 0 ε₂ @ 0.87 eV ε₂ @ 1.24 eV ε₂ @ 1.61 eV 2.8 1.46 1.26 data data fit data 1.44 1.24 2.78 fit 1.42 1.22 2.76 1.4 1.2 1.38 2.74 1.18 1.36 2.72 1.16 1.34 2.7 1.14 1.32 2.68 1.3 1.12 0 т 100 200 0 т 100 200 0 т 100 200 $\Delta \mathsf{R}$ $\Delta \epsilon_1$ Δσ 0.02 0.04 4 0.015 0.02 2 0.01 0 0 0.005 -0.02 -2 0 $8\Delta A_{LB}^{(2)} = 0.005 \text{ eV}^2$ -0.04 -4 -0.005 0.5 0 ω 1 1.5 ω 1 2 3 ω 1 2 3 Δτ 100 50 -50 -100 -150 -200 -250 -300 -350 -400

$Bi_2Sr_2CaCu_2O_{8+\delta}$, $T_c=88K$

Model with 3 interband oscillators and 1 Drude oscillator. Parameters allowed to change: ϵ_{∞} , ω_p and γ of the first interband osc and ω_p and γ of the Drude osc.

Figure 3.25: The measured temperature dependent data together with the fits.

Model with 3 interband oscillators and 1 Drude oscillator. Parameters allowed to change: ϵ_{∞} , ω_p and γ of the first interband osc and ω_p and γ of the Drude osc.



Figure 3.26: The temperature dependence of the parameters that are allowed to change.



Figure 3.27: The measured temperature dependent data together with the fits.

8A(1) [eV model parameters 8AI+D [eV 4.72 3.7 eps.inf. : ε..=2.93584 3.695 4.71 third interband osc : ω0=4.843, ω0=4.662, γ=2.386 3.69 4.7 second interband osc : ω_0 =3.821, ω_p =1.099, γ =0.497 3.685 4.69 3.68 first interband osc : ω0=2.528, ωp=1.790, γ=1.889 4.68 3.675 second MIR osc : wn=0.824, wn=0.339, v=0.477 4.67 3.67 first MIR osc : ω0=0.264, ω0=1.733, γ=0.742 4.66 3.665 gap : ω_n=0.192, δ_n=0.88404, y_n=0.131585 4.65 3.66 gapped Drude osc : ωn=1.263, γ=0.047 0 Т 100 200 0 Т 100 200 eps.inf. : ε first interband osc : ω_p² [eV²] first interband osc : y [eV] 2.955 3.9 2.2 3.8 2.15 2.95 3.7 2.1 3.6 2.945 2.05 3.5 2 2.94 3.4 1.95 3.3 2.935 1.9 3.2 2.93 3.1 1.85 т 200 0 т 100 200 0 100 0 Т 100 200 [eV²] first MIR osc : y [eV] first MIR osc : ω_n^2 [eV] gap : ω_g 3.02 3.015 3.01 0.746 0.21 0.744 0.205 3.005 0.742 0.2 3 2.995 0.74 2.995 2.99 2.985 2.98 0.195 0.738 0.19 0.736 2.975 0.734 0.185 2.97 0 т 100 200 0 т 100 200 0 т 100 200 gap : y_c gap : δ gapped Drude osc : ω_n² [eV2 0.8 1.6 1 1.595 0.95 0.7 1.59 0.9 0.6 1.585 0.85 0.5 1.58 1.575 0.8 0.4 1.57 0.75 0.3 1.565 0.7 0.2 1.56 0.65 0.1 1.555 0 T 100 0 100 0 Т 200 Т 200 100 200 gapped Drude osc : y [eV] 0.07 0.065 0.06 0.055 0.05 0.045 0 т 100 200

$Bi_2Sr_2CaCu_2O_{8+\delta}$, $T_c=66K$

Figure 3.28: The temperature dependence of the parameters that are allowed to change.

0

ω

0.5

1

1.5

R @ 0.06 eV R @ 0.25 eV R @ 0.12 eV 0.99 0.985 0.98 0.92 0.838 data data fit data fit • 0.918 • 0.836 ٠ fit 0.834 0.916 0.975 0.97 0.965 0.832 0.914 0.83 0.912 0.828 0.96 0.91 0.826 0.955 0.908 0.824 0.906 0.945 0.822 0.94 0.904 0.82 0 Т 100 200 0 т 100 200 0 Т 100 200 ε₁ @ 1.25 eV $\epsilon_1 @ 1.62 eV$ ε₁ @ 1.01 eV 2.7 0.4 1.7 data data fit 0.38 ٠ da ٠ 2.69 ٠ 1.68 0.36 fit 2.68 1.66 0.34 2.67 0.32 1.64 2.66 0.3 1.62 2.65 0.28 1.6 2.64 0.26 1.58 0.24 2.63 0.22 1.56 2.62 0 т 100 200 0 т 100 200 т 100 200 0 ε₂ @ 1.01 eV ε₂ @ 1.25 eV ε₂ @ 1.62 eV 1.885 1.875 1.875 1.865 1.865 1.865 1.855 1.855 1.845 1.845 1.845 1.845 1.36 1.35 1.34 1.33 1.32 1.31 1.29 1.28 1.27 1.26 1.25 1.18 data fit • 1.17 1.16 1.15 1.14 1.13 1.12 1.11 1.83 0 т 100 200 0 т 100 200 0 100 200 ΔR Δε Δσ 0.02 0.04 4 0.015 0.02 2 0.01 0 0 0.005 -0.02 -2 0 -0.04 $8\Delta A_{LB}^{(2)} = 0.014 \text{ eV}^2$ -4 -0.005 0.5 2 3 0 ω 1 1.5 ω 1 ω1 2 3 Δτ 150 100 50 -50 -100 -150 -200 -250 -300 -350 Ē

$Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$, $T_c=95K$

Figure 3.29: The measured temperature dependent data together with the fits.

