TEMPERATURE DEPENDENCE OF INFRARED AND OPTICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

By

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TEMPERATURE DEPENDENCE OF INFRARED AND OPTICAL PROPERTIES OF HIGH TEMPERATURE SUPERCONDUCTORS

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The infrared properties of the newly discovered high temperature superconductors are extremely unusual. We have extensively studied two cuprate families: La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$. The former is the material where high $T_c$ was first discovered; the latter is the first substance with a transition temperature above the liquid nitrogen boiling point. The samples studied were $ab$-plane-oriented superconducting thin films deposited on insulating substrates. Optical transmittance and reflectance measurements were made with the films in both the normal and superconducting states. Other superconducting samples in forms of randomly oriented or textured polycrystallines and granular films were also measured.

The infrared conductivity of these cuprates in the normal state showed a strong, nearly temperature-independent broad band in the mid-infrared region in addition to a strongly temperature-dependent narrow Drude band in the far infrared. Most of the
free-carrier oscillator strength was found to shift into the zero-frequency delta-function conductivity in the superconducting state as the free carriers condense into Cooper pairs. The CuO$_2$-plane London penetration depth $\lambda_L$ ($\sim$2700 Å for La$_{2-x}$Sr$_x$CuO$_4$, $\sim$1700 Å for YBa$_2$Cu$_3$O$_{7-\delta}$) was estimated from the superfluid density. The low-frequency tail of the midinfrared absorption, a direct particle-hole excitation, remained for $T \ll T_c$.

One striking result observed was the linear temperature dependence of the quasiparticle scattering rate above $T_c$, followed by a rapid drop just below $T_c$. Another was that the $T$-dependent conductivity of the YBa$_2$Cu$_3$O$_{7-\delta}$ films at low frequencies exhibited a peak just below $T_c$, resembling the "coherence peak" of ordinary superconductors, yet having a different origin. This peak is associated with the dramatic decrease of the scattering rate rather than with the coherence effect.

Finally, the superconducting gap absorption was invisible in the infrared spectra, suggesting that these cuprates were "clean-limit" superconductors. The energy gap for YBa$_2$Cu$_3$O$_{7-\delta}$ might be deduced indirectly from the $T$-dependence of the far-infrared vibrational features of the polycrystalline samples, suggesting $3.0 < 2\Delta/k_BT_c < 4.2$. 
CHAPTER I
INTRODUCTION

This dissertation describes a detailed study of the optical properties—from far infrared through ultraviolet frequencies—of the newly discovered copper oxide materials which have high superconducting transition temperatures. It concentrates on the investigations on La$_{2-x}$Sr$_x$CuO$_4$ ($T_c \approx 30$ K) and YBa$_2$Cu$_3$O$_{7-\delta}$ ($T_c \approx 90$ K) thin films and polycrystalline samples through measurement and analysis of optical transmittance and/or reflectance as a function of incident photon frequency ($\omega$) and sample temperature ($T$). Much effort in this work has been devoted to study the anomalous non-Drude response in the mid-infrared region, the behavior of superconducting energy gap, and the role of phonon and low-lying excitations.

The discovery of high temperature superconductors (HTSC) by Bednorz and Müller\(^1\) in 1986 and Wu et al.\(^2\) in 1987 has stimulated considerable interest in the scientific world. These new materials are interesting because they present an exciting new regime for superconductivity and have the potential of valuable practical applications. The most fundamental properties of these high-$T_c$ cuprates are threefold: high superconducting transition temperature ($T_c$), short coherence length ($\xi$), and large anisotropy. The conventional mechanism of pairing \textit{via} electron-phonon interaction cannot describe this oxide materials simply because $T_c$ is to high. Attempts have been made to determine whether these high-$T_c$ superconductors are fundamentally different from the conventional superconductors, which have been well described by the Bardeen-Cooper-Schrieffer (BCS) theory.\(^3\)

Infrared spectroscopy, a powerful and successful technique for studying classical superconductors,\(^4-8\) has been widely used to study such fundamental physical proper-
ties as superconducting gaps, crystal vibrations, electron-phonon couplings, low-lying excitations, density of states, and electronic band structure.

In the framework of BCS theory, the existence of an energy gap means that a bulk superconductor at $T \ll T_c$ is a perfect reflector of electromagnetic radiation for photon energy ($\hbar \omega$) less than the gap energy ($2\Delta$). Photons with $\hbar \omega > 2\Delta$ can disassociate the Cooper pairs and cause quasiparticle transitions to unoccupied levels above the gap, making the superconductor behave like a normal metal. This is indeed the case for conventional superconductors, as first verified by Glover and Tinkham.\textsuperscript{4}

However, the high-$T_c$ superconductors show much more complicated behavior. A major difficulty with the observability of the superconducting gap in the infrared spectra is that the reflectance of HTSC can hardly be distinguished from unity at low frequencies within which a gap is expected. Because the transition temperature is comparable to the Debye temperature ($T_c \approx T_\theta$), the superconducting gap energies of HTSC are expected to lie in the frequency range where infrared active optical phonons are present. In return, these phonons (if not well screened by free carriers) may obscure the observation of the energy gap. It has been reported\textsuperscript{9} by direct bolometric absorption measurements that these materials have a finite absorption down to the frequencies well below the BCS gap at $T \ll T_c$. In both the normal and superconducting states, a non-Drude low-lying excitation spectrum is present in the mid-infrared region. Added to the complexity is the anisotropy of these materials, which means that for polycrystalline and twinned samples, only an effective response can be measured. Furthermore, thin film measurements are complicated by contributions from the substrates. Although the optical results generally agree among different investigators, the interpretation in many ways—particularly about the infrared determinations of the gap and the origin of the mid-infrared band—still remains controversial and is not clearly understood.
One feature common to all cuprate superconductors is the existence of quasi-two-dimensional Cu-O planes, which appear to play a major role in high-$T_c$ superconductivity. Therefore, it is of primary importance to investigate the intrinsic electronic responses of these planes. Most optical studies to date have concentrated on the 90-K transition temperature $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) system, which contains both CuO$_2$ planes and CuO chains. (For reviews, see Refs. 10–13.) It has been observed, however, that the quasi-one-dimensional CuO chains in YBCO have a substantial contribution to the optical conductivity,\textsuperscript{14,15} which has complicated the analysis of this material. In contrast, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) system, which has the simplest crystal structure in the cuprate family and contains only single CuO$_2$ layer per formula unit, has been studied in most cases on the sintered polycrystalline samples.\textsuperscript{16–23} Because the LSCO materials are strongly anisotropic, it is difficult to determine the intrinsic nature of the CuO$_2$ layers from measurements of polycrystalline samples. A few optical measurements, mostly restricted to the composition-dependence studies at room temperature, on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals or thin films have been made,\textsuperscript{24–29} and most recently, a systematic temperature-dependent optical study on oriented samples of this material has been reported.\textsuperscript{30}

In no case can the normal-state infrared conductivity be described by a simple Drude model. In many studies,\textsuperscript{10–12,30–36} this non-Drude conductivity observed in ceramics, crystals and thin films has been described by a two-component approach: a narrow, strongly temperature-dependent Drude absorption centered at the origin and a broad, nearly temperature-independent mid-infrared (MIR) band. The Drude absorption is due to the free carriers which are responsible for the dc transport and which condense into a superfluid below $T_c$ whereas the MIR absorption is due to the bound carriers which have a semiconductor-like gap. This approach has been adopted because it is clear that a single, strongly damped, Drude term, used to model the infrared date in many early measurements, does not work.\textsuperscript{10,12} An alternative
is a single-component approach: all of the infrared absorption is due to one type of carriers, with a strong frequency dependence in the scattering rate and effective mass. This approach also leads to a broad range of optically inactive excitations in the mid-infrared region while at low frequencies (including dc) the conductivity goes inversely with the temperature. This approach has been described in the framework of the “marginal Fermi liquid” (MFL) theory of Varma et al.\textsuperscript{37} and the “nested Fermi liquid” (NFL) theory of Virosztek and Ruvalds.\textsuperscript{38,39}

Attempts have been made\textsuperscript{10,15,40–46} to assign the superconducting energy gap either to the edge of a rapid drop in the ratio $\mathcal{R}_s(\omega)/\mathcal{R}_n(\omega)$ of the superconducting to normal reflectance or to the absorption onset of the conductivity, $\sigma_{1s}(\omega)$, in the superconducting state. The values of $2\Delta(0)/k_BT_c$ obtained in this way range between 2.5 and 8. There has been a controversy, however, whether these structures are due to the energy gap or are part of the midinfrared absorption.\textsuperscript{32–35,47–49}

Most of the work to date determines the frequency-dependent conductivity through Kramers-Kronig analysis of reflectance measurements.\textsuperscript{10–13,30–35,40–50} The main advantage of this technique is that a large amount of important information about the material can be extracted easily once the reflectance over a wide frequency range is measured. However, there is a drawback of artificial extrapolations beyond the measured frequency range, which is required by the Kramers-Kronig integral. Furthermore, the optical properties derived from this method is very dependent on the accuracy of the reflectance especially for highly reflecting materials. In contrast, the optical functions derived from transmission measurement are much less sensitive to the errors than from reflectance. In this work, both techniques are employed for data analysis. We will present a method of extracting the optical functions directly from combined measurements of reflectance and transmittance without referring to the Kramers-Kronig analysis.
The rest of this dissertation is organized as follows. The second chapter is a review of the previous research work on superconductivity and of some fundamental properties of HTSC. Chapter III discusses the basic theory about the general optical properties of solids and the phenomenological models in description of superconductivity. Chapter IV will describe the infrared technique and experimental apparatus used in this study. Sample preparation and characteristics will be presented in chapter V. Chapter VI explains the procedures of experimental measurement and low temperature technique along with data collecting and processing. Chapter VII, VIII and IX are devoted to data analysis and result discussion, in which the experimental optical spectra for several high-$T_c$ samples are presented and discussed in detail. Various theoretical models are used to describe the physical properties of the oxide materials in the normal and superconducting states. Finally, Summary and conclusions are given in chapter X.
CHAPTER II
BRIEF SURVEY OF SUPERCONDUCTIVITY

Since Kamerlingh Onnes' 1911 discovery of superconductivity in mercury cooled to 4.2 K, the observed transition temperatures, \( T_c \), have gradually moved upward but remained strictly a low temperature phenomenon. The most important developments of this area in the recent decades include: the Ginzburg-Landau theory,\(^{51}\) the Pippard nonlocal electrodynamics,\(^{52}\) and the discovery of isotope effect\(^{53,54}\) in early 1950's; the first satisfactory description of microscopic mechanism (in terms of energy gap and Cooper pairs) by the BCS theory\(^3\) in 1957; the prediction of Josephson effect\(^{55}\) in 1962; and, most recently, the discovery of high-\( T_c \) superconductors in late 1980's. The highest record for \( T_c \) before 1986 was 23.2 K in Nb\(_3\)Ge found by L. R. Testardi \textit{et al.}\(^56\) in 1973. The extraordinarily high \( T_c \) superconductivity era started in 1986 when J. G. Bednorz and K. A. Müller\(^1\) observed that La\(_{2-x}\)Ba\(_x\)CuO\(_4\) became superconducting below 35 K. This opened the way for intensive work on high temperature superconductors. Another breakthrough soon arrived by the announcement\(^2\) in 1987 of YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\), with \( T_c \) above 90 K capable of becoming superconducting in liquid nitrogen. In 1988, two families of copper oxide compounds with even higher values of \( T_c \), 110 K in Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\)\(^57\) and 125 K in Tl\(_2\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\)\(^58\) were found.

The discovery of high-\( T_c \) oxides has generated tremendous excitement in public because of the new technological promises of these materials. Superconductivity can now be achieved with a simpler coolant—liquid nitrogen. The electronic properties of HTSC can be exploited to make more efficient microelectronic components such as passive microwave devices, logic circuits, computer interconnect boards, and infrared detectors. The fabrication of ultra-sensitive sensors and production of Josephson...
microwave mixers with a wider electromagnetic wave windows become possible with the use of HTSC because of the larger energy gap expected for these materials.

**Fundamental Properties**

As stated in the introductory chapter, there are three unusual fundamental properties which distinguish these new materials from the conventional superconductors. First, the transition temperature \( T_c \) is high. Aside from the promising applications as stated above, high \( T_c \) also presents a new challenge to scientific investigators, as many low-lying excitations are present near \( T_c \). These excitations will affect some fundamental properties of the superconductors such as \( T_c \) and critical current \( J_c \) as well as the energy gap \( 2\Delta \), if such excitonic energies are large enough to break Cooper pairs. These high-\( T_c \) materials have low dc conductivity in the normal state due to lower conduction electronic concentration, which results in a longer penetration depth. The high value of \( T_c \) has turned out to complicate the behavior of the materials in both the normal state and superconducting state.

Second, as a consequence of higher \( T_c \) or larger superconducting gap compared to the classical superconductors, HTSC have a shorter coherence length \( \xi \), with typical value of \( \xi = \hbar v_F / kT_c \sim 10 \) Å, which is comparable to the unit cell dimensions. All HTSC are type II superconductors because of \( \xi < \lambda \), where \( \lambda \) is the electromagnetic penetration depth with a value of the order 1000 Å. The shortness of \( \xi \) makes the superconductivity sensitive to small scale structures. In turn the fluctuations play a much larger role in high-\( T_c \) materials than in classical superconductors. A small \( \xi \) also leads to a high value of upper critical magnetic field \( H_{c2} \).

Thirdly, HTSC show large optical anisotropy. The physical properties such as optical conductivity and other fundamental physical parameters vary in different directions. The resistivity, for instance, along the \( c \)-axis (\( \rho_c \)) is larger than within the CuO-plane (\( \rho_{ab} \)) by a factor of \( \sim 10^2 \). Therefore, high quality crystals and oriented
films are essential for experimental studies, because the anisotropy of the layered copper oxides requires that the samples be measured along different axes of the crystals.

Finally, it has been estimated and will be shown in this dissertation that the mean free path $l = v_F \tau \approx 100 \, \text{Å}$, making

$$\xi < l < \lambda.$$ 

It is this condition that places the HTSC in the "clean limit" which is sharply distinguished from most conventional superconductors. The latter ones at low temperatures are usually in the anomalous skin effect limit or dirty limit.

**Crystal Structure and Phase Diagram**

The crystal structure and the phase diagrams of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are shown in Figs. 1 and 2. Note that both figures show the structure in a unit cell which contains two formula units. The parent compounds of both materials are anti-ferromagnetic semiconductors. When doped with holes, they become metallic.

For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, it has the perovskite $\text{K}_2\text{NiF}_4$ structure and is the body-centered tetragonal Bravais lattice ($I4/mmm$). The typical values of lattice constants are: $a \approx b \approx 3.78 \, \text{Å}$, and $c \approx 13.2 \, \text{Å}$. As the temperature is lowered, the crystal exhibits a second order structural phase transition from tetragonal to orthorhombic phase ($Cmca$). This transition involves a staggered rotation of the CuO$_6$ octahedra as shown by the arrows in Fig. 1. Upon further cooling the crystal exhibits another transition from metallic to superconducting phase. The optimum Sr doping for superconductivity lies in the range of $0.1 \leq x \leq 0.2$. Since $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ does not have chains, one expects that the dynamic conductivity $\sigma(\omega)$ of an oriented crystal probed to be solely due to the intrinsic response from the CuO$_2$ planes, provided the electric field vector $\mathbf{E}$ is parallel to these planes.
In contrast with La$_{2-x}$Sr$_x$CuO$_4$ crystals, the presence of CuO chains, as shown in Fig. 2, along the $b$-axis in the YBa$_2$Cu$_3$O$_{7-\delta}$ system complicates the analysis of this materials. A great deal of effort has been devoted to distinguish the role of the quasi-one-dimensional chains from that of the quasi-two-dimensional planes in recent years. However, most of the YBa$_2$Cu$_3$O$_{7-\delta}$ samples are usually microtwinned, making it difficult to identify the difference. One the other hand, by far YBa$_2$Cu$_3$O$_{7-\delta}$ are the most studied material in high-$T_c$ family. The parent compound YBa$_2$Cu$_3$O$_6$ is tetragonal while the superconducting YBa$_2$Cu$_3$O$_{7-\delta}$ is orthorhombic. Typical values of the lattice constants are: $a = 3.82$ Å, $b = 3.88$ Å, and $c = 11.68$ Å. The transition temperature of this material is very dependent on the oxygen doping concentration as illustrated in Fig. 2.

**Other Physical Properties**

A good superconductor is usually a poor electric conductor in the normal state. The reason is that the conventional electron pairing requires a strong electron-phonon interaction in order to produce a high transition temperature. It is the same interaction that causes the large electronic scattering rate hence high resistivity in the normal state. The HTSC are quite poor electric conductors above $T_c$, thus one expects a strong electron scattering mechanism in these materials.

It is widely believed that the electron-phonon interaction plays a minor role in the superconductivity for YBa$_2$Cu$_3$O$_{7-\delta}$. However, a significant isotope shift ($\alpha \simeq 0.2$) due to partial substitution of $^{18}$O for $^{16}$O in La$_{1.85}$Sr$_{0.15}$CuO$_4$ has been observed and interpreted as evidence for strong electron-phonon coupling.$^{59,60}$ This implies that phonons may still play an important role, if not a key role, in the pairing mechanism. On the other hand, the observed linear behavior of the dc resistivity for La$_{2-x}$Sr$_x$CuO$_4$ up to 1100 K implies a weak electron-phonon coupling for the free
carriers.\textsuperscript{61} Therefore the La$_{2-x}$Sr$_x$CuO$_4$ system is expected to bridge the classical superconductors and HTSC.

In optical studies, a lot of effort has been made in recent years to study the non-Drude response in the mid-infrared region and to discover the superconducting energy gap. It has been observed that the MIR absorption is absent in the undoped parent compounds such as La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_6$. For La$_{2-x}$Sr$_x$CuO$_4$, Uchida et al.\textsuperscript{29} have reported that the MIR absorption band develops with increasing dopant concentration and then exhibits a saturation in the higher compositional range $0.1 \leq x \leq 0.25$. Similar effects are observed in doping of $n$-type Pr$_{2-x}$Ce$_x$CuO$_4$ by Cooper et al.\textsuperscript{62} As a consequence of the redistribution of the the O 2$p$ and Cu $3d$ orbitals upon doping, spectral weight is rapidly transferred from the in-plane O 2$p \rightarrow$ Cu $3d$ charge transfer (CT) excitations above 2 eV to the free-carrier absorption (Drude band) and the low-energy excitations (MIR band) below 1.5 eV. Therefore both the Drude and MIR absorptions in HTSC appear to be related to the introduction of holes on the CuO$_2$ layers (or CuO chains) by doping. For La$_{2-x}$Sr$_x$CuO$_4$, the CT gap becomes weaker or fills in and the phonons are obscured as holes are added upon substituting Sr$^{2+}$ for La$^{3+}$. In contrast to these changes, the plasma minimum in the reflectance is pinned at 0.9 eV and insensitive to the dopant concentration.\textsuperscript{22,23,63,64} This unusual behavior is in contradiction with the prediction that the plasma frequency should increase with increasing carrier concentration.

In summary, the high temperature superconductors are complex and have many unusual properties that we have been trying to understand. The major issues that challenge to the spectroscopists include: the normal transport properties, the superconducting mechanism and the energy gap, the roles of electron-phonon interaction and low-lying excitation. These issues will be addressed in the following chapters.
Fig. 1. Phase diagram for La$_{2-x}$Sr$_x$CuO$_4$ and crystal structure of the parent compound—La$_2$CuO$_4$ (Ref. 65). (Note that it has been reported recently that $T_c$ became zero near $x = 0.22$. See Ref. 66.)
Fig. 2. Crystal structure for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and phase diagram (Ref. 65) of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. AF: antiferromagnet, SC: superconducting.
CHAPTER III
THEORY

Optical Theory

The frequency dependent optical conductivity \( \sigma_1(\omega) \) and dielectric function \( \epsilon_1(\omega) \) are most directly connected to the absorptive and dispersive nature of a material. In the zero frequency limit, \( \sigma_1(0) \) becomes the ordinary dc conductivity, and \( \epsilon_1(0) \) is the static dielectric constant. However, neither \( \sigma_1(\omega) \) nor \( \epsilon_1(\omega) \) can usually be measured directly. Therefore, the optical properties are usually determined experimentally by measuring the reflectance or transmittance as a function of the energy of the incident light radiation, from which \( \sigma_1(\omega) \) and \( \epsilon_1(\omega) \) can be derived. The interaction between matter and the applied electromagnetic field is described by Maxwell’s equations and the boundary conditions.

Optical Response of the Medium

In the infrared through ultra-violet region, the wavelength of the light radiation is much larger than the dimensions of the unit cell. The propagation of electromagnetic wave in a medium can be described by a set of four differential equations (known as the macroscopic Maxwell’s equations):\(^{67}\)

\[
\begin{align*}
\nabla \cdot \mathbf{D} &= 4\pi \rho_f, \\
\nabla \cdot \mathbf{B} &= 0, \\
\n\nabla \times \mathbf{E} &= -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \\
\n\nabla \times \mathbf{H} &= \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c} \mathbf{J}_f,
\end{align*}
\]  \(1\)

where \( \mathbf{E} \) and \( \mathbf{H} \) are the electric and magnetic fields, \( \mathbf{D} \) and \( \mathbf{B} \) the displacement field and magnetic induction, \( \rho_f \) and \( \mathbf{J}_f \) the free-charge and free-current densities,
respectively. Gaussian units are used throughout this dissertation unless otherwise specified.

For weak electromagnetic field and in local limit, the response of the medium is linear and can be written by the constitutive relations:

\[
D = \epsilon_1 E, \quad B = \mu H, \quad J_f = \sigma_1 E,
\]

where \(\epsilon_1, \mu, \sigma_1\) are the frequency-dependent dielectric function, permeability, and conductivity, respectively, of the medium. For simplicity, we take \(\mu = 1\), the case for most non-magnetic materials. Thus, \(B\) can be replaced by \(H\). If the medium is isotropic and homogeneous, then \(\epsilon_1\) and \(\sigma_1\) are scalar quantities rather than tensors and have no space variation. Assume the fields have the plane-wave form:

\[
\left\{ \begin{array}{c} E \\ H \end{array} \right\} = \left\{ \begin{array}{c} E_0 \\ H_0 \end{array} \right\} \exp[i(q \cdot x - \omega t)],
\]

where the vectors \(E_0, H_0\) and \(q\) (wave vector) are in general complex and independent of space \(x\) and time \(t\), then \(\frac{\partial}{\partial t}\) can be replaced by \(-i\omega\), and \(\nabla\) by \(iq\), causing the curl equations in (1) become

\[
iq \times E = \frac{i}{c} \omega H, \quad (4)
\]

\[
iq \times H = \frac{4\pi}{c} (J_d + J_f + J_p) = -\frac{i}{c} \omega E + \frac{4\pi}{c} \left[ \sigma_1 + i\frac{\omega}{4\pi} (1 - \epsilon_1) \right] E, \quad (5)
\]

where the first term in Eq. (5) is the displacement current, the second is free (conduction) current, and the third is polarization (bound) current. One can introduce a complex conductivity \(\sigma = \sigma_1 + i\sigma_2\) with \(\sigma_2 = \omega(1 - \epsilon_1)/4\pi\), or a complex dielectric function \(\epsilon = \epsilon_1 + i\epsilon_2\) with \(\epsilon_2 = 4\pi\sigma_1/\omega\) such that

\[
iq \times H = -\frac{i}{c} \omega E + \frac{4\pi}{c} \sigma E = -\frac{i}{c} \omega \epsilon E. \quad (6)
\]
Finally, Eqs. (4) and (6) are simplified as

\[
\begin{align*}
q \times E &= \frac{\omega}{c} H, \\
q \times H &= -\frac{\omega}{c} eE.
\end{align*}
\]  

Equation (7) implies that these three vectors are mutually perpendicular with one other \((q \perp E, H)\) if \(\epsilon\) is a scalar, the case for isotropic materials. Such a wave is the well known transverse wave. The solution of Eq. (7) is \(q^2 = \left(\frac{\omega}{c}\right)^2 \epsilon\). One can also define a complex refractive index \(N\), yielding the very useful dispersion relationship:

\[
q = \frac{\omega}{c} N = \frac{\omega}{c} (n + i \kappa).
\]  

Consider the case of normal incidence and \(q \parallel x\), then Eq. (3) has the form:

\[
\begin{bmatrix} E \\ H \end{bmatrix} = \begin{bmatrix} E_0 \\ H_0 \end{bmatrix} e^{i\left(\frac{\omega}{c} N x - \omega t\right)} = \begin{bmatrix} E_0 \\ H_0 \end{bmatrix} e^{-\omega \kappa x} e^{i\left(\frac{\omega}{c} n x - \omega t\right)}.
\]  

This solution is an attenuated wave with a skin depth \(\delta = c/\omega \kappa\) or a power absorption coefficient \(\alpha = 2/\delta = 2\omega \kappa /c\); the phase velocity is \(v_p = c/n\).

In summary, the optical response of a material can be described by various quantities (called optical "constants") which are not independent and are interrelated by

\[
N^2 = \frac{1}{Z^2} = \epsilon = 1 + \frac{4\pi}{\omega} \sigma,
\]

where the complex surface impedance \(Z = R + iY\), with \(R\) and \(Y\) being the impedance and reactance, has been introduced. Note all the optical "constants" introduced are (in general) frequency dependent.
We are particularly interested in the real part of the optical conductivity, \( \sigma_1 \), because it is directly proportional to the power dissipation of the electromagnetic field per unit volume by the medium:

\[
\frac{dP_{\text{dissip}}}{dV} = \frac{1}{2} \text{Re}(J \cdot E^*) = \frac{1}{2} \text{Re}[(\sigma E) \cdot E^*] = \frac{1}{2} \sigma_1 |E|^2.
\]  

(11)

Here \( J = J_f + J_p = \sigma E \), defined by Eq. (5), is the total charge current induced by the electric field \( E \). This indicates that only the in-phase conduction current \( J_f = \sigma_1 E \) dissipates power, while the displacement current \( J_d = -i\varepsilon_0 \dot{E} \) and the polarization current \( J_p = i\sigma_2 E \) do not because they are 90° out of phase with \( E \) thus the time average of energy flow is zero.

**Determination of Optical Constants**

One useful experimental technique to determine the frequency dependence of the optical constants is to measure the fraction of power intensity reflected by, \( \mathcal{R}(\omega) \), or transmitted through, \( \mathcal{I}(\omega) \), by a sample. The incident photons of energy \( \hbar \omega \) interact with the electrons, ions, spinons ..., causing electronic transitions from occupied states below the Fermi energy \( (E_F) \) to unoccupied states above \( E_F \); or interact with lattice vibrations (phonons), causing polariton excitations. Transmittance measurements require good quality films with thicknesses \( (d) \) being shorter than the electromagnetic penetration depths \( (\delta) \), which are not usually feasible. Thus, reflectance measurements are more frequently adopted in optical experiments. Here we will describe the background of the theory and the techniques of extracting the optical constants from \( \mathcal{R}(\omega) \) in a wide frequency range or from a combination of \( \mathcal{R}(\omega) \) and \( \mathcal{I}(\omega) \). The details of the optical measurements and the experimental approaches for the optical constants will be given in chapter VI.
Reflectance of thick crystals

The expression for the reflectance will be rather simple for normal incidence on bulk samples with surface dimensions much greater than the skin depth \((d \gg \delta)\). In this case, both \(E\) and \(H\) are parallel to the sample surface. In the absence of the idealized surface current, the boundary conditions require that the tangential components of \(E\) and \(H\) are continuous at the interface:

\[
\begin{align*}
E_i + E_r &= E_t, \\
H_i - H_r &= H_t, \\
& \text{(12)}
\end{align*}
\]

where the subscripts \(i\), \(r\), and \(t\) denote the incident, reflected, and transmitted fields, respectively, at the interface. Note that, in Eq. (12), \(E_r\) and \(E_i\) are assumed in the same direction. Thus \(H_r\) is opposite to \(H_i\) to maintain the relation \(q \parallel E \times H\) as required by Eq. (7) for a plane wave.

The scalar relation between \(E\) and \(H\) can be simplified as \(H = NE\) according to Eqs. (7) and (8). Thus, when a plane wave is propagating across the interface between medium \(a\) and medium \(b\), it satisfies

\[
\begin{align*}
H_i &= N_a E_i, \\
H_r &= N_a E_r, \\
H_t &= N_b E_t, \\
& \text{(13)}
\end{align*}
\]

where \(N_a\) and \(N_b\) are, respectively, the complex refractive indices in medium \(a\) and medium \(b\). From Eqs. (12) and (13), it is straightforward to find the complex amplitude coefficients of the reflected \((r)\) and transmitted \((t)\) electric field:

\[
\begin{align*}
& \begin{cases} 
  r = \frac{E_r}{E_i} = \frac{N_a - N_b}{N_a + N_b}, \\
  t = \frac{E_t}{E_i} = 1 + r = \frac{2N_a}{N_a + N_b}.
\end{cases} \\
& \text{(14)}
\end{align*}
\]
The light is usually incident from vacuum onto a sample surface so that we take $N_a = 1$, and $N_b = N = n + i\kappa$. The power (intensity) reflectance is then given by

$$\mathcal{R} = \mathcal{R} = \frac{(1 - n)^2 + \kappa^2}{(1 + n)^2 + \kappa^2}. \quad (15)$$

The measured reflectance $\mathcal{R}$ and $\phi$, the phase change of the reflected electric field wave, are related to $n$ and $\kappa$ by

$$\sqrt{\mathcal{R}} e^{i\phi} = r = \frac{(1 - n) - i\kappa}{(1 + n) + i\kappa}, \quad (16)$$

and

$$\tan \phi = -\frac{2\kappa}{1 - n^2 - \kappa^2}. \quad (17)$$

Note again that all quantities in the above equation are frequency dependent.

**Kramers-Kronig relations**

If $\mathcal{R}(\omega)$ is measured over a wide frequency range, the phase dispersion $\phi(\omega)$ can be evaluated using the Kramers-Kronig relations

$$\phi(\omega) = \frac{\omega}{\pi} \int_0^\infty \frac{\ln \mathcal{R}(\omega') - \ln \mathcal{R}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

$$= \frac{1}{2\pi} \ln \frac{\omega' - \omega}{\omega' + \omega} \frac{d\ln \mathcal{R}(\omega')}{d\omega'} d\omega'. \quad (18)$$

The second expression, obtained from the first by integrating by parts, indicates that the far-away spectral regions ($\omega' \ll \omega$ and $\omega' \gg \omega$) and the regions in which $\mathcal{R}(\omega')$ is flat ($d\mathcal{R}/d\omega' \approx 0$) have very small contributions to the integral. After $\mathcal{R}(\omega)$ and $\phi(\omega)$ are determined, one can invert Eq. (16) to obtain

$$n(\omega) = \frac{1 - \mathcal{R}(\omega)}{1 + \mathcal{R}(\omega) - 2\sqrt{\mathcal{R}(\omega)} \cos \phi(\omega)}, \quad (19)$$
Finally, other optical constants, such as $\epsilon(\omega)$, $\sigma(\omega)$, skin depth $\delta$, absorption coefficient $\alpha$, and electronic loss function $-\text{Im}(1/\epsilon)$, can be obtained from Eq. (10), i.e.,

$$\begin{align*}
\epsilon_1 &= n^2 - \kappa^2, \\
\epsilon_2 &= 2n\kappa, \\
\sigma_1 &= \omega\epsilon_2/4\pi, \\
\sigma_2 &= \omega(1 - \epsilon_1)/4\pi, \\
\delta &= c/\omega\kappa, \\
\alpha &= 2\omega\kappa/c.
\end{align*}$$

Other commonly used Kramers-Kronig equations are

$$\begin{align*}
\epsilon_1(\omega) - 1 &= \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega'\epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \\
\epsilon_2(\omega) &= -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega',
\end{align*}$$

where $\mathcal{P}$ stands for principle part of the integral. These equations relate a dispersive process to an absorptive process due to the requirement of causality for linear response functions. In other words, the real and imaginary parts of a linear response function (such as $\ln r = \frac{1}{2} \ln \mathcal{R} + i\phi$, $N = n + i\kappa$, $\epsilon = \epsilon_1 + i\epsilon_2$, $\sigma = \sigma_1 + i\sigma_2$, etc.) are not independent with each other. Rather, they are rigorously related by the Kramers-Kronig dispersion relations.

Equation (18) shows that $\phi$ at a single frequency must be determined from $\mathcal{R}$ at all frequencies (and vise versa). In practice, $\mathcal{R}(\omega)$ can be measured only in a limited discrete frequency range $\omega_1 \leq \omega \leq \omega_2$. Therefore, reasonable extrapolations beyond the region of the experimental data must be made. This procedure will be discussed later in detail (see p. 69) for our La$_{2-x}$Sr$_x$CuO$_4$ thin film data.
A drawback of the Kramers-Kronig technique is obviously the requirement of a large frequency range measurements, which are not always possible. Errors will be introduced by the artificial extrapolations. Furthermore, if the sample is thin, the single bounce assumption will be no longer valid, hence, the determination of the optical constants become difficult. The situation is even more complicated for a thin sample (film) deposited on a substrate. In such case, it is possible to extract $\sigma_1$ and $\sigma_2$ (without the Kramers-Kronig analysis) from combined reflectance and transmittance measurements over any finite frequency range. This technique will be presented below.

Combination of reflectance and transmittance of thin films

For a film of thickness $d \ll \lambda$, the wavelength of the far-infrared radiation, and $d \ll \lambda_L, \delta$, the penetration depth, the film may be treated as a sheet of conductor of complex admittance $y_1 + iy_2$. In this case, the transmission through, $T_f$, and reflection from, $R_f$, a film on a supporting substrate with index $n$ can be approximated as

$$T_f = \frac{4n}{(y_1 + n + 1)^2 + y_2^2},$$  \hspace{1cm} (24)

and

$$R_f = \frac{(y_1 + n - 1)^2 + y_2^2}{(y_1 + n + 1)^2 + y_2^2}. \hspace{1cm} (25)$$

These single-layer equations are generalizations of expressions given by Glover and Tinkham. The dimensionless complex admittance of the thin film is related to the conductivity $\sigma$ by

$$y = Z_0 \sigma d \quad \text{or} \quad y_1 + iy_2 = Z_0 (\sigma_1 + i\sigma_2) d. \hspace{1cm} (26)$$

Here, $d$ is the film thickness and $Z_0 = 377 \ \Omega = 4\pi/c$ (esu) is the impedance of free space.
The exact expressions for the composite Fresnel coefficients of transmission and reflection in normal incidence can be derived easily. A thin film on a substrate can be considered as sandwiched by two media, the air and substrate. Consider a three medium system with complex refractive indices of \( N_1, N_2 \) and \( N_3 \), respectively, where \( N_j = n_j + i\kappa_j \) \((j = 1, 2, 3)\), the transmission coefficient (from medium 1 through medium 2 and into medium 3) is

\[
t_f = t_{12}t_{23}e^{i\delta} \left[ 1 + r_{23}r_{21}e^{i2\delta} + (r_{23}r_{21}e^{i2\delta})^2 + \cdots \right]
\]

\[
= \frac{t_{12}t_{23}e^{i\delta}}{1 - r_{23}r_{21}e^{i2\delta}},
\]

where \( r_{ij} = (N_i - N_j)/(N_i + N_j) \) and \( t_{ij} = 2N_i/(N_i + N_j) \) as already derived in Eq. (14). The complex phase depth \( \delta \) of medium 2 with thickness \( d \) is defined by

\[
\delta = \frac{2\pi N_2 d}{\lambda} = N_2 \frac{\omega}{c} d.
\]

Similarly, the reflection coefficient is

\[
r_f = r_{12} + t_{12}r_{23}t_{21}e^{i2\delta} \left[ 1 + r_{21}r_{23}e^{i2\delta} + (r_{21}r_{23}e^{i2\delta})^2 + \cdots \right]
\]

\[
= \frac{r_{12} + t_{12}r_{23}t_{21}e^{i2\delta}}{1 - r_{21}r_{23}e^{i2\delta}}
\]

\[
= \frac{r_{12} + r_{23}e^{i2\delta}}{1 - r_{21}r_{23}e^{i2\delta}}.
\]

Note the identity \( t_{12}t_{21} - r_{12}r_{21} \equiv 1 \) has been used in deriving the last expression in Eq. (29). The power transmittance and reflectance are finally obtained:

\[
\mathcal{I}_f = \frac{n_3}{n_1} |t_f|^2 \quad \text{and} \quad \mathcal{R}_f = |r_f|^2.
\]

The subscript \( f \) has been chosen for Eqs. (27)–(30) to consist with the notations of Eqs. (24) and (25). The denominators in Eqs. (27) and (29) account for the multiple
internal reflections. One can recover the approximations of Eqs. (24) and (25) easily from the rigorous expressions of Eqs. (27)–(30). This can be done as follows: first, take medium 1 as vacuum \( (N_1 = 1) \), medium 2 as a metal film with thickness \( d \) and refractive index \( N_2 \), and medium 3 as a weakly absorbing semi-infinite slab with index \( N_3 \); then, substitute the following approximations into Eqs. (27)–(30),

\[
\begin{align*}
\left| N_2 \right| & \gg N_1 = 1, \\
\left| N_2 \right| & \gg \left| N_3 \right| \approx n_3 \equiv n, \quad (\kappa_3 \ll n_3), \\
e^{i2\delta} & \approx 1 + i2\delta, \\
-iN_2\delta & \approx \frac{4\pi}{c} \sigma d = \gamma.
\end{align*}
\]

Here we have applied the long wavelength (or low frequency) limit and assumed that film is thin enough such that \( \delta \ll 1 \). The calculation is straightforward and is left as an exercise to the interested readers.

In reality, the substrate has a finite thickness and it is a four medium problem with medium 4 being air. For a nearly opaque metal film, the overall reflectance of film plus substrate in this 4-medium system is

\[ R \approx R_f. \] (32)

Equation (24) gives the transmittance across the film into the substrate. This quantity is related to the measured transmittance \( T \) (across the film and substrate into the air) by

\[ T = \frac{(1 - R_s)e^{-\alpha x}}{1 - R_s R_f e^{-2\alpha x} T_f}, \] (33)

where \( x \) is the thickness and \( \alpha \) the absorption coefficient of the substrate (for example, MgO). The other terms in Eq. (33) are the substrate-incident internal reflection of the film,

\[ R'_f = \frac{(y_1 - n + 1)^2 + y_2^2}{(y_1 + n + 1)^2 + y_2^2}, \] (34)
and the single bounce reflection of the substrate,

$$R_s = \frac{(1 - n)^2 + \kappa^2}{(1 + n)^2 + \kappa^2} \approx \left(\frac{1 - n}{1 + n}\right)^2. \quad (35)$$

The approximation in Eq. (35) holds when $\kappa \equiv c \alpha / 2 \omega \ll n$, the case of weakly absorbing medium. Equation (33) assumes a thick or wedged substrate, so that there is no coherence among multiple internal reflections within the substrate.