8A⁽¹⁾ 8A_{I+D} [eV²] [eV2 model parameters 4.92 4.15 eps.inf. : E..=2.36736 4.9 4.14 third interband osc : ω0=5.128, ω0=5.837, γ=2.343 4.88 4.13 second interband osc : ω_0 =3.848, ω_p =1.399, γ =0.583 4.86 4.12 first interband osc : ω_0 =2.373, ω_p =1.686, γ =1.850 4.84 4.11 second MIR osc : ωn=0.734, ωn=0.436, γ=0.412 4.82 4.1 first MIR osc : ω₀=0.136, ω_n=1.657, γ=0.642 4.8 4.09 gap : ω_q=**0.129**, δ_g=**0.490827**, y_g=**0** 4.78 4.08 gapped Drude osc : ωn=1.410, γ=0.027 0 Т 100 200 0 Т 100 200 first interband osc : ω_p^2 [eV²] first interband osc : y [eV] eps.inf. : ε_∞ 3.4 2.37 2.1 3.35 3.3 3.25 2.08 2.06 2.04 2.368 2.366 2.364 3.2 3.15 2.02 2.362 2 2.36 3.1 2.358 3.05 1.96 2.356 3 2.95 1.94 2.354 1.92 2.352 2.9 1.9 т 100 200 0 100 200 0 Т 0 т 100 200 first MIR osc : y [eV] first MIR osc : ω_p^2 [eV²] gap:ωg [eV] 2.825 0.62 0.13 2.82 0.12 0.615 2.815 0.61 0.11 2.81 0.605 0.1 2.805 0.6 0.09 2.8 0.595 0.08 2.795 0.07 2.79 0.59 0 т 100 200 0 Т 100 200 0 т 100 200 [eV²] gap : y gap : gapped Drude osc : $\omega_{\rm p}^2$ 0.65 0.9 1.92 0.8 0.6 1.9 0.55 0.6 1.88 0.5 0.5 0.45 1.86 0.4 0.4 0.3 1.84 0.35 0.2 1.82 0.3 0.1 0.25 0 1.8 Т 200 0 Т 0 100 0 T 100 200 100 200 gapped Drude osc : y [eV] 0.028 0.026 0.025 0.024 0.023 0.022 0.02 0.019 0.018 0 т 100 200

$Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$, $T_c=95K$

Figure 3.30: The temperature dependence of the parameters that are allowed to change.

YBa₂**Cu**₃**O**_{7- δ}, *T*_c=91K

Model with 4 interband oscillators and 2 Drude oscillators. Parameters allowed to change: ϵ_{∞} , ω_p and γ of the second interband osc, ω_0 , ω_p and γ of the first interband osc, ω_p and γ of the second Drude osc and ω_p of the first Drude osc.



Figure 3.31: The measured temperature dependent data together with the fits.

YBa₂**Cu**₃**O**_{7- δ}, T_c =91K and oscillators and 2 Drude oscillators. Parameters allow

Model with 4 interband oscillators and 2 Drude oscillators. Parameters allowed to change: ϵ_{∞} , ω_p and γ of the second interband osc, ω_0 , ω_p and γ of the first interband osc, ω_p and γ of the second Drude osc and ω_p of the first Drude osc.



Figure 3.32: The temperature dependence of the parameters that are allowed to change.

CHAPTER 4

TEMPERATURE DEPENDENCE OF OPTICAL CONSTANTS IN BCS SUPERCONDUCTORS

4.1 INTRODUCTION

The¹ BCS theory for superconductivity in normal metals predicts that, while crossing T_{c} , the interaction energy is lowered [43]. The kinetic energy on the other hand is increased, but by a smaller amount and the total free energy is lowered, favoring the superconducting state. A gap Δ opens up in the excitation spectrum which is observable in the optical conductivity. For photon energies smaller than two times the gap energy the pairs of electrons can not be broken and therefore there is no absorption: the conductivity is zero (in the clean limit) or at least reduced [80, 81].

The integrated optical conductivity represents the number of electrons in the solid, which is of course unchanged. Therefore the reduction of optical conductivity for energies below 2Δ must be recovered elsewhere [82], and is indeed recovered in the superconducting delta peak at zero energy, representing the zero DC resistivity of the superconductor. Even above 2Δ there is a reduction of conductivity [80, 83] and for BCS superconductors one needs to evaluate the integrated optical conductivity up to an energy of approximately 8Δ to obtain a

¹The measurements presented in this chapter were done in close collaboration with Fabrizio Carbone.

temperature independent value. For a superconductor with a critical temperature of 15K this is about 20 meV. Therefore one does not expect to see any signs of superconductivity in the optical spectrum above these energies and certainly not around 1 eV, as has been observed for the cuprates [57].

In the cuprates, the observed change in the dielectric function around 1 eV ($\approx 100\Delta$) indicated a change in low frequency spectral weight. Besides the BCS like redistribution of spectral weight due to the opening of the gap, there is an extra overall increase of the spectral weight at low energies. Within the nearest neighbor tight-binding model this can be interpreted as a lowering of kinetic energy.

Suppose a similar effect would take place for a BCS superconductor. We assume that the nearest neighbor tight-binding model is applicable and the kinetic energy change (increase) is of the order of the condensation energy. From BCS theory [43] the condensation energy is given by $E_c = \frac{1}{2}D(E_F)\Delta^2$, where $D(E_F)$ is the density of states at the Fermi energy and $2\Delta = 3.53k_BT_c$. Assuming that the conduction electrons can be described by a Fermi gas [84], we can use the following well known results. k_F is the Fermi wave vector and can be expressed in the dimensionless ratio r_s/a_0 : $k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{3.63}{3\pi^2}$ in Å⁻¹, where a_0 is the Bohr radius and r_s is the radius in atomic units of the sphere which encloses one unit of electron charge. The electron density is $n = \frac{k_F^3}{3\pi^2}$ and the density of states at the Fermi energy is $D_{E_F} = \frac{mk_F}{h^2\pi^2}$, where *m* is the mass of the electrons. The plasma frequency is $\omega_p^2 = \frac{4\pi ne^2}{m}$, where *e* is the charge of the electrons.

The relation between the kinetic energy *K* and the integrated spectral weight is [49]:

$$\frac{\omega_p^2}{8} = \int_0^{\Omega_c} \sigma_1(\omega) \, \mathrm{d}\omega = -\frac{4\pi e^2 a^2}{\hbar^2} K \tag{4.1}$$

where *a* is the lattice parameter and Ω_c is a cut-off frequency to indicate that we want to integrate only over the low energy region of the optical conductivity $\sigma_1(\omega)$. A change in the kinetic energy would result in a change of the plasma frequency. Suppose that the change in kinetic energy is of the same order as the condensation energy: $\Delta K = K_s - K_n = E_c$. The change of the plasma frequency, $\omega_{p,s} - \omega_{p,n}$, would be

$$\delta\omega_p = -\frac{e^2 a^2 m k_F}{\pi \omega_b \hbar^4} (1.76 k_B T_c)^2 \tag{4.2}$$

where $\omega_{p,n} = \omega_p$ and $\omega_{p,s} = \omega_p + \delta \omega_p$, keeping only terms linear in $\delta \omega_p$.

Fitting the spectrum of niobium with a Drude-Lorentz model and extracting the plasma frequency of the Drude peak gives: $\omega_p = 7.7$ eV. Using $r_s/a_0 = 3.07$

and a = 3.30 Å [84] we get a theoretical value for ω_p of 8.7 eV, which is quite close to the measured value. Now we can calculate the expected shift in the plasma frequency if the onset of superconductivity would result in a increase of the kinetic energy of the order of the condensation energy. Given T_c =9K we get $\delta \omega_p \approx 2 \cdot 10^{-6}$ eV. This corresponds to an upward shift of the real part of the dielectric function at 1 eV of about $2.8 \cdot 10^{-5}$. Considering the resolution of our spectrometer, we will not be able to observe this. We try nevertheless to observe an effect, because, after all, the theoretical considerations pointed out above have not been tested experimentally in this way in the past.

4.2 SAMPLES AND EXPERIMENTS

We measured three samples that are considered to be BCS superconductors. That is, the BCS theory should apply to these samples to describe the superconducting properties. The first sample is a crystal of V_3 Si with a shiny metallic surface of roughly 3mm by 3mm and a critical temperature of 15K. The second sample was a Nb polycrystalline disk of 4mm diameter with a shiny metallic surface and a critical temperature of 9K. The third sample was a pellet of pressed polycrystalline MgB₂.

The measurements were done using ellipsometry in the energy range from 0.75 eV to 4.5 eV. The samples were mounted in a UHV He flow cryostat with a pressure of typically $3 \cdot 10^{-9}$ mbar. First measurements of the entire spectrum were taken at selected fixed temperatures. Then measurements were done for fixed frequencies while slowly increasing the temperature to well above T_c , resulting in a temperature resolution of 0.1 to 0.5 K.

Figure 4.1 shows the measured real part of the dielectric function $\epsilon_1(\omega)$ as a function of photon energy, together with the real part of the optical conductivity $\sigma_1(\omega)$. Figures 4.2 to 4.4 show the measured dielectric function for a selection of representative frequencies. The MgB₂ shows a weak overall temperature dependence, but no extra change at T_c (39K). Also the Nb shows little temperature dependence and within our experimental resolution there is no observable change at the critical temperature (9K). For this sample we also measured the entire spectrum in the energy range from 0.75 eV to 2.5 eV for temperatures from 5K to 20K with 0.5K intervals. For each temperature we fitted the spectrum with a Drude-Lorentz model, simulating one Drude peak and four interband transitions (table 4.5). We extracted the model parameters as a function of temperature and calculated the low frequency spectral weight, which is shown in figure 4.6. Here as well we do not observe a significant change at the critical temperature.



Figure 4.1: Frequency dependence of optical conductivity σ_1 and dielectric function ϵ_1 of V_3Si , Nb and MgB₂.



Figure 4.2: Temperature dependence of the optical conductivity σ_1 and dielectric function ϵ_1 of V_3Si for some frequencies.



Figure 4.3: Temperature dependence of the optical conductivity σ_1 and dielectric function ϵ_1 of *Nb* for some frequencies.



Figure 4.4: Temperature dependence of the optical conductivity σ_1 and dielectric function ϵ_1 of MgB_2 for some frequencies.

ω_0	ω_p	γ
4.38	10.31	2.4
2.46	6.27	1.48
1.91	1.78	0.59
1.43	2.75	1.04
0	7.74	0.17
$\epsilon_{\infty} = 1.13$		

Figure 4.5: Lorentz fit parameters for Nb. ω_0 is the center frequency in eV, ω_p is the strength in eV and γ is the width in eV.



Figure 4.6: Low frequency spectral weight of Nb as a function of temperature.

The V_3Si sample shows a spectacular temperature dependence. There are several temperatures where the slope of the temperature dependence changes, the most prominent one being around 22K. This is close to the cubic-to-tetragonal phase transition temperature in V_3Si . Indeed, thermal expansion measurements show a large change of the lattice parameter at this temperature [85, 86]. Repeating the arguments from the previous chapter we expect the plasma frequency to be proportional to the lattice parameter and the dielectric function in turn is proportional to the plasma frequency, giving $\epsilon \sim a^{\nu}$. When we compare $\frac{1}{\epsilon} \frac{\partial \epsilon}{\partial a} \frac{\partial a}{\partial T} = \nu \frac{1}{a} \frac{\partial a}{\partial T}$ with measurements of the thermal expansivity [85, 86] we see that we need a value of $|\nu|$ of the order 1, which is what we expect. Also the jump at the phase transition is of the same order in $\frac{1}{\epsilon} \frac{\partial \epsilon}{\partial T}$ as in the thermal expansivity data (opposed to the case for Bi₂Sr₂CaCu₂O_{8+ δ}, where the jump in our data was much larger than the jump in the thermal expansivity data). This indicates that the lattice expansion can be responsible for the observed changes in the optical response.