The index $n$ and the absorption coefficient $\alpha$ of a substrate can be obtained by measuring the overall transmittance $T_{\text{sub}}(\omega)$ and reflectance $R_{\text{sub}}(\omega)$ of the substrate. In general, for normal incidence, the formulas for $T_{\text{sub}}(\omega)$ and $R_{\text{sub}}(\omega)$ of an absorbing substrate of parallel faces with thickness $x$ are given by

$$T_{\text{sub}}(\omega) = \frac{\left[(1 - R_s)^2 + 4 R_s \sin^2 \phi e^{-\alpha x}\right]}{(1 - R_s e^{-\alpha x})^2 + 4 R_s e^{-\alpha x} \sin^2(\phi + \beta)}, \quad (36)$$

$$R_{\text{sub}}(\omega) = \frac{(1 - e^{-\alpha x})^2 + 4 e^{-\alpha x} \sin^2 \beta}{(1 - R_s e^{-\alpha x})^2 + 4 R_s e^{-\alpha x} \sin^2(\phi + \beta)} R_s. \quad (37)$$

Here $R_s$ and $\phi$ are defined by Eq. (35) and Eq. (17), respectively, and $\beta = n \frac{\omega}{c} x$. The expression of these two equations incorporates interference effects due to the substrate. [Equations (36) and (37) can also be derived from the expressions of Eqs. (27)–(30), taking medium 2 as the substrate and medium 3 the air.] In a low resolution measurement (for example, see p. 166), the periodic interference fringes are averaged out. The averages can be found by integrating Eqs. (36) and (37) over $d\beta$, to be

$$T_{\text{sub}}(\omega) = \frac{(1 - R_s)^2 e^{-\alpha x}}{1 - R_s^2 e^{-2\alpha x}}, \quad (38)$$

$$R_{\text{sub}}(\omega) = \frac{1 + (1 - 2 R_s) e^{-2\alpha x}}{1 - R_s^2 e^{-2\alpha x}} R_s. \quad (39)$$

Therefore, $n$ and $\alpha$ can be solved by inverting Eqs. (38) and (39).
After measuring $\mathcal{I}$ and $\mathcal{R}$ at each frequency, we can determine $y_1$ and $y_2$, hence $\sigma_1$ and $\sigma_2$ by inverting Eqs. (24), (25) and Eqs. (32)–(34). In this procedure, we can iterate for a self-consistent $\mathcal{R}_f$, using the values of $\alpha$ and $n$ measured for the substrate. This technique has been applied in data analysis of our YBa$_2$Cu$_3$O$_{7-\delta}$ films. The computer programming routines used for this computation are presented in Appendix B.

Lorentz and Drude Models

Two classical models (Lorentz and Drude) are frequently used to describe the optical properties of materials. The Lorentz model can be employed for either bound-carrier interband transitions or lattice vibrations whereas the Drude model is applicable to free-carrier intraband transitions. Thus we can model the dielectric function by a sum of three terms:

$$\epsilon = \epsilon_{Drude} + \epsilon_{Lorentz} + \epsilon_{\infty}. \quad (40)$$

Here $\epsilon_{\infty}$ is the contribution from the high frequency absorption beyond the measured range.

The Lorentz dielectric function $\epsilon_L$ can be derived by assuming that the electrons are bound to their cores by harmonic forces and are subject to viscous damping forces which represent the energy loss mechanism. $\epsilon_L$ is then given by

$$\epsilon_L = \sum_j \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\gamma_j\omega}, \quad (41)$$

where $\omega_j$, $\gamma_j$, and $\omega_{pj}$ are the resonant frequency, plasma frequency and damping constant, respectively, of the $j^{th}$ Lorentzian. The plasma frequency—defined by $\omega_{pj}^2 = 4\pi N_j e^2/m_j^*$ with $N_j$ and $m_j^*$ being the number density and effective mass of the bound carriers—may also be written as $\omega_p = \sqrt{S_j}\omega_j$ such that $S_j$ represents the contribution of the $j^{th}$ oscillator to the static dielectric constant.
From the quantum mechanical point of view, $\hbar \omega_j$ is the transition or gap energy between the initial and excited atomic states, $\gamma_j$ the inverse lifetime of the excited carriers or the energy width due to energy uncertainties in the initial and final excited states. The oscillator strength $\omega_{pj}$ is related to the transition probability.

The Drude model describes the optical response of free carriers in good metals. It is just a particular case of the Lorentz oscillator with the resonance frequency equal to zero (no restoring force for "free" carriers):

$$\epsilon_D = -\frac{\omega_{PD}^2}{\omega(\omega + i/\tau)}, \quad (42)$$

where the Drude plasma frequency is defined by $\omega_{PD}^2 = 4\pi Ne^2/m^*$ with $N$ being the charge concentration (do not be confused with the index of refraction) and $m^*$ the effective mass of the free carriers. The viscous damping mechanism—described by a relaxation time $\tau$—is associated with collisions between electrons (or holes) and impurities or lattice vibrational phonons in metals. The real part of the Drude conductivity is

$$\sigma_{1D} = \frac{1}{4\pi} \frac{\omega_{PD}^2 \tau}{1 + \omega^2 \tau^2} = \frac{\sigma_0}{1 + \omega^2 \tau^2}, \quad (43)$$

with the zero frequency limiting value

$$\sigma_0 = \frac{\omega_{PD}^2 \tau}{4\pi} = \frac{Ne^2 \tau}{m^*} \quad (44)$$

being the ordinary dc conductivity.

Since the reflectance can be calculated using Eqs. (15) and (21), therefore, as an alternative to the KK analysis, we can in return fit the experimental reflectance data with a combined Drude-Lorentz model of Eq. (40) to extract the optical parameters. This procedure turns out to be very successful as will be discussed in our data analysis later.
Sum Rule

One of the most important sum rules is called the $f$-sum rule. It states that the area under the conductivity $\sigma_1(\omega)$ is conserved:

$$\int_0^\infty \sigma_1 d\omega = \frac{\omega_p^2}{8} = \frac{\pi Ne^2}{2m}.$$  \hspace{1cm} (45)

Here $m$ and $e$ are the bare mass and electric charge of a free electron. This sum rule means that the area, or oscillator strength, is independent of factors such as the sample temperature, the scattering rate, phase transition, etc. The sum rule has an important impact on a superconductor, in which an energy gap develops below the transition temperature $T_c$; the spectral weight at $\omega < 2\Delta$ shifts into the origin, causing an infinite dc conductivity.

Superconductivity

Perfect Conductor

A perfect conductor has no scattering, namely $1/\tau = 0$. This is the case for ideal metals with perfect translationally invariant periodic lattice described by Bloch’s theorem. The complex conductivity in this case can be obtained by

$$\sigma(\omega) = \lim_{\tau \to \infty} \frac{i\omega_p^2}{4\pi(\omega + i/\tau)} = \frac{\omega_p^2}{4} \left[ \delta(\omega) + i \frac{1}{\pi \omega} \right],$$  \hspace{1cm} (46)

or

$$\sigma_1 = \frac{\omega_p^2}{4} \delta(\omega), \hspace{1cm} \sigma_2 = \frac{\omega_p^2}{4\pi \omega}.$$  \hspace{1cm} (47)

For simplicity, here $\omega_p$ is used instead of $\omega_pD$ to represent the Drude plasma frequency.

Note Eq. (47) satisfies the sum rule required by Eq. (45), considering $\delta(\omega)$ is an even function thus $\int_0^\infty \delta(\omega) d\omega = 1/2$. Equation (46), or (47), implies that a perfect conductor has an infinite dc conductivity but $\sigma_1 = 0$ for $\omega \neq 0$, and the inductive
response (represented by $\sigma_2$ which goes as $1/\omega$) is dominant at low frequencies. The dielectric function $\epsilon$ is

$$\epsilon_2 = \sigma_1 = 0, \quad \epsilon_1 = 1 - \frac{\omega_p^2}{\omega^2}, \quad (\omega \neq 0)$$

(48)

thus

$$N = n + i\kappa = \sqrt{\epsilon} = \begin{cases} 
    i(\omega_p^2/\omega^2 - 1)^{1/2}, & (0 < \omega < \omega_p) \\
    (1 - \omega_p^2/\omega^2)^{1/2}, & (\omega > \omega_p) 
\end{cases}$$

(49)

Therefore, because $R = [(n - 1)^2 + \kappa^2]/[(n + 1)^2 + \kappa^2]$, a bulk perfect conductor is also a perfect reflector ($R = 1$) for $\omega \leq \omega_p$.

**Superconductor**

The optical response of a superconductor is similar to that of a perfect conductor. One major distinction is that a BCS superconductor has an energy gap, $2\Delta$, in the excitation spectrum and the electrons are paired when the temperature is lowered below $T_c$. In the BCS weak-coupling theory, the energy gap for $T < T_c$ is given by $^{71}$

$$\frac{1}{VN(0)} = \int_0^{\hbar \omega_c} \frac{\tanh \frac{1}{2} \beta (\xi^2 + \Delta^2)^{1/2}}{(\xi^2 + \Delta^2)^{1/2}} \, d\xi,$$

(50)

where $N(0)$ is the density of states at the Fermi level, $V$ is the electron-phonon interaction potential, $\beta = 1/k_B T$, and $\omega_c$ is the typical phonon frequency or Debye frequency. The transition temperature is predicted as

$$k_B T_c = 1.13 \hbar \omega_c e^{-1/NV(0)}.$$  

(51)

In the vicinity of $T_c$, the theory gives

$$\Delta(T) \approx 1.74 \Delta(0) \left( 1 - \frac{T}{T_c} \right)^{1/2}.$$  

(52)

The limiting value at $T = 0$ is

$$2 \Delta(0) = 3.5 k_B T_c.$$  

(53)

[For a $T_c = 90$ K superconductor, for example, this would give $2\Delta(0) = 220$ cm$^{-1}$, a range in the far infrared.] Consequently, one expects $\sigma_1 = 0$ in the range
$0 < \hbar \omega < 2\Delta$. This means that photons of energy less than $2\Delta$ are not absorbed because their energies are not sufficient to break Cooper pairs. The incident light is therefore 100% reflected because the impedance mismatch at the interface ($n = 0$ in the superconducting sample, and $n = 1$ in vacuum). This property agrees with the Meissner effect that the electromagnetic field is zero in the interior of a bulk superconductor.

However, part of the field still does penetrate into the superconductor and is exponentially damped within a length scale called the London penetration depth:

$$
\lambda_L = \sqrt{\frac{m^* c^2}{4\pi N_s e^2}}
$$

(54)

with $N_s$ being the superfluid density. If all free carriers condense completely into pairs, then $\lambda_L = c/\omega_p$. The fraction of the transmitted electric field at the sample surface can be found from Eqs. (14) and (49),

$$
t = \frac{2}{1 + N} \approx -\frac{2\omega}{\omega_p},
$$

(55)

for $\omega < 2\Delta \ll \omega_p$. This indicates that the transmitted electric field $E_t$ has a $-\frac{\pi}{2}$ phase shift related to, and is much less than, the incident field $E_i$. Note the transmitted power is zero, namely $\mathcal{S} = n|t|^2 = 0$, because $n = 0$ ($\sigma_1 = 0, \epsilon_1 < 0$). The induced inductive current (associated with $\sigma_2$) in the superconductor is $90^\circ$ out of phase with $E_i$ and hence does not dissipate energy. The transmitted magnetic field given by

$$
H_t = NE_t \approx \frac{i\omega_p}{\omega} E_t = 2H_i
$$

(56)

is much larger than $E_t$ and is in phase with the incident $H_i$. This is a consequence of the continuity of $H$ at the interface and the $180^\circ$ reversal of $E_r$, the reflected wave.
At $\omega > 2\Delta$ (taking $\hbar = 1$), the photon energy is high enough to disassociate Cooper pairs, causing quasiparticle excitations across the superconducting gap to the unoccupied normal levels. The conductivity thus approaches the normal state value.

At finite temperature below $T_c$, the conductivity $\sigma_1$ at $\omega < 2\Delta$ is no longer zero, shown in Fig. 3, due to the existence of thermally excited quasiparticles. The temperature dependence of the low-frequency conductivity exhibits a peak below $T_c$ (illustrated in Fig. 4) which has been explained by the coherence effect. In BCS theory, the perturbation Hamiltonian can be written as

$$H_1 = \sum_{kk'} B_{k'k} C_{k'}^+ C_k.$$  \hspace{1cm} (57)

Here the subscript $k$ represents the quantum state for momentum and spin, $C_{k'}^+$ and $C_k$ are the quasiparticle creation and annihilation operators, and $B_{k'k}$ are matrix elements of the perturbation operator. In the normal state, each term in the sum is independent. At $T < T_c$, however, there exists phase coherence between the wave functions of the occupied states. This interference leads to $B_{k'k} = \pm B_{-k'-k}$, where the upper sign for "case I" and the lower sign for "case II" interactions.

The Hamiltonian for interaction of electromagnetic radiation with matter is represented by a term $p \cdot A$, where $p$ is the momentum of the electrons and $A$ is the vector potential of the external field. Since this term is odd with $p$ (or $k$), the interaction obeys the case II process. Tinkham\textsuperscript{71} has shown that this interference will result a coherence factor for scattering:

$$F(\Delta, E, E') = \frac{1}{2} \left( 1 + \frac{\Delta^2}{EE'} \right),$$  \hspace{1cm} (58)

where $E$ is the quasiparticle energy measured from the Fermi level and $E' = E + \hbar \omega$.

The superconducting to normal-state conductivity can be expressed as

$$\frac{\sigma_{1s}}{\sigma_n} = \frac{1}{\hbar \omega} \int_{-\infty}^{\infty} F(\Delta, E, E') N_s(E) N_s(E + \hbar \omega) \left[ f(E) - f(E + \hbar \omega) \right] dE$$

$$= \frac{1}{\hbar \omega} \int_{-\infty}^{\infty} \frac{|E(E + \hbar \omega) + \Delta^2|[f(E) - f(E + \hbar \omega)]}{(E^2 - \Delta^2)^{1/2}[(E + \hbar \omega)^2 - \Delta^2]^{1/2}} dE,$$  \hspace{1cm} (59)
where \( f(E) \) is the Fermi distribution function and \( N_s(E) \) is the superconducting density of states given by

\[
N_s(E) = N(0) \operatorname{Re} \frac{|E|}{(E^2 - \Delta^2)^{1/2}}.
\] (60)

Here \( \operatorname{Re} \) stands for real part. Equation (60) indicates that \( N_s = 0 \) for \( |E| < \Delta \). It diverges near \( \Delta \) and approaches the normal state value at \( |E| \gg \Delta \). Note the case II coherence factors have been used in Eq. (59).

The resulting conductivity calculated from Eq. (59) are shown in Figs. 3 and 4. The low-frequency upturn in Fig. 3 is due to the coherence factor, and the minimum moves to higher energy as \( T \) is lowered, indicating an opening superconducting gap. At \( T = 0 \), \( \sigma_{1s}(\omega) = 0 \) up to \( \omega = 2\Delta \); above this frequency, \( \sigma_{1s}(\omega) \) begins to rise due to the photo-excited quasiparticle absorption. The difference between \( \sigma_{1n}(\omega) \) and \( \sigma_{1s}(\omega) \) disappears at higher frequencies. The oscillator strength below \( 2\Delta \) (or the "missing" area) shifts into the origin to form the superconducting condensate. Figure 4 shows that, at small frequency \( \omega \), the integral in Eq. (59) gives a peak below \( T_c \) because of the divergence of the density of states \( N_s(E) \) at \( E \approx \Delta \). The peak gradually disappear with increasing frequency. Such peak due to the case II coherence factor has been observed in the nuclear relaxation rate\(^7\) and the optical conductivity\(^8\) for classical superconductors.
Fig. 3. The conductivity ratio of a superconductor vs. frequency at $T \leq T_c$ in the framework of Mattis-Bardeen theory.
Fig. 4. Conductivity ratio as a function of temperature at low frequencies, showing a coherence peak below $T_c$. 

Mattis–Bardeen theory

$2\Delta_0 = 200 \text{ cm}^{-1}$

$1/\tau = 100 \text{ cm}^{-1}$

$T_c = 90 \text{ K}$
CHAPTER IV
INFRARED TECHNIQUES

This chapter describes the principles of Fourier transform interferometry and spectrometers used in this work. The optical response is determined experimentally by measurements of reflectance or transmittance of the sample as a function of a wide range of incident photon energies. This range extends from about 20 cm\(^{-1}\) to 40,000 cm\(^{-1}\) (2.5 meV–5 eV) using variety of optical spectrometers, light sources and detectors.

The following conversion factors for energy units are useful:

\[
E : \quad 1 \text{ meV} = 11.6 \text{ K} = 8.066 \text{ cm}^{-1} = 0.242 \text{ THz}
\]

\[
f : \quad 1 \text{ THz} = 4.133 \text{ meV} = 33.33 \text{ cm}^{-1} = 48 \text{ K}
\]

\[
\omega : \quad 1 \text{ cm}^{-1} = 0.124 \text{ meV} = 1.44 \text{ K} = 30 \text{ GHz}
\]

\[
T : \quad 1 \text{ K} = 0.086 \text{ meV} = 0.695 \text{ cm}^{-1}.
\]

Interferometry

The spectrometers used to measure the optical spectra of the samples in the far-infrared (20–600 cm\(^{-1}\)) and mid-infrared (500–3000 cm\(^{-1}\)) region are a slow-scan Michelson interferometer and a fast-scan 113 V Bruker Fourier Transform Interferometer. (A Perkin Elmer 16 U Grating Monochromator, which will be discussed later, is used to collect data at higher frequencies of 1000–40,000 cm\(^{-1}\)).

Infrared Radiation at Low Frequencies

Interferometry is widely used for measurements in the far-infrared region primarily due to the fact of energy-starvation for all thermal sources at low frequencies. This fact can be seen from the Plank law for the spectral distribution of black-body
radiation. The power $p(\omega)$ emitted per unit area of the light source at temperature $T$ and in frequency range between $\omega$ and $\omega + d\omega$ is given by:

$$p(\omega)d\omega = \frac{\hbar}{4\pi^2c^2} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega. \quad (61)$$

The radiation spectra are peaked near $\hbar\omega = 2.82kT$ (or $\omega \approx 2T$ for $\omega$ in cm$^{-1}$ and $T$ in kelvin). Figure 5 plots the spectrum of Eq. (61) using logarithmic scales. The intensity is normalized to the peak value at 1000 K. It can be shown that the peak power $p_m(T) \sim T^3$ and is given by

$$p_m(T) = 1.42 \left( \frac{\hbar}{2\pi c} \right) \left( \frac{kT}{\hbar} \right)^3 \approx 1.26 \left( \frac{T}{1000 \text{ K}} \right)^3 \text{mW/cm}. \quad (62)$$

Note that the result in Eq. (62) is for per one unit wavenumber (1 cm$^{-1}$) interval. To stress and illustrate the strong temperature dependence, the same spectral distributions are also plotted in linear scale, shown in Fig. 6. The total radiation power $P_0$ emitted from a source of area $A$ can be obtained by integrating Eq. (61) over all frequencies

$$P_0 = A \int_0^\infty p(\omega) d\omega = \sigma T^4 A \quad (63)$$

with

$$\sigma = \frac{\pi^2 k^4}{60 c^2 \hbar^3} = 5.67 \times 10^{-12} \text{ W/cm}^2 \text{ K}^4 \quad (64)$$

being the Stefan-Boltzmann constant.

Consider a mercury arc lamp source with $A = 3$ cm$^2$ at $T = 5000$ K, the total emitted power is $P_0 = 1.1 \times 10^4$ W. To estimate the fraction of radiation power in
the far-infrared region, remembering $1 \text{ K} = 0.7 \text{ cm}^{-1}$, one can approximate Eq. (61) in the low frequency limit $x \equiv \hbar \omega / kT \ll 1$:

$$p(\omega) = \frac{kT}{4\pi^2 c^2} \omega^2.$$  \hfill (65)

This $\sim \omega^2$ dependence, as seen from the slopes of the curves plotted in Fig. 5, indicates that $p(\omega)$ decays rapidly with decreasing frequency, which can also be seen in Fig. 6. The emission power up to a frequency $\omega$ is therefore

$$P(\omega) = A \int_0^\omega p(\omega') d\omega' = \frac{kT}{12\pi^2 c^2} \omega^3 A.$$  \hfill (66)

Of the total radiation power $P_0$, only a fraction

$$\eta = P(\omega)/P_0 = \frac{5}{\pi^4} \left( \frac{\hbar \omega}{kT} \right)^3$$  \hfill (67)

is emitted below $\omega$. For $\omega = 100 \text{ cm}^{-1}$ and $T = 5000 \text{ K}$, this fraction is $\eta = 1.2 \times 10^{-6}$, i.e., only a tiny amount of power, 13 mW out of 11 KW (taking $A = 3 \text{ cm}^2$), is emitted at $\omega \leq 100 \text{ cm}^{-1}$. Therefore, a dispersion spectrometer such as grating monochromator, which measures a one resolution width at a time, is obviously inefficient in the far-infrared measurement.