At the critical temperature of 17K a very small change is visible in some temperature dependent measurements. This could again be related to small changes in the thermal expansivity, as observed in [86], but could also be related to spectral weight transfer. The noise however is too large to make definite conclusions (especially in $\epsilon_1(T)$) and more accurate measurements are needed.

4.3 CONCLUSION

We measured the dielectric function and optical conductivity of the BCS superconductors Nb, V₃Si and MgB₂ with a high temperature resolution around their critical value, in the energy range from 0.75 eV to 4.5 eV. From theoretical considerations we do not expect to see any changes related to the onset of superconductivity. Indeed, the Nb and MgB₂ showed no anomalies at the superconducting phase transition. The V₃Si sample showed changes in the dielectric function a few degrees above T_c which could be related to the the cubic-to-tetragonal phase transition. At T_c something interesting might be happening. Still, the results are preliminary and more accurate measurements are in progress.

CHAPTER 5

QUANTUM CRITICALITY IN CUPRATE SUPERCONDUCTORS

Quantum criticality is associated with a system composed of a nearly infinite number of interacting quantum degrees of freedom at zero temperature, and it implies that the system looks on average the same regardless of the time- and length scale on which it is observed. Electrons on the atomic scale do not exhibit such symmetry, which can only be generated as a collective phenomenon through the interactions between a large number of electrons. In materials with strong electron correlations a quantum phase transition at zero temperature can occur, and a quantum critical state has been predicted [39, 32] which manifests itself through universal power-law behaviors of the response functions. Candidates have been found both in heavy-fermion systems [87] and in the high-transition temperature (high- T_c) copper oxide superconductors [88], but the reality and the physical nature of such a phase transition are still debated [2, 89, 90].

5.1 PHASE TRANSITIONS

In general a second order phase transition¹ is a continuous phase transition between an ordered and an disordered state of the system, characterized by an order parameter r, which is zero in the disordered state and finite in the ordered state. While the thermodynamic average of the order parameter is zero in the disordered phase, its fluctuations are non-zero. If the critical point is approached,

¹This introduction is largely inspired by the work by Sachdev and Vojta [32, 91].

the spatial correlations of the order parameter fluctuations become long-ranged. Close to the critical point their typical length scale, the correlation length ξ , diverges as

$$\xi \sim |t|^{-\nu} \tag{5.1}$$

where *t* is a dimensionless measure of the distance from the critical point, for example $t = \frac{|T-T_c|}{T_c}$ if there is a phase transition at temperature T_c . The correlation length critical exponent ν is a number which depends on various non-miscroscopic details of the system. In addition to the long-range correlations in space there are analogous long-range correlations of the order parameter fluctuations in time. The typical timescale for a decay of the fluctuations is the correlation (or equilibrium) time τ_c . As the critical point is approached the correlation time diverges as

$$\tau_c \sim \xi^z \sim |t|^{-\nu z} \tag{5.2}$$

where *z* is the dynamical critical exponent. Close to the critical point there is no characteristic length scale other then ξ and no characteristic time scale other then τ_c . At the phase transition point the correlation length and time are infinite, fluctuations occur on all length scales and timescales and the system is said to be scale invariant. As a consequence, all observables depend via power laws on the external parameters. If we observe the system at a scale *x* or λx , scale invariance states that the correlation functions are described by the same function *F*, apart from an overall constant, indicating that $F(\lambda x) = c F(x)$. Functions with this property are power laws, $F(x) = ax^{\eta}$.

For a crystal the Hamiltonian has operators that are defined on a lattice. Since close to the transition only large scale properties are relevant, we can go over from a description with operators on a discrete lattice to a description with operators that are defined for all points in space. We then use field operators and the resulting model will be a field theory. For a phase transition at finite temperature this results in a *d*-dimensional field theory, where *d* is the number of space dimensions. This approach is well studied for classical transitions.

As the transition point is approached the time scale τ_c diverges and consequently the corresponding frequency scale ω_c goes to zero. At finite temperature this has to be compared with the energy scale of the thermal fluctuations, k_BT . For a quantum mechanical system the character of the order parameter fluctuations crosses over from quantum to classical when $\hbar\omega_c$ becomes smaller then k_BT , indicating that classical thermal fluctuations are dominant. Therefor, close enough to the critical point any quantum mechanical system at finite temperature can be described with a classical (field) theory. Consequently, if we probe the system on a timescale larger than 1/T (or with a frequency $\hbar \omega < k_B T$) we are in the classical regime.

At the critical point all scales diverge and there is no relevant internal energy scale anymore. If we probe the system with a certain energy, then the only energy scale to which we can compare this energy is temperature itself. This leads to response functions being a function of frequency and temperature alone, known as ω/T scaling.

5.1.1 QUANTUM PHASE TRANSITIONS

In some systems the phase transition is not at a finite critical temperature, but at zero temperature and at a critical value of some other parameter, for example pressure, magnetic field or doping. The phase transition then takes place in the absence of thermal fluctuations. Quantum mechanical fluctuations will dominate and the previous mentioned cross over from a quantum theory to a classical theory can not be applied.

The Hamiltonian of such a system is typically of the form

$$H = H_1 + gH_2 \tag{5.3}$$

where *g* is related to the order parameter. At zero temperature the ground state is an eigenfunction of either H_1 or H_2 , depending on the value of *g*. As *g* is changed we get a phase transition from the ordered (say) ground state of H_1 if $g < g_c$ to the disordered ground state of H_2 if $g > g_c$. If there is an ordered state at finite temperature this system has a rich phase diagram (figure 5.1).

Although the quantum critical point is not experimentally accessible, a good description is still relevant, because the finite temperature properties are excitations of the zero temperature ground state of the system. At finite temperature and $g < g_c$ the excitations of the system are the quasiparticles of H_1 and the influence of H_2 makes them dynamic. At some finite temperature thermal fluctuations become strong and there can be a finite temperature phase transition to a thermally disordered state (if a finite temperature ordered state exists). The critical point at $g = g_c$ is then the endpoint of a line of finite temperature transitions and close to this line the system can be described by a classical theory. When $g > g_c$, in the quantum disordered state, the quasiparticles are given by H_2 which can be of completely different character.

Around $g = g_c$ and at finite temperature the system state can no longer be distinguished as an eigenstate of H_1 or H_2 , due to thermal fluctuations. The system then enter the quantum critical regime of the phase diagram. The quasiparticles are no longer those of either H_1 or H_2 but are of a more complex nature. At finite



Figure 5.1: The typical phase diagram of a system with a quantum critical point and order at finite temperatures. For zero temperature and $g < g_c$ the system is in an ordered state, while for $g > g_c$ the system is in an ordered state, while for $g > g_c$ the system is in and disordered state. If $g < g_c$ and the temperature is increased then one first finds the system in a still ordered state (light gray region), which is at some temperature destroyed by thermal fluctuations (black line). Around this critical line these thermal fluctuations dominate quantum processes and the phase transition is of a classical character. For temperatures higher then this phase transition the system is thermally disordered. If $g > g_c$ and one starts to raise the temperature from zero one finds the system disordered. At some temperature the system crosses over to a regime of the phase diagram where no well defined quasiparticles are present. It is then in the quantum critical regime. Because of thermal fluctuations both parts of the Hamiltonian (H₁ and H₂) contribute equally to the character of the excitations. The same thing happens for $g < g_c$ and the cross over temperature is lower when g is closer to g_c .

temperature the system 'looks critical' with respect to the parameter g, but it is driven away from criticality by thermal fluctuations. The T > 0 region in the vicinity of a quantum critical point therefor offers a fascinating interplay of effects driven by quantum and thermal fluctuations. Sometimes, as in the shaded region of figure 5.1, we can find some dominant fluctuations which are purely classical and thermal, and then the classical theory will apply. However, outside this region a new description is needed.

Thermodynamical properties of the system can be calculated from the partition function z, given by $z = \text{Tr e}^{-H/k_BT}$. If we identify $1/k_BT$ with $i\tau/\hbar$, then this
looks like a time evolution operator in imaginary time, $e^{-iH\tau/\hbar}$. This brings the *d*-dimensional quantum system from a state at time zero to a state at imaginary time τ . It turns out that this is equivalent to another, classical system evaluated in D = d + z dimensions, where z is the dynamical critical exponent (the dimensionality of the imaginary time axis). To understand this, imagine a single site quantum system (d = 0). Applying the imaginary time evolution operator brings the system from an initial state to a new state, during which (for $g < g_c$) the influence of H_2 is to mix the eigenstates of H_1 into (quantum mechanically) entangled states, making the system 'disordered' to a certain degree, with respect to the eigenstates of H_1 . The time $L_{\tau} = \frac{\hbar}{k_B T}$ is a measure of how long it takes the system to become maximally disordered, given a certain value of T. This now is equivalent to a 1-dimensional classical system with each site in an eigenstate of H_1 (and no entanglement), but with interaction between the sites of the 1-dimensional system. Each site is an eigenstate of H_1 and therefor 'ordered'. The role of H_2 is similar to the hopping term in a 1-dimensional chain of atoms. Maximal order corresponds to all sites being in the same eigenstate, but this does not necessarily have to be the case. Neighboring sites can be in different eigenstates due to the interactions given by H_2 . Interaction between the sites (due to H_2) can result in the entire 1-dimensional system being less then maximally ordered. Evaluating the single site quantum system from time zero to L_{τ} corresponds to evaluating the classical system with all the inter site interactions over a length L_{τ} . The extent to which the single site quantum system is ordered or disordered (entangled) corresponds to the extent to which the 1-dimensional classical chain is ordered. Therefor the *d*-dimensional quantum system corresponds to a D = d + z dimensional classical system where the extra dimension is an imaginary time dimension with length L_{τ} . Again, if the correlation length ξ is large and only large scale properties are important, we can go over from a discrete model to a continuous model. The resulting model is a classical field theory in D-dimensional space-time with imaginary time (that is, Euclidean space-time), where the imaginary time direction is periodic with length L_{τ} . Note that this is a quantum to classical mapping of a system in the vicinity of a critical point at zero temperature. It is therefor different from the previous quantum to classical mapping at finite temperature.

Using this formalism we can calculate correlators of some observable, which will be in imaginary time. To find the correlators in real time an analytical continuation needs to be done. For an exact solution of the Hamiltonian this is not a problem, but any approximation will give an unreliable result for the analytical continuation to real time. At the critical point thought, due to the scale invariance of the system, the exact form of the correlators is known to be a power law and the analytical continuation to real time is unproblematic.

Close to the critical point the microscopic details of the system are no longer important. The only parameters needed to describe the system are the correlation length (correlation time) and its critical exponent and external parameters, like temperature, pressure or magnetic field. Very different systems can then be described by the same class of models, and correlators of the system are given by universal scaling functions with have dependence on the microscopic details of the system (like the lattice constant).

5.2 QUANTUM CRITICAL BEHAVIOR IN $Bi_2Sr_2CaCu_2O_{8+\delta}$

In the quantum theory of collective fields one anticipates order at small coupling constant, and for increasing coupling one expects at some point a phase transition to a quantum-disordered regime. Quantum criticality in the copper oxides, if it exists, occurs as a function of charge carrier doping x, at a particular doping level x_c close to where the superconducting phase transition temperature reaches its maximum value. When this phase transition is continuous, a critical state is realized right at the transition, which is characterized by scale invariance resulting in the above-mentioned power-law response up to some (non-universal) high-energy cutoff Ω . Here we report a universal behavior that is characteristic of the quantum critical region. We demonstrate that the experimentally measured phase angle agrees precisely with the exponent of the optical conductivity. This points towards a quantum phase transition of an unconventional kind in the high- T_c superconductors.