The situation can be greatly improved if one uses an interferometer, in which entire radiation power at all frequencies is utilized. Consequently, the signal-to-noise ratio can be greatly enhanced which is called the Fellgett advantage.\textsuperscript{73} The details of interferometry have been described in literature,\textsuperscript{74–76} and here only a brief discussion will be given.
Fourier Transform Spectroscopy

The principle of interferometry is based on the idea of the Michelson interferometer as sketched in Fig. 7. Light radiation from an extended source $S$ is divided by a semi-reflecting beam splitter $B$ (mylar film or thin Ge layer) into two parts of approximately equal intensity. These two beams are reflected by a stationary mirror $M_1$ and a movable mirror $M_2$, and are then recombined to enter the detector $D$. As $M_2$ moves a distance of $x/2$ away from its neutral position, a path difference between the two beams, $x$, is introduced before they are combined, yielding a phase difference $\delta = 2\pi x/\lambda = 2\pi \nu x$. Here $\lambda$ and $\nu$ are wavelength and wave number, respectively, of the incident light. Assuming these two beams have an equal amplitude $a(\nu)$, then the complex amplitude of the combined beam reaching the detector is

$$A(\nu) = a(\nu)(1 + e^{i2\pi \nu x}).$$  \hspace{1cm} (68)

In the ideal case, $a(\nu) = \sqrt{S(\nu)}/2$, where $S(\nu)$ is the spectral intensity of the radiation source (as modulated by losses due to detector absorptivity, transmission of filters, lenses, beamsplitter, windows and samples, and reflection of the mirrors or samples, etc.). From Eq. (68), one can obtain the intensity at the detector as a function of path difference $x$ at frequency $\nu$

$$I(x, \nu) = AA^* = 2a^2(1 + \cos 2\pi \nu x) = \frac{1}{2} S(\nu)(1 + \cos 2\pi \nu x).$$  \hspace{1cm} (69)

For a polychromatic source emitting a continuous spectrum from $\nu = 0$ to $\nu = \infty$, Eq. (69) must be integrated to obtain the total intensity which gives

$$2I(x) = \int_0^{\infty} S(\nu) d\nu + \int_0^{\infty} S(\nu) \cos 2\pi \nu x \, d\nu.$$  \hspace{1cm} (70)

$I(x)$ is called the interferogram. The first term in Eq. (70) is constant and is the total intensity, $S_0$, emitted from the source. As $x \to \infty$, there is no correlation between the
two beams, the second term, which is just the Fourier transform of \( S(\nu) \), vanishes because of the rapid oscillation of the cosine function. At \( x = 0 \), the interference is constructive for all frequencies hence the detector receives a maximum signal \( I(0) \) called centerburst or "white light" (see the upper panel of Fig. 8). It is straightforward to see from Eq. (70) the relation between these two limits:

\[
I(0) = 2I(\infty) = S_0,
\]

where \( I(\infty) \) is the average or dc value of the interferogram. One can extend the lower limit in Eq. (70) by noting that \( S(\nu) \) an even function, i.e., \( S(-\nu) = S(\nu) \). By defining \( D(x) = 4[I(x) - I(\infty)] \), which is linearly related to the signal at the detector, one finds

\[
D(x) = \int_{-\infty}^{\infty} S(\nu)e^{-i2\pi\nu x} d\nu = FT[S(\nu)],
\]

\[
S(\nu) = \int_{-\infty}^{\infty} D(x)e^{i2\pi\nu x} dx = FT^{-1}[D(x)],
\]

or

\[
D(x) \xleftarrow{FT} S(\nu),
\]

where \( FT \) represents the Fourier transformation and \( FT^{-1} \) is the inverse \( FT \). Therefore, if one knows the interferogram, \( D(x) \), for a continuous path difference, the spectral intensity distribution of the radiation, \( S(\nu) \), can be determined by the Fourier transform of the interferogram. This computation has turned out to be accessible in practical applications with the development of the fast Fourier transformation (FFT) and the availability of modern computers.

In practice, however, it is impossible to measure a continuous interferogram over a infinite path difference. Instead, one samples a finite number of discrete points up
to some maximum path difference $x_m$ and replaces the Fourier integral by Fourier series. The finite maximum path difference approximation introduces side lobes near sharp spectral structures. This problem can be repaired by applying the apodization technique.\textsuperscript{76} Another problem, caused by the discrete sampling, is the so-called aliasing effect which must be reduced by using some cut-off filters to suppress the high frequency components. Figure 8 illustrates spectra of the real time interferogram $D(x)$ and its Fourier transformation—single beam spectrum—measured by the Bruker interferometer. As we can see, the interferogram is not symmetric about its central position, which is caused by the phase error and sampling.

**Optical Spectrometers**

**Bruker Interferometer**

Most of the measured reflectance and transmittance spectra in this work is obtained by using an IBM–Bruker fast-scan Fourier transform interferometer, the principle of which being similar to that of a Michelson interferometer. The frequency range covered is 20–5000 cm\(^{-1}\).

As illustrated in Fig. 9, the system is divided into four chambers—source, interferometer, sample and detector. A Hg arc lamp is used for far infrared (20–700 cm\(^{-1}\)) and a globar source for mid infrared (400–5000 cm\(^{-1}\)). The sample chamber consists of two identical channels which can be used for either reflectance or transmittance measurements. For reflectance measurement, an optical stage, shown in the top part of Fig. 9, is place into the sample chamber. The entire system is evacuated to avoid H\(_2\)O and CO\(_2\) absorption during measurements.

Light from the source is focused onto the beamsplitter and is then divided into two beam—one reflected, and one transmitted. Each beam is imaged onto the faces of a movable two-sided mirror. These two beams retrace their route back to the beamsplitter for recombination. The recombined beam is sent into the sample chamber.
and then into the detector. When the two-sided mirror moves at a constant speed, $v$, a path difference $x = 4vt$ is made, where $t$ is the time since the mirror is at the zero-path-difference position. Suppose the light is a monochromatic wave of wavenumber $\nu_o$ so that $S(\nu) = S_0 \delta(\nu - \nu_o) + S_0 \delta(\nu + \nu_o)$, [the second term is needed to make $S(\nu)$ an even function,] then Eq. (72) gives

$$D(t) = D_0 \cos 2\pi f_a t, \quad (75)$$

where $D_0 = 2S_0$ and $f_a = 4v\nu_o = (4v/c)f_o$. This indicates that the optical frequency of the radiation, $f_o$, is reduced by a factor of $4v/c$. In other words, the detector sees a signal with an audio frequency $f_a$ instead of the much higher optical frequency $f_o$. This signal is amplified by a wide-band audio preamplifier and then digitized by a 16-bit analog-to-digital converter. The digital data are transferred into the Aspect computer system and are Fourier transformed into a single-beam spectrum, as shown in Fig. 8, after some necessary corrections such as apodization and phase correction.\textsuperscript{77,78}

**Bolometric detectors.** The fact of weak infrared signals requires not only the use of interferometry techniques, as described earlier in this chapter, but also a detector of high sensitivity. One kind of detector with adequate sensitivity is the He-cooled bolometer. The detectors used in this work are a 4.2 K Si bolometer for FIR, and a 4.2 K Si:B photodetector for MIR. Pyroelectric deuterated triglycine sulfate (DTGS) detectors are also available. The cooled detectors have much better signal-to-noise (S/N) ratio as compared with the DTGS. The bolometer system consists of three main parts: detector, liquid helium (LHe) dewar, and preamplifier. Figure 10 illustrates a diagram of the bolometer detector mounting and the LHe dewar (HD-3). After the dewar is diffusion pumped to a pressure of $\sim 10^{-6}$ torr, it is pre-cooled with liquid nitrogen for about an hour. The pre-coolant is then removed and the liquid helium
is transferred in to the helium can to maintain the detector at 4.2 K. (A temperature as low as 1.2 K can be achieved by reducing the vapor pressure above the liquid helium.) A thermal radiation shield is placed between the helium can and the case to reduce the head load on the cold area. The Si detector is mounted on a cold surface under the helium can. The optical signal is guided by the pipe along the optical axis through a window (poly for FIR, KRS-5 for MIR) and optical filters before it finally arrives at the detector. The output electric signal from the detector is amplified and then sent to the A/D converter of the Bruker interferometer.

**Michelson Interferometer**

The far-infrared (10–600 cm\(^{-1}\)) data are also measured with a slow-scan Michelson interferometer. In comparison with the Bruker, it has an even better S/N ratio at low frequencies (particularly below 50 cm\(^{-1}\)) due to a larger and brighter mercury source. The disadvantage, however, is that it runs much slower.

As shown in Fig. 11, the light is interrupted periodically by a rotating chopper in order to allow lock-in detection. A beam splitter with various thicknesses of mylar films is used in combination with different optical filters to cover the corresponding frequency range. The detector used is a 4.2 K bolometer as illustrated in Fig. 10. Like the Bruker interferometer, the whole system is evacuated during measurements.

**Perkin-Elmer Monochromator**

Optical Spectra from mid infrared through visible and ultraviolet (UV) at frequencies of 1000–40,000 cm\(^{-1}\) (0.12–5eV) are measured using a model 16U Perkin-Elmer (PE) monochromator. During measurements, the tank is kept under vacuum to prevent from water absorption, particularly for the mid- and near-infrared regions. As shown in Fig. 12, three sources—globar, quartz-envelope tungsten lamp, and deuterium lamp—are used to cover this frequency range. A proper source can be selected by turning \(M_2\) from outside the vacuum tank. The light is chopped and
passes through one or two of a set of band-pass filters. These filters reject the unwanted higher order diffraction from the grating, which occurs at the same angle as the desired first-order component. This case can be seen from a simple diffraction equation: \( a \sin \theta = n \lambda = n/\nu \), where \( a \) is the grating constant. At an angle \( \theta \), the first-order component of wavelength \( \lambda \) satisfying \( \lambda = a \sin \theta \) is selected. Meanwhile, any higher order components with wavelengths \( \lambda_n = \lambda/n \), or \( \nu_n = n\nu \) \((n = 2, 3, \ldots)\), which could also pass through the slit are absorbed by the filter.

Light enters the grating monochromator through an entrance slit and leaves through an exit slit. The dispersed spectrum is scanned across the exit slit as the grating is rotated. The resolution of the monochromator is determined by the slit widths. Increasing the slit widths increases the intensity of the emerging radiation (higher S/N ratio) at cost of lower resolution. Mirror \( M_1 \) is a reference mirror which can be rotated or replaced by a sample for reflectance measurements. For transmission measurements, the sample is mounted in a "sample rotator," as indicated in Fig. 12. The positions of the sample on the rotator and of the detector are the two focal points of an ellipsoidal mirror. Three detectors are used to cover the different photon energy regions: a thermocouple for 0.11–0.9 eV, a lead sulfur (PbS) photoconductor for 0.5–2.5 eV, and a silicon photodiode for 2.2–5 eV. Table 1 lists the parameters used to cover each frequency range.

The electric signal from the detector is sent to a lock-in amplifier (Ithaco model 393). The output signal from the lock-in system is then averaged over a given time interval and converted into digital data by an integrating digital voltmeter (Fluke 8520A). The data are finally transmitted through the IEEE-48 Bus and a general purpose interface box to a PDP 11-23 computer and recorded on the hard disk for subsequent analysis.
Table 1. Pekin-Elmer Grating Monochromator Parameters

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Grating (^a) (line/mm)</th>
<th>Slit width (micron)</th>
<th>Source (^b)</th>
<th>Detector (^c)</th>
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<tbody>
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<td>101</td>
<td>2000</td>
<td>GB</td>
<td>TC</td>
</tr>
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<td>2400</td>
<td>700</td>
<td>D(_2)</td>
<td>576</td>
</tr>
</tbody>
</table>

\(^a\) Note the grating line number per cm should be the same order of the corresponding measured frequency range in cm\(^{-1}\).

\(^b\) GB: Globar; W: Tungsten lamp; D\(_2\): deuterium lamp.

\(^c\) TC: Thermocouple; PbS: Lead sulfite; 576: Silicon photocell.
In the grating monochromator, depicted in Fig. 13, the reflecting grating diffraction equation is satisfied:

\[ a(\sin \alpha + \sin \beta) = n\lambda, \quad (n = 0, 1, 2 \ldots) \]  

(76)

where \( a \) is the grating constant (cm/line), \( \alpha \) and \( \beta \) are angles of the incident and diffracted rays, respectively, and \( n \) is the order of diffraction. When Eq. (76) is satisfied, the interference is constructive. One can then rewrite Eq. (76) as

\[ n\lambda = 2a \cos \delta \sin \theta, \]  

(77)

where \( \delta = (\alpha - \beta)/2 \) and \( \theta = (\alpha + \beta)/2 \). In practice, \( \delta \) is fixed \((2\delta = 4^\circ)\) regardless of the grating position because the incident and diffracted light paths are predetermined by the physical geometry, whereas \( \theta \) changes as the grating (or its surface normal) is rotated. It can be seen from Eq. (77) or Fig. 13 that at \( \theta = 0 \), [i.e., \( \beta = -\alpha \)], the incident and diffracted rays are on both sides of and symmetric to the normal of the grating surface \( N(0) \) it will give a zero-order diffraction (white light) for all frequencies. Therefore, \( \theta \) is the rotation angle of the grating surface normal, \( N(\theta) \), with respect to the zero-order position, \( N(0) \), as illustrated in Fig. 13.

The first order is the desired one and the higher orders \((n \geq 2)\) are removed by the proper optical filters as described earlier. Taking \( n = 1 \), one gets

\[ \nu = 1/\lambda = C \csc \theta \]  

(78)

with \( C = 1/2a \cos \delta \) being a constant. Equation (78) indicates that the frequency is linearly related to \( \csc \theta \). As the grating is rotated, a single component at frequency \( \nu \) satisfying Eq. (78) is selected and emerges through the exit slit into the sample.
chamber. The monochromator is mechanically designed such that the grating, driven by a stepping motor, is moved linearly with $\csc \theta$, thus the scanning is linear in wavenumber. The rotation angle has been designed in the range $15^\circ \leq \theta \leq 60^\circ$, the optimum quasi-linear range in the cosecant function. To find the resolution of the monochromator, one simply needs to take the derivatives of Eq. (78) in its logarithm form:

$$\ln \nu = \ln C - \ln \sin \theta, \quad (79)$$

$$\frac{d\nu}{\nu} = -\cot \theta \, d\theta, \quad (80)$$

where $d\theta$ is the angle subtended by the slit (with a width $s$) at the collimator with a focal length $f = 26.7$ cm, i.e., $d\theta = s/f$. Equation (80) implies that a larger $\theta$ will give a better resolution. Consider the worst case at the maximum slit opening, $s = 2000 \mu\text{m}$, Eq. (80) gives $0.4\% < |d\nu/\nu| < 2.8\%$, which is adequate since most of the solid materials are lack of sharp features at frequencies above the mid-infrared band. A more detailed description of the grating monochromator can be found elsewhere.\textsuperscript{79}
Fig. 5. Blackbody radiation spectra using log-log scales at three temperatures.

The power intensity is normalized to the maximum value at $T = 1000$ K [see Eq. (62) for maximum power]. The slopes are equal to 2 at low frequencies, indicating an $\sim \omega^2$ dependence.
Fig. 6. Normalized blackbody radiation spectra using a linear scale. Note that the relative scale is expanded by factors of 10 for $T = 300$ K and of 100 for $T = 100$ K.
Fig. 7. Schematic of Michelson interferometer.
Fig. 8. The interferogram $D(x)$ (upper panel), and its Fourier transformation $S(\nu)$ (lower panel) measured by a fast-scanning Bruker interferometer. (Note we have used $\omega$ instead of $\nu$ to label the frequency axis for all figures throughout this dissertation for consistency.)
Fig. 9. Schematic diagram of IBM-IR/98 BRUKER interferometer. The top part of the figure (enlarged scale) is an optical stage setup for measuring reflectance.
Fig. 10. Bolometer detector. The dimensions are in inches.
Fig. 11. Michelson interferometer.
Fig. 12. Schematic diagram of Perkin-Elmer monochromator spectrometer.
Zero order position

Rotatable grating

Fig. 13. Schematic of the grating monochromator showing the incident and diffracted rays and the operation of the grating. Note that the grating constant, $a$, is significantly exaggerated in order to illustrate the path difference given by Eq. (76).
CHAPTER V
SAMPLE PREPARATION AND CHARACTERISTICS

Various high-$T_c$ superconducting samples have been investigated in this work. This dissertation will concentrate on the La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$ oriented thin films as well as YBa$_2$Cu$_3$O$_{7-\delta}$ polycrystalline samples. Other samples such as YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$ ceramics, YBa$_2$Cu$_4$O$_8$ textured pellets, YBa$_2$Cu$_3$O$_{7-\delta}$ granular films and ultra-thin YBa$_2$Cu$_3$O$_{7-\delta}$ film (96 Å) were also measured but in less detail.

La$_{2-x}$Sr$_x$CuO$_4$ Epitaxial Films

Three La$_{2-x}$Sr$_x$CuO$_4$ thin films were prepared at Westinghouse Research Center in Pittsburgh using off-axis dc magnetron sputtering technique. Two of them are deposited on LaAlO$_3$ substrates with dimensions of 6 mm × 6 mm × 270 nm, and the third is grown on the (100) face of a SrTiO$_3$ substrate with dimensions of 10 mm × 10 mm × 820 nm. Both kinds of substrates have a perovskite structure which makes a good lattice match with the films. Figure 14 illustrates the diffractometer position 2\theta and x-ray counts measured at Westinghouse, showing that the films are highly ab-plane oriented. In addition to the c-axis texture, the films are epitaxial. In other words, the [100] and [010] directions which lie in the plane of the films are parallel to the [100] and [010] directions in the substrates. The properties of the samples are summarized in Table 2.

The CuO$_2$ plane dc resistivity of a La$_{2-x}$Sr$_x$CuO$_4$ film, shown in Fig. 15, exhibits a sharp superconducting transition near 30 K. Above approximately 100 K, the resistivity for all films is roughly of the form of $\rho(T) = \rho_0 + \alpha T$, linear in temperature ($\alpha = 1.2 \sim 1.5 \mu\Omega \text{ cm/K}$), with a nearly zero extrapolated intercept. Deviations from this behavior are evident in the plateau below ~ 100 K. The inset of Fig. 15 shows
Table 2. \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) Thin Films Characteristics.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Thickness (nm)</th>
<th>Area (mm(^2))</th>
<th>( x )</th>
<th>( T_c ) (K)</th>
<th>( \Delta T_c ) (K)</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>270</td>
<td>6.3 ( \times ) 6.3</td>
<td>0.15</td>
<td>27</td>
<td>1.5</td>
<td>\text{LaAlO}_3</td>
</tr>
<tr>
<td>3</td>
<td>820</td>
<td>10 ( \times ) 10</td>
<td>0.17</td>
<td>31</td>
<td>1.5</td>
<td>\text{SrTiO}_3</td>
</tr>
</tbody>
</table>

an expanded view near \( T_c \) for \( \rho(T) \) and the inductive transition measured by the change of inductance of a coil placed against the film. The composition of the films is \( x = 1.5-1.7 \), near the optimum values for superconducting \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) films. The resistivity is consistent with the published reports of good quality \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) films.\(^{28,29}\) Details of sample preparation and dc transport properties can be found elsewhere.\(^{80}\)

YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) Oriented Films

The far-infrared spectra (both reflectance and transmittance) of three YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) thin films have been measured. The samples were prepared by the research group at Bell Communication Research (Bellcore). The films were deposited on 1-mm-thick MgO substrates by pulsed-laser ablation from a stoichiometric target.\(^{81}\) Other commonly used substrates for high-\( T_c \) superconducting films are \text{LaAlO}_3, \text{SrTiO}_3 (as used in our \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) films), \text{LaGaO}_3, and yttria-stabilized zirconia (YSZ). These substrates are usually good for epitaxial growth and for reflectance measurements of thin films. However, they are not suitable for thin film transmission studies as all of them are opaque in much of the far-infrared region. In contrast, MgO is reasonably transparent up to 330 cm\(^{-1}\) at low temperatures and is
also a good substrate for oriented growth. These properties make it the best choice as a substrate for far-infrared transmission studies of high-$T_c$ films. Film thicknesses for two films (480 and 1560 Å) were measured by Rutherford backscattering (RBS) and step profilometry. These two techniques agreed to within 100 Å. Thickness for the third film (1800 Å) is estimated from growth conditions. Table 3 lists the parameters of the YBa$_2$Cu$_3$O$_{7-\delta}$ samples.