5.3 METHODS

5.3.1 EXPERIMENTAL DETERMINATION OF THE OPTICAL CONDUCTIVITY

As detailed in earlier chapters, the most direct experimental technique, that provides the optical conductivity $\sigma_1(\omega)$ and its phase is spectroscopic ellipsometry. Another popular approach is the measurement of the reflectivity amplitude over a wide frequency region. Kramers-Kronig relations then provide the phase of the reflectivity at each frequency, from which (with the help of Fresnel equations) the real and imaginary part of the dielectric function, $\epsilon(\omega)$, is calculated. We used reflectivity for 6.2 meV $< \omega < 0.74$ eV, and ellipsometry for 0.18 eV $< \omega < 4.46$ eV. This combination allows a very accurate determination of $\epsilon(\omega)$ in the entire frequency range of the reflectivity and ellipsometry spectra. Owing to

the off-normal angle of incidence used with ellipsometry, the ab-plane pseudodielectric function had to be corrected for the c-axis admixture. We used previously published [71] c-axis optical constants of the same compound. The data files were generously supplied to us by S. Tajima. The effect of this correction on the pseudo dielectric function turns out to be almost negligible, in accordance with Aspnes [92].

The optical conductivity, $\sigma(\omega)$, and its phase, $\arctan(\sigma_2/\sigma_1)$, are obtained using the relation $\epsilon(\omega) = \epsilon_{\infty} + 4\pi i \sigma(\omega)/\omega$, where ϵ_{∞} represents the screening by interband transitions. In the copper oxide materials $\epsilon_{\infty} = 4.5 \pm 0.5$. For $\omega = 0.5$ eV an uncertainty of 0.5 of ϵ_{∞} propagates to an error of 2° of the phase of $\sigma(\omega)$. This accuracy improves for lower frequencies.

5.3.2 FREQUENCY DEPENDENT SCATTERING RATE

For an isotropic Fermi liquid, the energy dependent scattering rate of the quasiparticles can be readily obtained from the optical data, using the relation $1/\tau(\omega) = \text{Re}\left[\omega_p^2/4\pi\sigma(\omega)\right]$. In spite of the fact that the notion of a quasi-particle in the spirit of Landau's Fermi liquid is far from being established for the copper oxides, during the past 15 years it has become a rather common practice to represent infrared data of these materials as $1/\tau(\omega)$. The dynamical mass is defined as $m^*(\omega)/m = \text{Im}\left[\omega_p^2/4\pi\sigma(\omega)\right]$. To obtain absolute numbers for $1/\tau(\omega)$ and $m^*(\omega)/m$ from the experimental optical conductivity, a value of the plasma frequency, ω_p , must be adopted. With our value of ω_p the dynamical mass converges to 1 for $\omega \to \infty$ (figure 5.2).

Sometimes the renormalized scattering rate, $1/\tau^*(\omega) = 1/\tau(\omega) \cdot m/m^*(\omega) = \omega \sigma_1(\omega)/\sigma_2(\omega)$, is reported instead of $\tau(\omega)$. If the frequency dependence of the conductivity is a power law, $\sigma(\omega) = (-i\omega)^{\gamma-2}$, then $1/\tau^*(\omega) = -\omega \cot(\pi\gamma/2)$, which is a linear function of frequency [93]. The value of the slope reveals the exponent, and corresponds to the phase of the conductivity displayed in figure 5.5 and figure 5.6.

5.4 MEASUREMENTS

In figure 5.3 we present the experimental optical conductivity function $\sigma_1(\omega)$ of an optimally doped Bi₂Sr₂Ca_{0.92}Y_{0.08}Cu₂O_{8+ δ} single crystal (T_c = 96K [69]). In order to facilitate comparison with earlier publications [60, 94, 95] we also present $1/\tau(\omega)$ for a number of temperatures, adopting ω_p = 2.4 eV for the plasma frequency. The scattering rate $1/\tau(\omega)$ increases approximately linearly as a func-



Figure 5.2: The dynamical mass versus photon energy for $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$, using a value of $w_p = 2.4 \text{ eV}$ which results in $m^*(\omega)/m \to 1$ for $\omega \to \infty$.



Figure 5.3: The optical conductivity $\sigma_1(\omega)$ and frequency dependent scattering rate $1/\tau(\omega)$ of $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$.

tion of frequency, and when the temperature *T* is increased, the $1/\tau(\omega)$ curves are shifted vertically proportional to *T*. The notion that $1/\tau(\omega, T) \sim \omega + T$ in the copper oxides forms one of the center pieces of the marginal Fermi liquid model [39, 38, 96], and it has been shown to be approximately correct in a large number of experimental papers [60, 94, 95]. This phenomenology stresses the importance of temperature as the only relevant energy scale near optimal doping, which has motivated the idea that optimally doped copper oxides are close to a quantum critical point [39]. As can be seen in figure 5.3, $1/\tau(\omega)$ has a negative curvature in the entire infrared region for all temperatures, and it saturates at around 0.5 eV. Although this departure from linearity may seem to be a minor detail, we will see that it is a direct consequence of the quantum critical scaling of the optical conductivity.

If a quantum phase transition indeed occurs at optimal doping $x = x_c$, then three major frequency regimes of qualitatively different behavior are expected [32]: (1) $\omega < T$; (2) $T < \omega < \Omega$; (3) $\Omega < \omega$. We find direct indications of these regimes in our optical conductivity data.