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Area (mm$^2$)</th>
<th>$T_c$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>$\sigma_{dc}$ (at 300 K) (Ω$^{-1}$ cm$^{-1}$)</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>5 x 5</td>
<td>89</td>
<td>2</td>
<td>~2000</td>
<td>MgO</td>
</tr>
<tr>
<td>1560</td>
<td>5 x 5</td>
<td>90</td>
<td>1</td>
<td>2500</td>
<td>MgO</td>
</tr>
<tr>
<td>480</td>
<td>5 x 5</td>
<td>83</td>
<td>3</td>
<td>1600</td>
<td>MgO</td>
</tr>
</tbody>
</table>

Figure 16 illustrates the temperature dependence of the dc resistivity, $\rho_{dc}$, for a YBa$_2$Cu$_3$O$_{7-\delta}$ film measured by four-probe technique. In comparison with La$_{2-x}$Sr$_x$CuO$_4$, the YBa$_2$Cu$_3$O$_{7-\delta}$ films have higher $T_c$'s (~90 K) and show a T-linear resistivity over most of the temperature region above $T_c$. One striking feature is that, however, the magnitudes of $\rho(T)$ are close for all high-$T_c$ films as represented by Fig. 15 and Fig. 16.

**YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$ Polycrystalline Samples**

The samples were first prepared at 3M center. The starting compounds were Y$_2$O$_3$, BaCO$_3$ and CuO. The powders were combined to make a homogenous mixture.
After a set of lengthy firings, grindings and jet-millings, the compound is pressed (with carbonwax) into pellets before the final firing and annealing in a slow steady oxygen flow. The strontium concentration of these YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$ samples was in the range $0 \leq x \leq 1.3$. Trarascon et al. have observed that the upper limit of Sr doping is at $x \simeq 1.4$, beyond which the materials are multiphase. The transition temperature of this compound decreases gradually from 93 K ($x = 0$) to 80 K ($x \simeq 1.4$). Typical parameters of our original samples are listed in Table 4. The table gives the Sr composition, the dc resistivity at room temperature, the mass density and unit cell volume. It appears that the sample density is significantly lower than the theoretical prediction, indicating porous behavior. The detailed information about the preparation procedures of these ceramic samples can be found in Ref. 82.

We noted that the initial measurements of these samples showed strong vibrational features in the far-infrared region and there were differences but no systematic variations with $x$ in the reflectance and conductivity spectra. This result was most likely due to oxygen deficiency or a mixed phase in the samples as indicated by a large number of vibrational phonons in the infrared spectra. The Cu-O plane phonons, if not well screened, would show up as a result of reduced carrier concentration. The O$_2$ deficiency was further confirmed by placing the samples in a 0.3 Tesla magnetic field, with the result that most of the samples did not show a magnetic levitation when they were cooled by liquid nitrogen, implying that they were not superconducting. We also found there were green grains on some sample surfaces. The presence of this "green phase" (2112) indicated that the samples were in mixed phase. It was clear that O$_2$ had to be added into these samples to recover their superconducting phase for further study.
Table 4. Typical parameters of YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$ polycrystalline samples

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\rho$ (300 K) (m$\Omega$ cm)</th>
<th>Density$^a$ (g/cm$^3$)</th>
<th>Density$^b$ (g/cm$^3$)</th>
<th>Volume$^c$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.0</td>
<td>5.741</td>
<td>6.347</td>
<td>173.55</td>
</tr>
<tr>
<td>0.13</td>
<td>18.9</td>
<td>4.992</td>
<td>6.332</td>
<td>172.97</td>
</tr>
<tr>
<td>0.26</td>
<td>10.8</td>
<td>6.013</td>
<td>6.292</td>
<td>172.38</td>
</tr>
<tr>
<td>0.39</td>
<td>1.7</td>
<td>4.819</td>
<td>6.252</td>
<td>171.79</td>
</tr>
<tr>
<td>0.52</td>
<td>2.5</td>
<td>4.921</td>
<td>6.211</td>
<td>171.20</td>
</tr>
<tr>
<td>0.65</td>
<td>3.4</td>
<td>4.216</td>
<td>6.169</td>
<td>170.62</td>
</tr>
<tr>
<td>0.78</td>
<td>5.1</td>
<td>3.498</td>
<td>6.127</td>
<td>170.04</td>
</tr>
<tr>
<td>0.91</td>
<td>15.8</td>
<td>5.420</td>
<td>6.084</td>
<td>169.46</td>
</tr>
<tr>
<td>1.04</td>
<td>21.0</td>
<td>5.460</td>
<td>6.048</td>
<td>168.90</td>
</tr>
<tr>
<td>1.17</td>
<td>2.5</td>
<td>4.191</td>
<td>5.995</td>
<td>168.30</td>
</tr>
</tbody>
</table>

$^a$ Measured mass density.
$^b$ Theoretical density calculated from the atomic mass and the volume in one unit cell.
$^c$ Unit cell volume (from Ref. 83).

Reannealing Procedures for YBa$_2$Cu$_3$O$_{7-\delta}$

As the Sr doping in YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$ hardly affected the transition temperature, we turned our attention to the fully oxygenated ceramics and their temperature dependence, which appeared more interesting. Therefore, we tried to reanneal two YBa$_2$Cu$_3$O$_{7-\delta}$ ($x = 0, \delta \geq 0.5$) samples in order to increase their oxygen content in two step procedures.
First, the green-black pellets were ground into powder using a freezer mill at liquid nitrogen (LN2). The powder was then placed in a platinum foil and an alumina crucible to fire at 920 °C for 12 hours in order to release any water content. (Care must be taken that the sample should not be overheated as the melting point is around 1000 °C). After having been cooled gradually to room temperature, the product was removed from the furnace.

Second, this dark and brittle bulk product was reground and pressed into pellets with a pressure of ~10^5 psi. These pellets, blackish with very smooth surfaces, were returned to the oven for a second refiring. Having been sintered at 920 °C for a 12 hour period, the pellets were annealed in a 1 atm O_2 steady flow to start the oxygen doping process with a gradual temperature decrease. The timetable of this firing is illustrated in Fig. 17.

Meissner Effect Test and Susceptibility.

After the reannealing procedures, we immediately tested the samples in the magnetic field. As the samples were cooled to 77 K (LN2) in the field, we found both pellets levitated. The levitation lasted for more than 25 sec after the LN2 was removed from the samples, indicating that they had returned to good quality superconductors. This test, known as the Meissner Effect, showed that the magnetic flux originally present was expelled from the interior of the bulk samples. The magnetic susceptibility measurements also showed that the samples had an onset of diamagnetism at \( T_c \approx 92 \) K as illustrated in Fig. 18, suggesting that the YBa_2Cu_3O_{7-\delta} pellets had been greatly improved and become almost fully oxygenated (\( \delta \lesssim 0.1 \)). It turned out later that they had a very stable transition temperature and showed very little degradation over time.

The improvement can also be seen in Fig. 19 which shows the reflectance \( \mathcal{R}(\omega) \) and conductivity \( \sigma_1(\omega) \) of one YBa_2Cu_3O_{7-\delta} sample at room temperature, before
and after the reannealing treatment. In contrast to the initial measurement (dashed curves), the post-reannealing spectra (solid curves) had higher overall levels in both $\Re(\omega)$ and $\sigma_1(\omega)$ and just displayed five pronounced peaks which had been clearly identified as $c$-axis phonons. Phonons confined in the CuO$_2$ planes are screened by the conduction carriers thus only those phonons oscillating along the $c$-axis are visible.
Fig. 14. X-ray diffraction pattern measured at Westinghouse for a La$_{2-x}$Sr$_x$CuO$_4$ film used in this work. The film was grown on a SrTiO$_3$ substrate, and the growth orientation can be seen in this figure.
Fig. 15. Resistivity in the $ab$-plane, as a function of temperature, for a La$_{2-x}$Sr$_x$CuO$_4$ thin film ($x \sim 0.17$) used in this study. The inset figure shows an expanded view of the region near $T_c$ for the same sample and compares the resistive transition to the inductive transition.
Fig. 16. Measured dc resistivity in the Cu-O plane for a 156-nm thick YBa$_2$Cu$_3$O$_{7-\delta}$ film. It demonstrates a sharp superconducting transition near 90 K. The inset illustrates an expanded view around $T_c$. 
Fig. 17. Reanneal schedule for YBa$_2$Cu$_3$O$_{7-\delta}$ samples used in this study.
Fig. 18. Measured ac magnetic susceptibility of a YBa$_2$Cu$_3$O$_{7-\delta}$ pellet after reannealing. The lower branch is the "zero-field-cooled" curve (ZFC), and the upper one is "field-cooled" (FC) which characterizes the true Meissner effect.
Fig. 19. Comparison of the IR spectra of a YBa$_2$Cu$_3$O$_{7-\delta}$ pellet before and after reannealing treatment. The before-reannealing sample shows rich phonons, an indication of mixed phase.
CHAPTER VI
EXPERIMENTS AND LOW TEMPERATURE TECHNIQUES

This chapter describes the experimental techniques used to perform the optical measurements on various samples over wide ranges of frequencies and temperatures. Measurements of other physical properties and the experimental apparatus are also discussed.

Low Temperature Apparatus

The cooling system consists of three major parts: Hansen High-Tran refrigerator (cryostat), transfer line and helium supply dewar. The sample temperature can be varied from 4 K to 300 K by a controlled operation of liquid helium transfer. Figure 20 illustrates the flow diagram of the experimental set-up. The sample holder is attached to the cryo-tip end of the refrigerator. An optical spectroscopy vacuum shroud is used to isolate the cold tip from the outside environment. Optical windows can be installed on the vacuum shroud to allow the reflection and transmission measurements. The sample temperature is sensed by a calibrated silicon diode thermometer (Si-410A) buried into the cold finger. The accuracy of the diode is ±1 K. The sample can be warmed by adding electrical heat to the tip heater and the temperature is controlled automatically and monitored by a temperature controller (Hansen & Associates 8000). A thermal radiation shield is attached to the second cold stage to protect the sample and to absorb the 300 K black body radiation from the vacuum shroud, hence the heat load near the cold tip can be reduced. All these steps are necessary in order to minimize the systematic error in temperature recording. Before the helium flow is started, the cryostat is evacuated to a pressure of $10^{-4}$ torr or less in the vacuum shroud. By pressurizing the He dewar, the liquid helium is transferred from the dewar.
through the transfer line to the cryostat. The flow rate can be regulated by two flow meters with hoses and shut off valves which control the tip flow and shield gas flow.

Reflectance Measurements and Uncertainties—$La_{2-x}Sr_xCuO_4$ Films

The reflectance measurements were performed using two spectrometers with a variety of light sources, beamsplitters and detectors for different overlapping frequency ranges. The angle of incidence of the incident light was about 11° from the surface normal, so that the electric field of the infrared radiation was dominantly parallel to the $ab$-plane. The reflectance was calibrated with a reference mirror of 2000 Å thick aluminum evaporated on an optically polished glass substrate. The sample and Al mirror reference were mounted on a helium-cooled cold tip, along with a silicon thermometer and a resistance heater, to allow the temperature to be varied from 5 K to 350 K. The sample and reference could be exchanged by rotating the cryostat.

As the overall scale of the reflectance is very crucial to the analysis of HTSC, we carefully tested the stability and measured the absolute reflectance at each temperature. Thermal contraction of the sample holder and position variation between the sample and reference were also taken into account. In order to study the temperature dependence of the mid-infrared band and the plasma edge, we measured the reflectance at each temperature up to 4000 cm$^{-1}$ (0.5 eV), and at selected temperatures up to 40,000 cm$^{-1}$ (5 eV). The coincidence of spectra in each of the overlap frequency range was usually within 0.5%. As the film thickness (820 nm) was much greater than the penetration/skin depth ($\sim$ 250 nm), features attributable to the SrTiO$_3$ substrate effect were not detected. Because the sample surface was extremely smooth and shiny, specular reflection was assumed and there was no need to coat the sample with a metal film to correct for diffuse scattering losses. Also, the large sample area ($1 \times 1$ cm$^2$) enabled us to obtain a high signal-to-noise ratio, making it unnecessary to smooth the data for analysis.
The experimental uncertainty in our reflectance measurements is estimated to be ±0.5%. This error arises mainly from the difficulty in establishing precise optical alignment as the reference and the sample are interchanged, and partly from the slight temperature dependence of the Al reflectance at low frequencies. This small uncertainty in $\mathcal{R}(\omega)$, however, will cause a larger propagated error at low frequencies in the optical conductivity $\sigma(\omega)$ generated by the Kramers-Kronig transformation.

**Procedures in Kramers-Kronig Analysis**

After obtaining satisfactory results for a wide range of reflectance spectra $\mathcal{R}(\omega)$, we have confidence in using the Kramers-Kronig (KK) transform to determine the real part of the optical conductivity $\sigma_1(\omega)$, a more fundamental quantity than $\mathcal{R}(\omega)$ in description of particle-hole excitations of a material by absorption of photons of energy $\hbar \omega$. In principle, the KK integral requires a knowledge of $\mathcal{R}(\omega)$ at all frequencies\textsuperscript{68} as described on p. 18 of chapter III. Thus reasonable and careful extrapolations of the reflectance beyond the measured range must be made.

**High-frequency extrapolation**

The high-frequency extrapolation usually has a significant influence on the results, primarily on the sum rule derived from the optical conductivity. This effect has been reduced by merging our data to the reflectance spectra of Tajima et al.,\textsuperscript{27} which extend up to 37 eV (300,000 cm$^{-1}$). We find their spectra are in excellent agreement (within 5% in relative difference; 0.8% in absolute reflectance) with our high frequency data at room temperature.

After careful measurements, however, we observe a significant decrease in the overall level of $\mathcal{R}(\omega)$ at frequencies above the plasma edge ($\sim$ 7000 cm$^{-1}$) as the temperature is lowered below 250 K. This decrease persists up to 40,000 cm$^{-1}$, the upper limit of our experimental data, the reflectance at 250 K being about 80% of that at room temperature in this frequency region. However, as the temperature is further
decreased below 250 K, aside from the steepening of the plasma edge, there is very little temperature dependence down to 5 K in this high frequency region as shown in Fig. 21. We have carefully repeated the measurements several times and found this behavior reproducible in both the cooling and warming processes. At the same time, we have observed no change at all temperatures in the signal level reflected from the Al reference which has been mounted near the sample. In addition, the reflectance remains unchanged as the sample is heated up from 300 K to 350 K. These tests have convinced us that the extraneous influence such as thermal expansion/contraction of the sample holder or condensation of water on the sample surface can be ruled out. We therefore have readjusted the high-frequency room-temperature reflectivity given by Tajima et al.27 with a relative factor of 5% increase in the range of 5 ~ 8 eV, but no change above this range, before appending it to our data for temperatures below 250 K. After doing so, we have assumed $\mathcal{R}(\omega) \sim \omega^{-4}$, a free-electron asymptotic behavior, above 37 eV. These changes preserve the sum rule at 20 eV.

Low-frequency extrapolation

The low-frequency extrapolation is equally important. We find that using the Hagen-Rubens relation, $\mathcal{R}(\omega) = 1 - A\sqrt{\omega}$, for the normal state leads to a slightly depressed conductivity near the low frequency end, followed by a sharp rise towards zero frequency. This distortion may affect the estimate of the dc conductivity and also of the sum rule, from which we want to find the superconducting condensate by calculating the missing area below $T_c$. Since the Hagen-Rubens relation, a good approximation for ordinary metals, appears to be inappropriate for the HTSC because of the presence of phonons and of low-frequency (midinfrared) absorption processes, First, we make a least-square fit to the optical conductivity, $\sigma_1(\omega)$, derived from the initial KK transform of $\mathcal{R}(\omega)$. In this procedure, we use a two-component dielectric function (Drude plus mid-infrared and phonon oscillators):
\[
\epsilon(\omega) = -\frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{j=1}^{N} \frac{\omega_p^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j} + \epsilon_\infty,
\]

where the first term is a Drude oscillator described by a plasma frequency \(\omega_p\) and a relaxation time \(\tau\) of the free carriers; the second term is a sum of oscillators for mid-infrared and phonon absorptions with \(\omega_j\), \(\omega_p\), and \(\gamma_j\) being the resonant frequency, strength, and width of the \(j^{th}\) Lorentz oscillator; and the last term \(\epsilon_\infty\) is the high-frequency limit of \(\epsilon(\omega)\). This last parameter is found from a fit to \(\mathcal{R}(\omega)\).

Using the fit parameters, we recalculate the low frequency reflectance for the normal state. Then, after extending the experimental \(\mathcal{R}(\omega)\) with calculated reflectance, a second KK transform is made. The results of this "second" \(\sigma_1(\omega)\) give a more reasonable low frequency behavior. In the superconducting state, we have used the formula \(\mathcal{R} = 1 - B\omega^4\), as the way that \(\mathcal{R}\) goes to unity. For temperatures well below \(T_c\), the low frequency reflectance is nearly constant, with some noise fluctuations around unity. We have set \(\mathcal{R} = 1\) in this region for the KK transformation. As mentioned earlier, the experimental uncertainty in \(\mathcal{R}(\omega)\) is about \(\Delta\mathcal{R} = \pm 0.5\%\). As \(\mathcal{R}(\omega) \to 1\) at low \(\omega\) and low \(T\), the KK transform will give propagated error in \(\sigma_1(\omega)\)—primarily coming from the propagated error in the real index of refraction \(n(\omega)\)—roughly equal to

\[
\frac{\Delta\sigma_1}{\sigma_1} = \frac{1}{1 - \mathcal{R}} \frac{\Delta\mathcal{R}}{\mathcal{R}},
\]

namely, the percentage uncertainty in \(\sigma_1\) is about \(1/(1 - \mathcal{R})\) times higher than that in \(\mathcal{R}\). We will address this issue later.

Combination of \(\mathcal{R}(\omega)\) and \(\mathcal{I}(\omega)\) Measurements—\(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) Films

The far-infrared transmittance \(\mathcal{I}(\omega)\) and reflectance \(\mathcal{R}(\omega)\) measurements for the oriented \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) films deposited on \(\text{MgO}\) were made at temperatures from 6 K to 300 K, concentrated around \(T_c\) (\(\sim 90\) K). The light was incident nearly normal
(~ 10° for reflectance and ~ 0° for transmission) to the sample surfaces. In other words, the E vector is polarized on the CuO₂ plane of the YBa₂Cu₃O₇₋δ films. Reflectance measurement is similar to that discussed above for the La₂₋ₓSrₓCuO₄ films. For transmission measurements, the reference was a blank opening. The films, with surface dimensions of 5 × 5 mm², were circularly masked to reduce their areas to about 4 mm diameter. Transmittance spectra from 20 to 100 cm⁻¹ for the 480- and 1560-Å films, and 20–375 cm⁻¹ for the 1800-Å film, were measured using the far-infrared beamline at the National Synchrotron Light Source (NSLS). Transmittance over 50–375 cm⁻¹ for the 480- and 1560-Å films and reflectance over 20–375 cm⁻¹ for all three films were measured using a Bruker Fourier-transform interferometer. Sample and reference spectra were measured three times each to estimate the random noise. In order to deal with the effect due to the underlying substrates, we have also measured a 1 mm-thick bare MgO at each temperature where film data were taken.

Measurement of YBa₂₋ₓSrₓCu₃O₇₋δ Pellets

Optical reflectance measurements were made with a slow-scan home made Michelson spectrometer and a fast-scan Bruker interferometer for the far- and mid-infrared regions and with a grating monochromator for higher frequencies up to ultraviolet region. Initial measurements were made on all pellets (x = 0–1.3) at room temperature. After the reannealing treatments, a fully oxygenated sample with x = 0 was chosen and carefully measured at temperatures between 7 K and 300 K. In order to study the role of lattice vibrations in the superconducting transition, a number of measurements were made around Tc. Room temperature data above 4000 cm⁻¹ were used in analysis for all temperatures. This approximation was justified by the fact of only little T-dependence throughout the midinfrared range.

Surface correction. One important difference between ceramic samples and smooth thin films is that diffuse scattering from the granular surface will cause a
rapid decrease in reflectance with increasing frequency, particularly when the wavelength is comparable to the grain sizes. To compensate for the scattering losses, all pellets were coated with a thin aluminum layer after the initial optical measurement was finished, and a second measurement was carried out on the coated samples at room temperature to estimate the losses due to non-specular reflection. Two factors must be considered in making the coating. First, it is important that the coating layer be thin enough so that the microstructure of the sample surface remains unaltered. Second, the layer must be thicker than the penetration depth of the coating material. In our case, the Al coating was ~2000 Å thick, smaller than the sample grain size (~15 μm) but greater than the Al penetration depth (~200 Å). The coating was made by using an ion milling (microetch) equipment.

The final corrected reflectance was obtained by evaluating the ratio of the initial reflectance (no coating) to the reflectance of the coated sample, then multiplying the ratio by the aluminum reflectance from the literature. After the reflectance spectra $\mathcal{R}(\omega)$ over a wide frequency range were measured, the optical conductivity $\sigma(\omega)$ was determined by performing the Kramers-Kronig transformation, with reasonable extrapolations similar to the case of our $La_{2-x}Sr_xCuO_4$ films described above.
Fig. 20. Schematic of low temperature apparatus.
Fig. 21. Temperature dependence of the reflectance in the interband region. There is a remarkable change in $R(\omega)$ between 300 K and 250 K but no appreciable change above or below this temperature range.
CHAPTER VII
OPTICAL STUDIES OF La$_{2-x}$Sr$_x$CuO$_4$ FILMS

In this chapter, we present the in-plane spectra of reflectance $\mathcal{R}(\omega,T)$ and conductivity $\sigma(\omega,T)$ of high quality La$_{2-x}$Sr$_x$CuO$_4$ films over a wide frequency range of 30–40,000 cm$^{-1}$ (4 meV–5 eV) and for temperatures between 5 K and 350 K. We make an extensive optical study on the infrared dynamics of the films.

Sample preparation and the characteristic transport properties have been described in chapter V. The parameters of the samples have been summarized in Table 2 (see p. 55), and the dc resistivity has been illustrated in Fig. 15.

Thinner films (270 nm thickness) were measured but transparent enough that some features of the substrate could be seen in the reflectance spectra. Consequently, the work described here will focus on an especially thick film with thickness (820 nm) greater than the electromagnetic penetration depth ($d > \delta$) to avoid the substrate complications. Details of optical measurement techniques and the uncertainties in the Kramers-Kronig (KK) analysis have been discussed in chapter VI. Here we will present the spectra of reflectance and other optical functions derived from the KK analysis. Details of the infrared phonons and optical conductivity $\sigma(\omega)$ in the normal and superconducting state are discussed. Comparisons of the normal state data to both two- and one-component descriptions of the optical dielectric function are also made.

Results and Discussion

Infrared Phonons

Figure 21 has showed the measured $ab$-plane reflectance $\mathcal{R}(\omega,T)$ of a La$_{2-x}$Sr$_x$CuO$_4$ thin film on linear scale over most of the measured range. The details
of the low frequency behavior are presented in Fig. 22 at several temperatures. The inset, which shows data plotted on a logarithmic frequency scale for the entire measured frequency range at three typical temperatures, illustrates the strongly damped plasma edge around 0.8 eV (6000 cm\(^{-1}\)) and the interband features around the visible region. As we can see from Fig. 22, \(\mathcal{R}(\omega, T)\) increases over a broad frequency range with decreasing temperature, as expected. A few infrared-active phonons in the ab-plane are visible. These phonons are more obvious in the spectrum than in the case of YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\).\(^{10-12,34-36}\) This indicates that La\(_{2-x}\)Sr\(_x\)CuO\(_4\) crystals have a lower free carrier concentration and a higher vibrational oscillator strength. The phonon parameters can also be extracted from \(\sigma_1(\omega)\), the real part of the optical conductivity, shown in Fig. 23. Of the seven IR-active phonon modes (3\(A_2u\) + 4\(E_u\)) expected at the \(\Gamma\) point for the body-centered tetragonal \(D_{4h}^{17} - I4/mmm\) symmetry, three distinct \(ab\)-plane \(E_u\) modes are observed at 126, 359, and 681 cm\(^{-1}\) for \(T = 300\) K. These eigenenergies are close to those previously reported by Collins \textit{et al.},\(^{26}\) 132, 358, and 667 cm\(^{-1}\), from a room-temperature reflectance study of a La\(_{2-x}\)Sr\(_x\)CuO\(_4\) single crystal. These three phonons have been assigned as external, bending and stretching modes, respectively.\(^{87,88}\) More details regarding the phonon mode assignment have been reported in Ref. 89.

Structural phase transition

We note that the lowest phonon mode at \(\omega = 126\) cm\(^{-1}\), corresponding to an in-plane translational vibration of the La atoms against the CuO\(_6\) octahedron unit, broadens and splits into two distinct modes as \(T\) decreases below 250 K. The splitting begins at the tetragonal-to-orthorhombic structural transition which involves a staggered rotation of CuO\(_6\) octahedra. At 200 K, the degeneracy of the two modes is lifted but their energies are so close that they can barely be resolved. The splitting develops upon further cooling as depicted in Fig. 24. This splitting is probably asso-
associated with the folding back of the zone-boundary mode to the zone center because of the unit cell doubling due to orthorhombic distortion ($D_{2h}^{18} - Cmca$ symmetry). Similar results in neutron scattering measurements have been reported and associated with a soft phonon mode. For comparison, the inset in Fig. 24 shows the results of Keane et al. for the in-plane lattice constants of a La$_{1.85}$Sr$_{0.15}$CuO$_4$ sample as a function of temperature. The structural distortion is evident in their data at $T \lesssim 200$ K.

**Frequency shift and lifetime**

We also observe that the Cu-O stretching mode at 681 cm$^{-1}$ hardens by 13 cm$^{-1}$ as the sample cools off from 300 to 100 K, as expected for thermal contraction. It stops shifting, however, upon further cooling. In contrast, the frequency of the Cu-O bending mode at 359 cm$^{-1}$ remains constant at all temperatures yet exhibits a discernible splitting at low $T$. We thus conclude that the stretching mode is much more sensitive to the Cu-O bond length than the bending mode. Tajima et al. have recently found a similar result when they measured the room temperature phonon frequencies of different cuprates with different lattice constants but almost the same reduced mass by substituting the La atom by other rare earth elements. A similar effect has also been observed in the $T'\!$-RE$_2$CuO$_4$ system by Herr et al. In our case the absence of further hardening at lower temperatures is probably due to the fact that the real part of the phonon self-energy $\Sigma_{ph} = \Delta + i\Gamma$ has three contributions:

$$\Delta(T) = \Delta^{(0)}(T) + \Delta^{(1)}(T) + \Delta^{(2)}(T)$$

(83)

where $\Delta^{(0)}$ accounts for thermal expansion, $\Delta^{(1)}$ and $\Delta^{(2)}$ for the cubic and quartic anharmonic terms in the lattice potential, respectively. These contributions are generally of the same order of magnitude but may have different signs. Thus $\Delta^{(0)}$ may be compensated by the sum of $\Delta^{(1)} + \Delta^{(2)}$ at low temperatures. Another possibility
is the saturation of the $T$-dependence of all three contributions below 100 K. Such an effect has been found in silver- and thallium-halides. Indeed, Tranquada et al. and Keane et al. have observed that the interatomic distances of La$_{2-x}$Sr$_x$CuO$_4$ saturate below 100 K.

It has been reported that the two lower-lying IR active phonons at 149 and 190 cm$^{-1}$ for YBa$_2$Cu$_3$O$_7$ ceramic samples narrow dramatically but have no softening upon entering into superconducting state. In contrast, the phonons above 275 cm$^{-1}$ exhibit opposite behavior (i.e., little change in width but apparently softening below $T_c$). The anomalous dramatic narrowing in phonon widths for YBa$_2$Cu$_3$O$_{7-\delta}$ has been attributed to the disappearance of interaction between electrons and phonons with energies less than the superconducting gap when the electrons condense into Cooper pairs below $T_c$. The phonon lifetime will increase as a result of decreased probability of colliding with quasiparticles, because the number of quasiparticle excitations decreases rapidly below $T_c$. This issue will be addressed in more details in chapter IX, where polycrystalline samples are discussed. In any event, here we do not see a dramatic $T$-dependence in the observed $ab$-plane phonons for La$_{2-x}$Sr$_x$CuO$_4$, perhaps because the lowest phonon mode at 126 cm$^{-1}$ is far above the BCS gap energy, which is $\sim$ 80 cm$^{-1}$ for a $T_c = 31$ K sample.

Two-Component Approach

Returning to the conductivity spectra as shown in Fig. 23, we note that the normal state $\sigma_1(\omega, T)$ at the low frequency limit is nearly equal to the dc conductivity and exhibits a Drude response. A remarkable depression can be seen at 30 K, just below $T_c$, for $\omega < 150$ cm$^{-1}$, indicating the shift of spectral weight into the origin due to the superconducting condensation. The inductive current represented by the imaginary part of the complex conductivity, $\sigma_2$, is dominant at $\omega < 100$ cm$^{-1}$ and it diverges as $\omega \rightarrow 0$ for $T < T_c$, as shown in Fig. 25. Above $T_c$, $\sigma_2$ changes slope
at low frequencies and heads for the origin, and the maximum moves to higher frequency and decreases rapidly with increasing temperature, as expected. On the other hand, at $\omega > 300$ cm$^{-1}$, the normal-state $\sigma_1(\omega)$ in Fig. 23 decays much more slowly than the free carrier $\omega^{-2}$-dependence as one expects in a Drude model. Additionally, $\sigma_1(\omega)$ has much weaker temperature dependence at high frequencies than at low frequencies. This “non-Drude” behavior, which is universal for all copper oxide superconductors,$^{10-13,31-36,40,42}$ can be described in a two-component picture, in which a narrow (with a width of order $k_B T$) and strongly $T$-dependent free carrier (Drude) absorption peaked at $\omega = 0$ combines with a broad bound-carrier (MIR) absorption centered at higher frequencies. According to this picture, the cuprates are viewed as consisting of two type of carriers: free carriers which track the dc conductivity above $T_c$ and which condense to superconducting pairs below $T_c$, and bound carriers which are responsible for the broad MIR excitation. The dielectric function is made up of four parts:

$$\epsilon(\omega) = \epsilon_D + \epsilon_{MIR} + \epsilon_{phonon} + \epsilon_\infty$$  \hspace{1cm} (84)

where $\epsilon_D$ is the free carrier or normal Drude intraband contribution; $\epsilon_{MIR}$ is the bound-carrier contribution; $\epsilon_{phonon}$ is the phonon contributions, a sum of harmonic oscillators; and $\epsilon_\infty$ is the high frequency contribution.

To decompose the total conductivity into two components, we can assume that the conductivity at 5 K, $\sigma_1(\omega,5K)$, is a good first approximation of $\sigma_{1MIR}$, namely $\sigma_{1MIR}^{(1)} \leftarrow \sigma_1(\omega,5K)$, for the Drude part is presumed to have collapsed to a $\delta(\omega)$ function (the optical spectra are dominated by the inductive response). Thus the Drude conductivity at higher temperatures can be initially estimated by subtracting $\sigma_1(\omega,5K)$ from the experimental $\sigma_1(\omega,T)$, namely $\sigma_{1D}^{(1)} \leftarrow \sigma_1 - \sigma_{1MIR}^{(1)}$. Here the superscripts denote the number of iterations. Since

$$\sigma_{1D} = \frac{1}{4\pi} \frac{\omega_p^2 \tau}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (85)
we can determine $\omega_{pd}$ and $1/\tau$ from a linear fit to $1/\sigma_{1D}^{(1)}$ vs. $\omega^2$. Once $\omega_{pd}$ and $1/\tau$ are determined from the slope and the intercept of this straight line, we can again estimate the mid-infrared conductivity from the difference between a calculated Drude conductivity and the measured conductivity, namely $\sigma_{1MIR}^{(2)} = \sigma_1 - \sigma_{1D}$, where $\sigma_{1D}$ is calculated according to Eq. (85). By averaging $\sigma_{1MIR}^{(2)}$ at temperatures above $T_c$, we find the average $\langle \sigma_{1MIR}^{(2)} \rangle \approx \sigma_{1MIR}^{(1)}$ [or $\sigma_1(\omega, 5K)$], but there are noticeable differences. Therefore we repeat the above procedure with $\sigma_{1MIR}^{(2)}$ replacing $\sigma_{1MIR}^{(1)}$, and find convergence after a few iterations.

The free-carrier component—$\omega_{pd}$ and $\tau$

Figure 26 illustrates the comparison between the free carrier contribution, $\sigma_1 - \langle \sigma_{1MIR} \rangle$, and the calculated Drude conductivity. This figure shows that the conductivity is in good agreement with the ordinary Drude behavior after the MIR component is subtracted. The Drude plasma frequency, $\omega_{pd} = 6300 \pm 100$ cm$^{-1}$, obtained from the above analysis is essentially $T$-independent, whereas $1/\tau$ is linear in $T$. Writing $\hbar/\tau = 2\pi\lambda k_B T$, we obtain a weak-coupling value for the coupling constant, $\lambda = 0.25$. This small value of $\lambda$ is consistent with the observed absence of saturation up to 1100 K for the dc resistivity.61 Taking the Fermi velocity in the basal plane to be $v_F = 2.2 \times 10^7$ cm/s, as calculated by Allen et al.97 for La$_{1.85}$Sr$_{0.15}$CuO$_4$, and using our relaxation rate we can estimate the mean free path to be

$$l = v_F \tau \approx (110 \text{ Å}) \frac{100 \text{ K}}{T}.$$ (86)

At $T = 1000$ K, $l \sim 11$ Å, which is still longer than the interatomic spacing $a$ (here taken to be 3.8 Å, the in-plane lattice constant). The resistivity is expected to saturate if $l \ll a$, because the mean free path can no longer be properly defined in this region.98 On the other hand, at temperature close to $T_c$, the mean free path $l$ [e.g., $l_{50K} \sim 220$ Å according to Eq. (86)] is much longer than the coherence length
\( \xi (\sim 10 \text{ Å}) \). It is this case that places the HTSC in the "clean limit", which in turn gives a significant impact on the observability of the superconducting gap.

Figure 27 depicts the temperature dependence of \( 1/\tau \) in comparison with \( (1/\tau)_{dc} \) calculated from the measured four-probe dc resistivity \( \rho_{dc} \) and the value of \( \omega_{pD} \) found above, \[
(1/\tau)_{dc} = \frac{\omega_{pD}^2}{4\pi} \rho_{dc}.
\] (87)

As seen in Fig. 27, \( (1/\tau)_{dc} \) or \( \rho_{dc} \) decreases quasi-linearly from room temperature followed by a plateau and then a sudden drop as the temperature approaches \( T_c \) whereas the far-infrared scattering rate shows a quasi-linear \( T \) variation followed by a faster-than-linear drop \( (1/\tau \sim T^2) \) below \( T_c \). This is evident when the same data are plotted on a log-log scale, as shown in the inset of Fig. 27. The excellent agreement in both the slopes and overall levels between the dc transport and infrared measurements strengthens our confidence in the determination of the normal state plasma frequency \( \omega_{pD} \) and scattering rate \( 1/\tau \). The sudden drop in \( 1/\tau \) just below \( T_c \) is interesting and has received considerable attention recently. Such observations on quasiparticle damping have been reported previously for laser-ablated \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) films\textsuperscript{99,36} and a free-standing \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \) crystal.\textsuperscript{100,101} Similar behavior has also been found for \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) and \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) in femtosecond optical transient absorption experiments.\textsuperscript{102} This result may suggest that the excitation that scatters the free carriers is also strongly suppressed below \( T_c \), or forms its own gap, as the free carriers condense. Another interpretation is that the number of unoccupied states available near the Fermi levels decreases rapidly as a result of the depression of the density of quasi-particle states near \( E_F \) as the gap opens, causing a dramatic decrease in the probability of quasiparticle elastic scattering. Nicol \textit{et al.}\textsuperscript{103} have recently calculated the quasiparticle scattering rate and found such a fast drop within the phenomenological Marginal Fermi Liquid model. However, on account of the
large error bars at low frequencies (below 100 cm\(^{-1}\)) and the limited number of temperatures below \(T_c\) (31 K) in our data, we are unable to observe a "coherence" peak in \(\sigma_1(T)\), as has been calculated by Nicol \textit{et al.}\(^{103}\) and found in YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) by Nuss \textit{et al.},\(^{104}\) and in Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_8\) by Romero \textit{et al.}\(^{101}\) This "coherence peak" has also been observed in our YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) thin films and will be discussed in detail in the next chapter.

The midinfrared absorption

Figure 28 presents the MIR conductivity in the normal and superconducting states. This quantity is obtained by subtracting the calculated free carrier contribution (shown in Fig. 26 as solid lines) from the total conductivity. Some features that are common at all temperatures include: an onset near 80 cm\(^{-1}\), a maximum around 250 cm\(^{-1}\), a notch-like structure at 400 cm\(^{-1}\), and a broad peak around 800 cm\(^{-1}\). As we can see, the MIR conductivity \(\sigma_{1\text{MIR}}(\omega,T)\) has a relatively weak temperature dependence. There do appear to be three distinct temperature regimes: \(\geq 250\) K, \(T_c-200\) K, and below \(T_c\). In each, there is a noticeable conductivity increase in the region of 150–1500 cm\(^{-1}\) with decreased temperature. The enhancement is more obvious for \(T < T_c\) and will be discussed below.

According to the data in Fig. 28, the "two-gap" structure of an onset near 80 cm\(^{-1}\) (3.7 \(k_B T_c\)) and a notch around 400 cm\(^{-1}\) (18 \(k_B T_c\)) is present both below and above \(T_c\). This structure is shown more clearly in Fig. 29, where we plot the average of the curves above and below \(T_c\). Thus we cannot associated either feature with the superconducting gap, since that presumably would not appear above \(T_c\). Furthermore, there is no shift in any feature in the superconducting state as would be expected for a Holstein sideband associated with condensate. Such features have also been observed\(^{35,100,105}\) in YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) and Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_8\) films. The structure at 400 cm\(^{-1}\) (50 meV), which appears common to the cuprate superconductors, has been
explained as due to strong bound carrier/phonon coupling.\textsuperscript{48} It can not be accepted as a superconducting gap simply because its magnitude is too large. The value of the lower-energy onset usually varies for different samples. The presence of this structure above $T_c$ and the lack of evidence of an energy shift with varying temperature below $T_c$ make it difficult to associate it with the BCS gap.

**Holstein effect**

Lee \textit{et al.}\textsuperscript{106} have calculated the dynamic conductivity in the framework of strong-coupling theory, including the Holstein mechanism.\textsuperscript{107,108} They obtain a two-gap structure in the superconducting state. The first onset is presumed to be the superconducting gap, while the “second gap” is interpreted as the consequence of inelastic scattering with phonons due to the Holstein effect.