5.4.1 THE CLASSICAL REGIME

Region 1 ($\omega < T$) corresponds to measurement times long compared to the compactification radius of the imaginary time, $L_{\tau} = \hbar/k_BT$. Sachdev [32] showed that in this regime the system exhibits a classical relaxational dynamics characterized by a relaxation time $\tau_r = AL_{\tau}$ (where A is a numerical prefactor of order 1), reflecting that temperature is the only scale in the system. For the low frequency regime we expect a Drude form $\sigma_1(\omega) = \frac{\omega_{pr}^2}{4\pi} \frac{\tau_r}{1+\omega^2\tau_r^2}$, where ω_{pr} is the plasma frequency. Then $T\sigma_1(\omega, T)$ becomes a universal function of ω/T , at least up to a number of order one:

$$\frac{\hbar}{k_B T \sigma_1(\omega, T)} = \frac{4\pi}{A\omega_{pr}^2} \left(1 + A^2 \left(\frac{\hbar\omega}{k_B T}\right)^2 \right)$$
(5.4)

In figure 5.4 we display $\hbar/(k_B T \sigma_1)$ as a function of $u = \hbar \omega/k_B T$. Clearly the data follow the expected universal behavior for u < 1.5, with A = 0.6. The experimental data are in this regard astonishingly consistent with Sachdev's predictions, including $A \approx 1$. From the fitted prefactor we obtain $\omega_{pr} = 1.3$ eV. Above we have already determined the total spectral weight of the free carrier response, $\omega_p^2 = 5.8 \text{ eV}^2$. Hence the classical relaxational response contributes 30% of the free carrier spectral weight. These numbers agree with the results and analysis of Quijada et al. [60]. This spectral weight collapses into the condensate peak



Figure 5.4: The data presented as $\hbar/(k_B T \sigma_1(\omega))$, demonstrating that for $\hbar\omega/k_B T < 1.5$ the conductivity obeys $\sigma_1(\omega, T) = T^{-1}f(\omega/T)$. The solid black line is a fit to equation 5.4, while the dashed black line is a fit to the scaling function proposed by Prelovsek [97].

at $\omega = 0$ when the material becomes superconducting. In figure 5.4 we also display the scaling function proposed by Prelovsek [97], $\sigma_1(\omega) = C \left(1 - e^{-\hbar \omega/k_B T}\right)/\omega$. The linear frequency dependence of this formula for $\hbar \omega/k_B T \ll 1$ is clearly absent from the experimental data. The universal dependence of $T\sigma_1(\omega, T)$ on ω/T also contradicts the "cold spot model" [98], where $T\sigma_1(\omega, T)$ has a universal dependence on ω/T^2 .

5.4.2 THE QUANTUM CRITICAL REGIME

In region 2 ($T < \omega < \Omega$) we can directly probe the scale invariance of the quantum critical state. The Euclidean (that is, imaginary time) correlator has to be known in minute detail in order to enable the analytical continuation to real (experimental) time. However, in the critical state invariance under scale transformation fixes the functional form of the correlation function completely: It has to be an algebraic function of imaginary time. Hence, it is also an algebraic function of Matsubara frequency $\omega_n = 2\pi n/L_{\tau}$, and the analytical continuation is unproblematic: (1) Scale invariance implies that $\sigma_1(\omega)$ and $\sigma_2(\omega)$ have to be algebraic functions of ω , (2) causality forces the exponent to be the same for $\sigma_1(\omega)$ and



Figure 5.5: *a*) Absolute value of the optical conductivity plotted on a double log scale. The dotted line corresponds to the power law $|\sigma(\omega)| = C\omega^{-0.65}$. *b*) The phase function of the optical conductivity.

 $\sigma_2(\omega)$, and (3) time reversal symmetry, implying $\sigma(\omega) = \sigma^*(\omega)$, fixes the absolute phase of $\sigma(\omega)$. Taken together

$$\sigma(\omega) = C \left(-i\omega\right)^{\gamma-2} = C\omega^{\gamma-2} e^{i\pi(1-\gamma/2)}$$
(5.5)

Hence the phase angle relating the reactive and absorptive parts of the conductivity, $\arctan(\sigma_2/\sigma_1) = (2 - \gamma) \cdot 90^\circ$, is frequency independent and should be set by the critical exponent γ . Power-law behavior of the optical conductivity of the copper oxides has been reported previously [99, 100, 93]. In figure 5.5 we display the frequency dependence of $|\sigma|$ in a log-log plot, and the phase in a linear plot. Although the temperature dependence 'leaks out' to surprisingly high frequency in the latter, the data are remarkably consistent with equation 5.5 for ω between k_BT and 0.9 eV. The observed power law of the conductivity, $|\sigma| = C/\omega^{0.65}$ corresponds to $\gamma = 1.35$, and the value of the phase, $\arctan(\sigma_2/\sigma_1) = 60^\circ \pm 2^\circ$, implies that $\gamma = 1.33 \pm 0.04$. The good consistency of γ obtained from two experimental quantities (that is, the exponent of a power law and the phase) is a strong test of the validity of equation equation 5.5. Frequency independence of the phase in region 2 and agreement between the two power laws (one from $\sigma(\omega)$ and the other from the phase angle spectrum) are unique properties of slightly overdoped samples, as demonstrated by figure 5.6, where we present the phase function for optimally doped (T_c =88K), underdoped $(T_c=66K)$, and overdoped $(T_c=77K)$ single crystals of Bi_{2.23}Sr_{1.9}Ca_{0.96}Cu₂O_{8+ $\delta}$ [68]} with different oxygen concentrations. The observed trend for different dopings



Figure 5.6: The absolute value and the phase of the optical conductivity for three $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples with different dopings: one underdoped (UD) with a T_c of 66K, one optimally doped with a T_c of 88K and one overdoped (OD) with a T_c of 77K. The solid black line in the log-log plots corresponds to the function $C\omega^{\gamma-2}$ and the dotted black line in the corresponding phase plot is $(2 - \gamma) \cdot 90^{\circ}$

suggests that optimal doping, with T_c =88K, and overdoping, with T_c =77K, are in the region of carrier concentrations where the optical conductivity obeys equation 5.5.

Because the phase is constant, the frequency dependent scattering rate $1/\tau(\omega) = \text{Re}\left[\omega_p^2/4\pi\sigma(\omega)\right] = C\omega^{2-\gamma} = C\omega^{0.65}$ can not be a linear function of frequency (but note that $1/\tau^*(\omega)$ is linear [93]). Our findings disqualify directly theories that do not incorporate a manifest temporal scale invariance. Luttinger liquids are quantum critical states of matter, and Anderson's results [93] based on one dimen-

sional physics are therefore of the correct form, equation 5.5. The exponent $\gamma = 4/3$ is within the range considered by Anderson, but differs significantly from the prediction based on the "cold spot" model [98], providing $\sigma(\omega) \sim (-i\omega)^{-0.5}$, which corresponds to $\gamma = 3/2$.

Let us now turn to the temperature dependence of the optical conductivity. From figure 5.7 we see that in this region the conductivity crosses over to a different dependence on ω and T. In region 1, for $\hbar\omega/k_BT < 2$, the data collapsed on a curve of the form $\sigma_1(\omega, T) = T^{-1}f'(\hbar\omega/k_BT)$ (equation 5.4), where f'(u) is a universal function. According to the simplest scaling hypothesis, $\sigma_1(\omega, T) \sim T^{-\mu}h'(\omega/T)$ with $h'(u) \rightarrow$ constant and $h'(u) \rightarrow u^{-\mu}$ in the limits $u \rightarrow 0$ and $u \gg 1$, respectively. For u > 3, h'(u) has a weak power-law dependence corresponding to a frequency dependence $\sigma_1(\omega, T) = C'\omega^{-0.65} = C'T^{-0.65}u^{-0.65}$, which means $\mu = 0.65$. Although this energy-temperature scaling is roughly satisfied in the high frequency regime, it is strongly violated at low frequencies, because equation 5.4 in the regime for $\hbar\omega/k_BT < 1.5$ (see figure 5.4) implies an exponent $\mu = 1$ at low frequencies instead. Bernhoeft has noticed a similar problem in the context of the heavy fermion critical points [101].

The crossover from one scaling function to the other for the different regimes implies that an energy scale is present in the system, in spite of the fact that for a quantum critical system temperature is the only relevant energy scale. In region 1 the scaling function can be written as $(\omega/\omega_0)\sigma_1(\omega, T) = f(u)$. In region 2 it can be written as $(\omega/\omega_0)^{\mu}\sigma_1(\omega, T) = h(u)$ where h(u) is a constant. At the crossover point, around u = 2, the two functions are the same and this sets the energy scale ω_0 . This energy scale was found to be $\omega_0 = 78 \pm 5$ meV with a corresponding characteristic temperature $T_0 = 450 \pm 100K$. The errorbars were obtained by varying the crossover point from u = 1.5 to u = 3.

5.4.3 THE INTERBAND REGIME

Region 3 ($\omega > \Omega$) necessarily has a different behavior of the optical conductivity, based on the following argument: the spectral weight of the optical conductivity integrated over all frequencies is set by the f-sum rule. However, since $\gamma > 1$, the integration over all frequencies of Re[$\sigma(\omega)$] of the form of equation 5.5 diverges. Hence we expect a crossover from the constant phase angle Arg[$\sigma(\omega)$] = (2 – γ) · 90° to the asymptotic value Arg[$\sigma(\infty)$] = 90°. The details of the frequency dependence of $\sigma(\omega)$ at the crossover point Ω depend on the microscopic details of the system. A (non-universal) example of an ultraviolet regularization with the required properties is [102] $\sigma(\omega) = (ne^2/m)(-i\omega)^{\gamma-2}(\Omega - i\omega)^{1-\gamma}$, which for $\omega \ll \Omega$ becomes of the form given by equation 5.5. Indeed the phase functions show a



Figure 5.7: Temperature/frequency scaling behavior of the real part of the optical conductivity of $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$. a) The data plotted as $(\omega/\omega_0)\sigma_1(\omega, T)$, which is equivalent to figure 5.4. b) The data plotted as $(\omega/\omega_0)^{0.65}\sigma_1(\omega, T)$. c) The data plotted as $(\omega/\omega_0)^{0.5}\sigma_1(\omega, T)$, which gives a slightly better collapse.

gradual upward departure from the plateau value for frequencies exceeding 0.6 eV (figure 5.5). This indicates that the 'ultraviolet' cut-off is on the order of 1 eV.

5.5 CONCLUSIONS

Do our observations shed light on the origin of the quantum criticality? In fact, they point unambiguously at three surprising features. First, the current correlator behaves singularly, and this implies that the electromagnetic currents themselves are the order parameter fields responsible for the criticality. Second, the criticality persists up to surprisingly high energies. Third, we have seen that the optical conductivity curves collapse on $\sigma_1(\omega,T) = T^{\mu}h(\omega/T)$, where $\mu = 1$ for $\omega/T < 1.5$, while $\mu \sim 0.65$ for $\omega/T > 3$. This disqualifies many theoretical proposals. Much of the intuition regarding quantum criticality is based on the rather well understood quantum phase transitions in systems composed of bosons. A canonical example is the insulator-superconductor transition in two spatial dimensions [103] where the optical conductivity is found to precisely obey the energy-temperature scaling hypothesis [104], characterized by a single exponent $\mu = 0$ governing both the frequency and temperature dependences [32, 104, 105]. Bosonic theory can be therefore of relevance in electron systems, but it requires the fermionic degrees of freedom to be bound in collective bosonic degrees of freedom at low energy.

In the copper oxides, it appears that the quantum criticality has to do with the restoration of the Fermi-liquid state in the overdoped regime characterized by a large Fermi surface. This implies that fermionic fluctuations play a central role in the quantum critical state, and their role has not yet been clarified theoretically. The absence of a single master curve for all values of ω/T is at variance with notions of quantum critical behavior, and its understanding may require concepts beyond the standard model of quantum criticality. We close with the speculation that the presence of bosonic fluctuations and fermionic fluctuations in the copper oxides is pivotal in understanding the quantum critical behavior near optimal doping of the copper oxides.

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