To estimate this effect, we have calculated the conductivity according to the Holstein theory for our film and find that the enhancement of the MIR strength below $T_c$ may not be accounted for by the inelastic scattering contribution. In the Holstein model, the scattering rate at low temperature can be obtained by\textsuperscript{108}

\[ 1/\tau(\omega) = \frac{2\pi}{\omega} \int_0^\omega \alpha^2 F(\Omega)(\omega - \Omega) d\Omega, \quad (88) \]

where $\alpha^2 F(\Omega)$ is the Eliashberg function or electron-phonon spectral density. The parameters used in our calculation were: $\omega_p = 6300$ cm$^{-1}$ (from the two component model fit outlined above), $\lambda(\omega=0) = 0.25$, and the average boson frequency $\Omega_0 = 75$ cm$^{-1}$. In general, the coupling parameter is given by\textsuperscript{108}

\[ \lambda(\omega) = -\frac{2}{\omega} \int_0^\infty \alpha^2 F(\Omega) \left[ \ln \left| \frac{\omega - \Omega}{\omega + \Omega} \right| - \frac{\Omega}{\omega} \ln \left| \frac{\omega^2 - \Omega^2}{\Omega^2} \right| \right] d\Omega \quad (89) \]

with a zero frequency limiting value

\[ \lambda = \lambda(\omega\to0) = 2 \int_0^\infty \frac{\alpha^2 F(\Omega)}{\Omega} d\Omega \quad (90) \]

For simplicity, we have assumed the Eliashberg function has the form (in an Einstein model) $\alpha^2 F(\Omega) = A\delta(\Omega - \Omega_0)$, where $A = \frac{1}{2}\lambda\Omega_0$ according to Eq. (90). The
calculated result is illustrated as the dash-dotted curve in Fig. 29. The size of the Holstein side band could be enlarged to match the measured MIR spectral weight by increasing $\lambda$ and $\omega_p$, but this would be in disagreement with the values determined experimentally.

**Superconducting-to-normal ratios**

Another unconventional behavior is seen in the superconducting to normal-state conductivity ratio shown in Fig. 30. Ratios of conductivity have been used frequently in the past to suggest superconducting gap structure.\textsuperscript{41,42} In Fig. 30, we compare $\sigma_{1s}$ and "$\sigma_{1n}$" at the same temperature. We note that if $\sigma_{1s}$ and $\sigma_{1n}$ are compared at different temperatures, the result is totally different as shown in the inset, resembling a BCS-like behavior as seen in Fig. 3 on p. 31. To estimate $\sigma_{1n}(\omega, T)$ below $T_c$, we presume that the "normal state" $\omega_pD$ and $1/\tau$ below $T_c$ follow the "normal" behavior, i.e., $\omega_pD$ remains a constant (6300 cm\textsuperscript{-1}) and $1/\tau$ follows the linear extrapolation of the relaxation rate above $T_c$. Then $\sigma_{1n}$ below $T_c$ can be calculated as the sum of the calculated Drude component and the averaged MIR conductivity $\langle \sigma_{1MIR} \rangle_n$, namely

$$
\sigma_{1n} = \begin{cases} 
\text{measured } \sigma_1, & T > T_c \\
\frac{1}{4\pi} \frac{\omega_p^2 D \tau}{1 + \omega^2 \tau^2} + \langle \sigma_{1MIR} \rangle_n, & T < T_c
\end{cases}
$$

(91)

As we can see in Fig. 30, the ratio $\sigma_{1s}/\sigma_{1n}$ exhibits a sharp edge near 100 cm\textsuperscript{-1} and has a peak around 180 cm\textsuperscript{-1}. The peak is suppressed but does not shift as $T$ approaches $T_c$ from below. $\sigma_{1s}$ "overshoots" $\sigma_{1n}$ up to 1000 cm\textsuperscript{-1} and then gradually joins the normal state conductivity at higher frequencies. This surprising result can be attributed first to the observed enhancement of the mid-infrared conductivity in the superconducting state, and second to the observed faster-than-linear decrease in the quasiparticle scattering rate as demonstrated in Fig. 27.
Extra absorption below $T_c$

We turn to the differences between the MIR conductivity above $T_c$ and the below-$T_c$ conductivity. The enhancement is evident in the raw data of Fig. 23, in which we can see the conductivity at 5 K is higher than that at 50 K, above $T_c$, for $\omega \gtrsim 360$ cm$^{-1}$. By calculating the difference between the averaged mid-infrared conductivity in the superconducting state, $\langle \sigma_{\text{MIR}} \rangle_s$, and the one in the normal state, $\langle \sigma_{\text{MIR}} \rangle_n$, we find an extra absorption below $T_c$ in the MIR region which counts for roughly 15% of the Drude oscillator strength. This difference is shown in Fig. 29. (Note that the actual fraction may be smaller for the reason of large error bars in $\sigma_1$ at low $\omega$ below $T_c$, as will be discussed below; thus the difference, $\langle \sigma_{\text{MIR}} \rangle_s - \langle \sigma_{\text{MIR}} \rangle_n$, may be exaggerated at low frequencies.) This anomalous behavior suggests the existence of another type of excitation visible in the superconducting state, with the normal Drude carriers not completely condensing into the superfluid below $T_c$. However, this argument can not be taken as rigorous, since our approach of extracting the Drude component has neglected the $\omega$-dependence of the electronic scattering rate, though it may be weak as suggested by the small value of coupling constant $\lambda \sim 0.25$.

To confirm our observation of the extra absorption below $T_c$ in the MIR conductivity obtained by the two-component analysis, we use two other independent methods to estimate the oscillator strength of the superconducting condensate: the dielectric function and the $f$-sum rule. According to the clean limit picture, when $2\Delta \gg 1/\tau$ the Drude oscillator strength will condense into a $\omega = 0$ delta function for $T \ll T_c$. Thus the real part of the dielectric function at low frequencies is

$$\epsilon_1(\omega) = \epsilon_{1b} - \frac{\omega_{ps}^2}{\omega^2},$$

(92)

where $\omega_{ps}$ is the superconducting plasma frequency defined as $\omega_{ps} = 4\pi n_s e^2/m_b$ with $n_s$ being the density of superfluid carriers; and $\epsilon_{1b}$ is the bound carrier contribution to
\( \epsilon_1(\omega) \), i.e., the low-frequency sum of all finite frequency absorption. In principle, \( \epsilon_{1b} \) is \( \omega \)-dependent. It is constant only at frequencies well below the lowest bound-carrier resonant frequency.

Figure 31 shows the plot of \( \epsilon_1(\omega) \) [obtained from KK transform of \( R(\omega) \)] as a function of \( \omega^{-2} \). The data fall on a straight line, as predicted by Eq. (92), in the low frequency range. The slope obtained from the linear regression fit at \( T = 5 \) K gives \( \omega_{ps} \approx 5800 \pm 100 \) cm\(^{-1} \), from which the London penetration depth can be estimated to be \( \lambda_L = 1/2\pi\omega_{ps} = 275 \pm 5 \) nm. This value, which is much less than the film thickness (820 nm), is comparable to the 250 nm in-plane \( \lambda_L \) found by muon-spin-relaxation (\( \mu \)SR) measurements\(^{109} \) for La\(_{1.85}\)Sr\(_{0.15}\)CuO\(_4\) at \( T = 6 \) K. We note that only a fraction \( f_s = \omega_{ps}^2/\omega_{pD}^2 \approx 85\% \) of the free carriers condense into superfluid, in good agreement with the observation that \( \sim 15\% \) of the Drude spectral weight has shifted to MIR region below \( T_c \) as outlined above. Further evidence that supports this argument is obtained from the \( f \)-sum rule that will be discussed next.

**Sum Rule—Superconducting Condensate**

Figure 32 illustrates the spectral weight, \( N_{\text{eff}}(\omega) m/m_b \), as defined according to

\[
N_{\text{eff}}(\omega) \frac{m}{m_b} = \frac{2mV_{\text{cell}}}{\pi e^2} \int_0^\omega \sigma_1(\omega') \, d\omega',
\]

where \( e, m \) are the free electron charge and mass, respectively. \( m_b \) is the averaged high-frequency optical or band mass, and \( V_{\text{cell}} \) is the volume (95 \( \text{Å} \)) of one formula unit. Note Eq. (93) is also called partial sum rule and is the generalization of Eq. (45). In this expression, \( N_{\text{eff}}(\omega) \) equals to the effective number of carriers per formula unit participating in optical transition at frequencies below \( \omega \).\(^{68} \) The normal state \( N_{\text{eff}}(\omega) \) curves at 10,000 cm\(^{-1} \) gives, if \( m_b = m \), roughly 0.18 hole per CuO\(_2\) layer, which is a value close to the dopant concentration of our film ( \( x \sim 0.17 \) ) assuming each Sr atom donates one hole to the CuO\(_2\) layer.
In the normal state, the curves exhibit a sharp rise in the far infrared followed by a broad plateau before another rise beginning near 10,000 cm\(^{-1}\) due to the charge-transfer transition. As the temperature is lowered, spectral weight transfers to lower frequency in response to a decreasing relaxation rate. Below \(T_c\), the spectral weight is reduced as expected due to superconducting condensation. From the difference between \(N_{\text{eff}}(\omega) m/m_b\) for the normal and the superconducting states, the plasma frequency of the superfluid charge carriers [or the missing area in the curve of \(\sigma_1(\omega)\)] can be estimated. This difference gives 
\[
\Delta(N_{\text{eff}} m/m_b) = \omega_{ps}^2 m V_{\text{cell}}/4\pi e^2,
\]
from which we find \(\omega_{ps} = 5800\) cm\(^{-1}\) at 5 K, in excellent agreement with the value determined from the real dielectric function as discussed earlier.

One surprising result of our measurements is that the \(N_{\text{eff}}(\omega) m/m_b\) in the charge transfer region is larger at \(T \geq 300\) K than at other temperatures below 250 K, as shown in the inset of Fig. 32. The mechanism that causes this difference is not clear at this moment. One speculation is that the structural transition at around 250 K may change the band structure due to the doubling of the unit cell. The transformation introduces new Brillouin zone planes at which the semiconductor-like gaps are opened, transferring oscillator strength to higher frequency regions. The band mass may also change accordingly. This difference disappears, however, above 15 eV, where the \(N_{\text{eff}}(\omega) m/m_b\) curves come together. 15 eV is the end point of the interband excitations from the O 2p valence bands to the La 5d/4f conduction bands above the the Fermi level and the starting point of excitations from the Cu 3d bands to the La 5d/4f bands.

Figure 33 shows the temperature dependence of the Drude \((\omega_{pD})\) and superconducting \((\omega_{ps})\) plasma frequencies. Here \(\omega_{pD}\) is determined from the fit to \(\sigma_1(\omega)\) as described earlier and is consistent with a picture of constant carrier concentration in the normal state. This magnitude of \(\omega_{pD}\) (~0.8 eV) is smaller in comparison with the values (~1.2 eV) obtained in YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) or BiSrCaCuO crystals, presumably
indicating lower carrier concentration on the CuO₂ planes. Below \( T_c \), \( \omega_{ps} \) is estimated from the sum rule, the linear fit to \( \epsilon_1(\omega) \) vs. \( \omega^{-2} \), and the least-squares fit to the reflectance data using a two-fluid model. These three approaches give very close results in \( \omega_{ps} \) and we take the average values. Shown in the inset is the superfluid electronic density fraction \( f_s(T) \). This superconducting condensate is calculated according to

\[
f_s(T) = n_s(T)/n = \frac{\omega^2_{ps}(T)}{\omega^2_{pD}} \text{ with } \omega_{pD} = 6300 \text{ cm}^{-1},
\]

the normal state value. This quantity \( f_s(T) \) is essentially a measure of the strength of the \( \delta \) function in \( \sigma_1(\omega, T) \), and is related to the \( T \)-dependence of the penetration depth \( \lambda_L(T) \). The solid curves in Fig. 33 and its inset show the phenomenological behavior predicted by BCS theory according to

\[
\frac{f_s(T)}{f_s(0)} = \left( \frac{\Delta(T)}{\Delta(0)} \right)^2,
\]

where \( \Delta(T) \) is the \( T \)-dependent BCS order parameter. It gives a nearly constant \( \Delta(T) \) at \( T \ll T_c \). Near \( T_c \), \( \Delta(T) \) drops to zero with a \( (1 - T/T_c)^{1/2} \) dependence. The behavior of \( f_s(T) \) in our data agrees with this expression and it demonstrates that the normal carriers condense rapidly into the superfluid below \( T_c \), as expected.

One-Component Approach

An alternative approach to analysis of the optical conductivity is the one-component model with a frequency dependent mass and scattering rate.\(^{40,110-112}\) In this approach, the infrared absorption is entirely due to free carriers, in which are divided into "coherent" and "incoherent" parts caused by the interaction of the free carriers with some sort of optically inactive excitations (charge or spin fluctuations).\(^{105}\) This approach has been proposed by Anderson\(^{113}\) and applied to heavy-Fermion superconductors\(^{114}\). The normal Drude component is regarded as the coherent part centered at \( \omega = 0 \). The incoherent part occurs at frequencies characteristic of the excitations and shifts away from \( \omega = 0 \) due to interactions with the excitations. In this
model, the complex dielectric function is described by a generalized Drude formula:

$$\epsilon(\omega) = \epsilon_h - \frac{\omega_p^2}{\omega[\omega - \Sigma(\omega)]},$$ (95)

where $\epsilon_h$ is the "background" dielectric constant associated with the high frequency contributions, $\omega_p$—defined by $4\pi Ne^2/m_b$—is the bare plasma frequency of the free carriers, and $\Sigma(\omega) = \Sigma_1(\omega) + i\Sigma_2(\omega)$ is the self energy of the carriers.

Because $\epsilon(\omega)$ is causal, $\Sigma_1(\omega)$ and $\Sigma_2(\omega)$ are related by the Kramers-Kronig equations. It is important to stress that the interband contributions, which can be lumped into $\epsilon_h$, are excluded from $\omega_p$ and $\Sigma(\omega)$. To find $\Sigma(\omega)$, knowledge of $\omega_p$ and $\epsilon_h$ is required. In order to identify the interband components, we fit the experimental $\sigma_1(\omega)$ at frequencies higher than 8000 cm$^{-1}$ with Lorentz oscillators to parameterize the interband absorption. By subtracting the contribution due to these interband oscillators from the total conductivity and calculating the area under $\sigma_1(\omega)$, we obtain $\omega_p = 13,000$ cm$^{-1}$, corresponding to a carrier density of $n = 1.8 \times 10^{21}$ cm$^{-3}(m_b/m)$ or 0.17 holes per CuO$_2$ unit if $m_b = m$. As we have found $\omega_{PD} = 6300 \pm 100$ cm$^{-1}$ in the two-component analysis, we can also estimate the strength of MIR absorption or the "incoherent" component as $\omega_{pm} = (\omega_p^2 - \omega_{PD}^2)^{1/2} \approx 11,370$ cm$^{-1}$. $\epsilon_h$ can be estimated from the interband oscillators, giving $\epsilon_h \sim 4$ in the far infrared region. At higher frequencies, $\epsilon_h$ becomes complex and $\omega$-dependent.

**Mass enhancement $m^*/m_b$ and self energy $\Sigma(\omega)$**

Once $\omega_p$ and $\epsilon_h$ are determined, the self energy $\Sigma(\omega)$ can be calculated at each frequency from the experimental $\epsilon(\omega)$ according to Eq. (95). If we rewrite Eq. (95) as

$$\epsilon(\omega) = \epsilon_h - \frac{\omega_{PD}^2}{\omega[\omega + i/\tau^*(\omega)]},$$ (96)
and compare Eq. (96) with Eq. (95), we can extract the renormalized scattering rate
\[ \frac{1}{\tau^*(\omega)} = -\sum_2(\omega) m_b/m^*, \]
and the effective plasma frequency
\[ \omega^*_p = \omega_p(m_b/m^*)^{1/2}, \]
where the effective mass enhancement is given by
\[ \frac{m^*/m_b}{m_b} = 1 - \frac{\Sigma_1}{\omega}. \tag{97} \]

Note both the real and imaginary parts of \( \Sigma(\omega) \) are negative definite. The computer routine for the one-component analysis is given in Appendix B. The resulting curves of \( m^*(\omega)/m_b \) and \( \Sigma_2(\omega) \) are shown in Fig. 34. The effective mass \( m^* \) is greatly enhanced at low \( \omega \) and \( m^* \approx m_b \) at high \( \omega \), as expected for the MFL and NFL theory.\(^{37,38}\)

The behavior of \( m^*(\omega)/m_b \) and \( \Sigma_2(\omega) \) as shown can be viewed as arising from a local Coulomb interaction of carriers with a broad spectrum of other excitations. At low frequencies, the carriers drag a low-energy excitation cloud along with them, causing a mass enhancement. As frequency increases, the scattering rate \( 1/\tau^* \) increases when the low-lying states are excited hence a new inelastic scattering occurs. The carrier mass decreases to approach the band mass as \( \omega \) increases, for the low-lying excitations cannot follow the rapid carrier motion. We can estimate the characteristic energy range of the low-lying excitations from the frequencies at which \( m^*(\omega) \) and \( \Sigma_2(\omega) \) change from their low to high frequency behavior. This range appears to be between 300–1000 cm\(^{-1} \) (0.04–1.2 eV). We note that a pronounced peak near 0.1 eV reported by Uchida et al.\(^{29} \) is not observed in our spectra of \( m^*/m_b \) and \( \Sigma_2 \). The present values of \( \Sigma_2 \) are comparable with their result for the unnormalized scattering rate. The mass enhancement here is, however, a factor of 0.15 smaller than their result. The high value of \( m^* \) in their data would imply an even stronger coupling between the free carriers and the low-lying excitations, which is difficult to understand.

Note that the value of \( m^*/m_b \) at low \( \omega \) and low \( T \) can also be predicted from the conductivity sum rule from Fig. 32 or simply from \( \omega_p^2/\omega_{PD}^2 \sim 4.2 \), which agrees well
with the result in Fig. 34. Writing $m^*/m_b = 1 + \lambda$, we find the low-frequency-limit value of coupling constant $\lambda \approx 3$ at low temperatures, suggesting strong interaction of carriers with a spectrum of other excitations. One major difficulty with this model is that this large $\lambda$ would give a high $T_c$, inconsistent with the actually measured $T_c$ value. To account for this large $\lambda$, one may speculate that the $T_c$ is suppressed by other mechanisms. However, such mechanisms, if any, are not clear at this point.

**Effective scattering rate $1/\tau^*(\omega)$**

A linear $T$-dependent scattering rate at $\omega \sim 0$ implies it is also linear in $\omega$ at higher frequencies. The effective renormalized scattering rate can be obtained by $1/\tau^* = -(m_b/m^*) \Sigma_2$. This quantity is shown in Fig. 35. The extrapolated $\omega = 0$ values of $1/\tau^*$ are compatible to those obtained above in the two-component fit by assuming a constant scattering rate. This is not surprising since both the one- and two-component approaches have described the dc transport behavior well. At higher frequencies, we observe $1/\tau^*$ is of order $\max(T, \omega)$ before it saturates. According to the MFL theory, however, it is not $1/\tau^*$ but the imaginary part of the quasi-particle self energy $\Sigma_2$ that has the form $-\Sigma_2 = \lambda \max(\pi T, \omega)$, as long as $\omega \lt \omega_c \approx 1000$ cm$^{-1}$. Thus $\Sigma_2$ would change from constant to linear in $\omega$ at $\omega > \pi T$. At low $\omega$, our results agree with this prediction, and $\Sigma_2$ tends to saturate at frequencies above $\omega_c$. Since $\lambda$ is in principle $T$-independent, one expects the slope of $\Sigma_2(\omega)$ to be constant at all temperatures in MFL theory. However, our data indicate a gradual decrease of slope with increasing temperature.

It is difficult to interpret the frequency dependent scattering rate as a consequence of inelastic scattering due to Holstein effect,$^{107,108}$ in which a carrier can absorb a photon of energy $\hbar \omega$, emit an excitation (or a phonon) of energy $\varepsilon$ ($\varepsilon \sim 300$ cm$^{-1}$ in this case), and scatter. First, the large value of $\lambda$ ($\sim 3$) derived from our data of Fig. 34 suggests a strong coupling between the conduction carriers and the excitation.
Therefore at $T > \varepsilon \sim 400$ K, the dc resistivity should significantly deviate from its linear $T$-dependent behavior. Such a large $\lambda$ would also imply that the mean free path is of the same order of the lattice constant at room temperature, thus the dc resistivity would be expected to saturate, inconsistent with the observed linear behavior which persists up to 1100 K for LSCO materials.\textsuperscript{61} Second, the Holstein sideband would shift upwards by $2\Delta$, the threshold energy for exciting two quasiparticles, in the superconducting state. On the contrary, our spectra in Fig. 23 do not show such shift. However, this structure could have been smeared out as the size of the Holstein effect depends sensitively on the shape of Eliashberg function $\alpha^2 F(\Omega)$ and impurity scattering.\textsuperscript{106} The possibility of Holstein effect therefore may not be completely ruled out.

**Loss Function**

In the temperature-dependent reflectance spectra of Figs. 21 and 22, we have observed that the reflectivity edge sharpens and slightly moves to higher frequency with decreasing temperature. This may be attributed mainly to the effect of volume contraction. The behavior can also been seen in the electronic loss function $\text{Im}(1/\epsilon)$ as demonstrated in Fig. 36. Upon cooling, the peak position at the screened plasma frequency $\tilde{\omega}_p \approx 6400 \text{ cm}^{-1} (\sim 0.8 \text{ eV})$ shifts to slightly higher energies along with a slight narrowing of the broad peak. This can be understood in terms of the generalized Drude model, in which the maximum value in $-\text{Im}(1/\epsilon)$ is given approximately by $\tilde{\omega}_p \tau^* (\tilde{\omega}_p) / \epsilon_h$ at $\omega = \tilde{\omega}_p \approx \omega_p / \sqrt{\epsilon_h}$ with a width of $1/\tau^*(\tilde{\omega}_p)$. This broad width (0.4 eV) is caused by the anomalous mid-infrared background absorption.

Bozovic\textsuperscript{115} found that $-\text{Im}(1/\epsilon) = \beta \omega^2$ for small $\omega$ in both Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O, and conjectured that the quadratic law to be universal for all layered cuprate superconductors. In addition, it has been suggested that the two-component oscillator model fails to reproduce accurately the experimental loss function.\textsuperscript{115} After
making careful analysis on our $\La_{2-x}\Sr_x\CuO_4$ film, however, we find our results do not support these conclusions. By using the dielectric function with a two-component model in the form of Eq. (81) to fit the room temperature reflectance, we obtain a set of oscillator parameters which can almost exactly reproduce the measured $\Re(\omega)$ as shown in the upper inset to Fig. 36. The oscillator parameters are listed in Table 5. When the same set of parameters is used to calculate the loss function, we see an excellent fit to the experimental $-\Im(1/\epsilon)$ curve throughout the entire measured range as illustrated in the main part of Fig. 36. We want to stress here that the peak in $-\Im(1/\epsilon)$ is determined not only by the free carriers, but also by the bound carriers participating the charge transfer and interband transitions. The loss function can be well fit only after the interband oscillators are taken into account.

When looking into the small $\omega$ behavior of the loss function, we note, for our film, the low-frequency quadratic law $-\Im(1/\epsilon) \sim \omega^2$ suggested by Bozovic et al.\textsuperscript{115,116} is valid only at low temperatures (or at higher frequencies). A linear $\omega$ dependence, instead, is more appropriate for high temperatures. The result is more evident when our data are plotted in log-log scale as shown in the lower inset of Fig. 36. This result can be understood quantitatively in the one-component approach. Starting with Eq. (95), one can derive the approximation for $\omega \ll \omega_p$:

$$-\Im(1/\epsilon) \approx -\frac{\omega \Sigma_2}{\omega_p^2} \propto -\omega \Sigma_2,$$

(98)

where $\omega_p = 13,000$ cm$^{-1}$ for our film. If $\Sigma_2$ has the form of $-\Sigma_2 = \lambda \max(\pi T, \omega)$ as suggested by Fig. 34, then $-\Im(1/\epsilon)$ will be quadratic in $\omega$ when $T < \omega/\pi$ but linear in $\omega$ when $T > \omega/\pi$. We can see the 300 K curve in the inset changes its slope at $\omega_c \simeq 700$ cm$^{-1} \sim \pi T$, giving a $\sim \omega^2$ dependence above $\omega_c$ and an $\omega$-linear dependence below $\omega_c$. [In fact, the 50 K curve also becomes linear in $\omega$ at frequencies below 100 cm$^{-1} \sim \pi T$ (not shown).] This behavior can also be explained qualitatively in the
Table 5. Parameters of a two-component oscillator fit to the measured $\mathcal{R}(\omega)$ at room temperature for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

<table>
<thead>
<tr>
<th>Oscillator #</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>$\omega_p$ (cm$^{-1}$)</th>
<th>$\gamma$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>0</td>
<td>6240</td>
<td>358</td>
</tr>
<tr>
<td>Mid-IR #1</td>
<td>250</td>
<td>2320</td>
<td>210</td>
</tr>
<tr>
<td>Mid-IR #2</td>
<td>950</td>
<td>10640</td>
<td>2850</td>
</tr>
<tr>
<td>Mid-IR #3</td>
<td>3180</td>
<td>6580</td>
<td>4330</td>
</tr>
<tr>
<td>Phonon #1</td>
<td>126</td>
<td>750</td>
<td>28</td>
</tr>
<tr>
<td>Phonon #2</td>
<td>359</td>
<td>455</td>
<td>22</td>
</tr>
<tr>
<td>Phonon #3</td>
<td>681</td>
<td>450</td>
<td>25</td>
</tr>
<tr>
<td>CT-band</td>
<td>11260</td>
<td>6720</td>
<td>4820</td>
</tr>
<tr>
<td>Interband #1</td>
<td>23650</td>
<td>16620</td>
<td>15630</td>
</tr>
<tr>
<td>Interband #2</td>
<td>59370</td>
<td>94290</td>
<td>33410</td>
</tr>
</tbody>
</table>

$\epsilon_\infty = 1.5$

two-component analysis. At small $\omega$, the dielectric function $\epsilon(\omega)$ is dominated by the Drude term, thus the loss function exhibits the ordinary $\omega$-linear dependence. At higher frequencies, the mid-infrared tail becomes important, causing the loss function to deviate from this linear behavior.

The Superconducting Gap

In the conventional BCS superconductors, it has been demonstrated successfully that the superconducting-to-normal ratio in transmission$^{4,5,117}$ would give a maximum very near $2\Delta$, the superconducting gap energy. Other experiments$^{7,8}$ showed
that the gap corresponded to a threshold in conductivity or surface resistance. Many attempts have been made to identify the superconducting gap of HTSC at the peak in the reflectance ratio $R_s(T)/R_n$ or at the onset of the conductivity $\sigma_{1s}(\omega)$. However, it is problematic to make such assignments. First, the reflectance data (see Fig. 22, for example) do not exhibit a clear edge. Second, the phonon structure and MIR absorption tail as well as the $T$-dependence of the scattering rate complicate this approach. Finally, the propagated errors in $\sigma_{1s}(\omega)$ at low frequencies are large due to the fact that $R(\omega)\rightarrow 1$. Since the experimental accuracy in $R(\omega)$ is not much better than $\pm 0.5\%$, we can estimate the uncertainties in $\sigma_1(\omega)$ by rescaling the reflectance level up and down by $0.5\%$, respectively, and performing the KK transformation to obtain the corresponding $\sigma_1(\omega)$ as illustrated in Fig. 37. The propagated uncertainty appears roughly $\Delta \sigma_1/\sigma_1 = \left(\frac{1}{1-\frac{\Delta R}{R}}\right)(\Delta R/R)$. As we can see, the absorption edge of $\sigma_{1s}(\omega)$, whose value ($\sim 3.7\ k_B T_c$) appears to coincide with the prediction by BCS theory, is largely dependent on the accuracy of $R(\omega)$. This prevents a precise gap assignment based on the onset of $\sigma_{1s}$.

Kamarás et al. have argued that a superconducting gap can not be unambiguously identified in the infrared spectra if the material is in the clean limit, $1/\tau \ll 2\Delta$ or $l \gg \xi$, with $l$ the electronic mean free path and $\xi$ the coherence length. In our sample, the free carrier relaxation rate is $1/\tau \sim 2.5\ k_B T_c$ at $50\ K$ ($\tau = 0.1$ pico-second), smaller than the expected BCS superconducting gap. One expects an even smaller value of $1/\tau$ well below $T_c$ thus the clean limit condition will be met. This low free-carrier relaxation rate implies that most of the free-carrier oscillator strength would move to the zero-frequency delta function of the superconductor, leaving little strength—only a factor $1/(\pi \tau \Delta)$ of the Drude spectral weight—available for the gap transition. As seen in Fig. 28, there is already considerable second component (MIR) absorption in the low frequency region, making it likely that any remaining gap structure is obscured by the intense mid-infrared absorption.
Summary

In this chapter, we presented a set of temperature- and frequency-dependent optical spectral functions from the far-infrared through the ultraviolet region. We made a systematic analysis for an epitaxial $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ thin film with a transition temperature $T_c = 31$ K. We emphasized the two-component analysis for both the normal and superconducting states. Then we discussed the alternative of a one-component approach.

Our results show that the temperature dependence of the $ab$-plane infrared phonons is sensitive to the tetragonal-to-orthorhombic phase transition near 250 K. One anomalous behavior which appears to be associated with the structural transition is that the reflectance in the charge-transfer region is significantly depressed below 250 K, implying a shift of spectral weight to the higher energy region. The electronic behavior is similar to that observed in other cuprate superconductors like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ or $\text{BiSrCaCuO}$ crystals. On the other hand, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ crystal has a lower free-carrier concentration but a higher phonon oscillator strength on the CuO$_2$ layers. The normal state infrared properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ materials exhibit an extremely unusual non-Drude response over most of the infrared range. This anomalous behavior can be interpreted either by absorptions due to free- and bound-carriers in two-component approach, or by a strong frequency dependent scattering rate and a mass enhancement in a single-component approach.

The two-component picture analysis shows a narrow (of order $k_BT$) Drude absorption and a broad, strong mid-infrared band. The Drude plasma frequency is essentially temperature independent, whereas the scattering rate is roughly linear in $T$ in the normal state followed by a fast drop below $T_c$. A weak coupling strength $\lambda \sim 0.25$ is derived. The mid-infrared absorption exhibits a weak temperature dependence in the normal state. In the superconducting state, the absorption is similar to the mid-infrared band, but is enhanced in the 150–1500 cm$^{-1}$ range. The super-
conducting condensate carries most (\(\sim 85\%\)) of the free-carrier oscillator strength. A superconducting gap is not discernible as the film is near the clean limit. The absorption edge near 80 cm\(^{-1}\) or 400 cm\(^{-1}\) can not be assigned as the superconducting gap and is attributed to the tail of low-energy excitations or to the strong bound carrier/phonon coupling. The single-component picture analysis in the normal state shows a strongly frequency dependent scattering rate of the order \(k_B T + \hbar \omega\) at low frequencies and a large mass enhancement, which leads to a strong coupling strength \(\lambda \sim 3\). This analysis has the features predicted by marginal Fermi liquid or nested Fermi liquid, but has a temperature dependent slope in the imaginary part of the quasiparticle self-energy.
Fig. 22. Measured reflectance $R(\omega)$ at selected temperatures between 5 K and 300 K. The inset shows the same data over the entire measured frequency range (note the logarithmic frequency scale).
Fig. 23. The real part of the \(ab\)-plane conductivity \(\sigma_1(\omega)\) derived from the Kramers-Kronig transformation of the reflectance data in Fig. 22. The inset shows the entire measured frequency range.
Fig. 24. The in-plane phonon frequency as a function of temperature. (The lines are guides for the eyes.) For comparison, the inset shows the results of Keane et al. (Ref. 91) for the $T$-dependent $ab$-plane lattice constants of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. 
Fig. 25. The imaginary part of the conductivity, \( \sigma_2(\omega) \), showing the inductive response. The inset plots the same data in the entire measured frequency range, showing the zero crossing near the screened plasma frequency.
Fig. 26. The Drude conductivity, obtained by subtracting the averaged mid-infrared contribution from the total conductivity as explained in the text on p. 80. The solid lines are Drude fits to the data.
Fig. 27. Drude scattering rate, $1/\tau$, as a function of temperature. For comparison, it shows the values obtained from fits to the infrared conductivity (diamond symbols) and the ones estimated from the measured dc resistivity (dashed lines). Note both of these two cases exhibit a small negative intercept due to a slight deviation from $T$-linear dependence. This is illustrated in the inset plotted on a log-log scale. The slope of the solid straight line gives a power of 1.1 instead of 1 to temperature $T$. Below $T_c$, the quasiparticle damping rate has a sudden drop and goes roughly as $1/\tau \sim T^2$. 
Fig. 28. $\sigma_{1\text{MIR}}$, the frequency dependent conductivity with Drude contribution subtracted. The data fall into three groups, 5–30 K, 50–200 K, and $\geq 250$ K.
Fig. 29. Averaged mid-infrared conductivity in the normal and superconducting states. Also shown is the difference between them. The dash-dotted curve is a calculation within the framework of Holstein theory.
Fig. 30. The ratio of the real part of the conductivity in the superconducting state to an estimated normal-state conductivity at the same temperature. For comparison, the inset demonstrates the ratio of the conductivity at a temperature $T$ to that at a fixed temperature of 100 K.
Fig. 31. Real part of the dielectric function $\varepsilon_1$ against $\omega^{-2}$ below $T_c$. The frequency range shown is 45–300 cm$^{-1}$. Inset: $\varepsilon_1$ versus $\omega$ at 5, 200 and 300 K, illustrating the $\omega$-dependent metallic response and the zero-crossing near the plasma edge (\~{}6000 cm$^{-1}$).
Fig. 32. Effective carrier density per Cu atom, $N_{\text{eff}} m/m_b$, as a function of frequency for various temperatures. The data are obtained from the area under the curves of $\sigma_1(\omega)$. The spectral weight of the superfluid condensate can be estimated from the difference of $N_{\text{eff}} m/m_b$ in the normal and superconducting states. The inset illustrates the behavior at higher energy for $T = 100, 300$ K where the high-frequency reflectivity data of Tajima et al. (Ref. 27) have been utilized.
Fig. 33. Temperature dependence of the Drude plasma frequency $\omega_{PD}(T)$, the superconducting plasma frequency $\omega_{ps}(T)$, and the superfluid density $f_s(T) = n_s(T)/n$. The solid lines for $\omega_{ps}$ and $f_s$ are calculated in the framework of the BCS theory, taking $f_s(0) = 0.85$ and $T_c = 31$ K. (The dash-dotted lines connecting points for $\omega_{PD}$ are guides to the eye.)
Fig. 34. Frequency-dependent mass enhancement (lower panel) and imaginary part of the self energy (upper panel) derived from the experimental complex dielectric function with interband contributions subtracted.
Fig. 35. Renormalized scattering rate given by $1/\tau^* = -(m_b/m^*)\Sigma_2$. 

Photon Energy (eV)

820-nm La$_{2-x}$Sr$_x$CuO$_4$ film

$1/\tau^*$ (cm$^{-1}$)

$\omega$ (cm$^{-1}$)

300 K
250 K
200 K
150 K
100 K
50 K
Fig. 36. Energy-loss function calculated from the Kramers-Kronig analysis of $\mathcal{R}(\omega)$ at selected temperatures. The solid line for $-\text{Im}(1/\varepsilon)$ in the main figure is calculated using the oscillator parameters (Table 5) obtained from a two-component model fit to $\mathcal{R}(\omega)$, shown in the upper inset. The lower inset illustrates the different low $\omega$-dependent behavior of the loss function at 50 and 300 K.
Fig. 37. The propagated uncertainty in values of the conductivity derived from the reflectance $R$, in which $R$ is close to unity and has uncertainty of $\pm 0.5\%$. The absorption onset in $\sigma_1(\omega)$ is sensitively dependent on the accuracy of $R(\omega)$. 
CHAPTER VIII
FAR-INFRARED STUDIES OF YBa2Cu3O7−δ FILMS

In this chapter, we present the results of a detailed study of the far-infrared properties of three YBa2Cu3O7−δ thin films, the materials with Tc above the liquid nitrogen boiling point. Both the transmittance (T) and reflectance (R) have been measured over the frequency range from 20 to 360 cm−1 at temperatures between 20 and 300 K. The films, grown on MgO substrates by pulsed laser ablation, are highly a-b-plane oriented. The characteristics of the samples have been listed in Table 3 on p. 56, and the dc resistivity has been presented in Fig. 16.

We use T and R to extract directly the optical conductivity without referring to the Kramers-Kronig relations, and find good agreement with results from Kramers-Kronig analysis of reflectance measurements alone. Although we have used different techniques, the results for the YBa2Cu3O7−δ films are in many ways similar to that of La2−xSrxCuO4 films discussed in the previous chapter. The transmittance is consistent with a two-component dielectric function consisting of Drude (free-carrier) and midinfrared (bound-carrier) absorption. Like the La2−xSrxCuO4 film, a superconducting gap for the YBa2Cu3O7−δ films is not observed in our spectra. There are some differences, however, compared with La2−xSrxCuO4. First, the transition temperature is much higher, thus the energy gap is expected larger. Second, the carrier density is higher, causing a larger plasma frequency. Third, no vibrational features are visible in the ab-plane spectra.

In agreement with earlier studies, we find a nearly T-independent non-Drude absorption in the far-infrared region below 300 cm−1. The temperature dependence of the normal-state Drude parameters agrees with the independently measured dc
resistivity of the same samples. Using a two-fluid model to fit the transmittance data in the superconducting state, we observe that the Drude contribution, which is still present, drops rapidly with decreasing temperature, suggesting that the normal carriers responsible for the dc transport condense rapidly into a superfluid state. The low-frequency tail of the mid-infrared band remains for $T \ll T_c$.

Results and Discussion

We focused our attention on the far-infrared region below 350 cm$^{-1}$ since the MgO substrate is opaque just above 350 cm$^{-1}$ at all temperatures due to a TO-phonon mode near 400 cm$^{-1}$. To average over interference fringes due to multiple internal reflections in the substrate, as stated on p. 23 and to be illustrated on p. 166, the measurements were made at relatively low resolution and interpolated to give smooth curves. In addition, we carefully measured both the reflectance $R_{\text{sub}}$ and transmittance $T_{\text{sub}}$ for a bare MgO substrate.

The spectra of the substrate are shown in Fig. 38. The transmittance indicates that MgO is reasonably transmitting below 300 cm$^{-1}$ for $T \leq 100$ K, reaching nearly 60% and with almost no absorption below 100 cm$^{-1}$. There is structure near 100, 155, and 290 cm$^{-1}$ caused by multiphonon processes. At low temperatures, the MgO acoustic phonons are frozen near the origin (zone center) and thus only those photons of energy higher than the TO phonon energy ($\sim 400$ cm$^{-1}$) can be strongly absorbed, resulting only small absorptions below this frequency. At higher temperatures, however, the acoustic phonons are thermally excited to populate up to the zone boundary. Therefore photons of energy less than 400 cm$^{-1}$ can now be absorbed as long as their energies are sufficient to excite the phonons across the gaps from the TA branch to the TO branch. In other words, phonon difference processes cause absorption below the TO-phonon frequency. The upper panel of Fig. 38 shows that MgO is $\sim 40\%$ reflecting for all temperatures at low frequencies, which means no absorption
in this frequency regime, for the rest 60% incident light is transmitted through the film as seen in the lower panel of Fig. 38. In the range $100 < \omega < 280 \text{ cm}^{-1}$, the incident light does not see the back surface of the substrate for $T > 200 \text{ K}$ due to multiphonon absorption processes. At lower temperatures, these processes are suppressed hence light can reach the back surface and is bounce back, causing a higher reflectance. At $\omega > 280 \text{ cm}^{-1}$, however, the reflectance is $T$-independent due to a strong TO-phonon absorption at all temperatures. This phonon absorption also affects the transmittance of the YBa$_2$Cu$_3$O$_{7-\delta}$/MgO samples. To account for substrate absorption, the frequency-dependent absorption coefficient $\alpha$ and the index of refraction $n$ of the MgO, shown in Fig. 39, were determined by solving $R_{sub}(\alpha, n)$ and $T_{sub}(\alpha, n)$ according to Eqs. (38) and (39). The computer software for this computation is presented in Appendix B. The dispersive curves, $n(\omega)$, are nearly constant in frequency and temperature, whereas the absorptive curves, $\alpha(\omega)$, show a strong dependence on both $\omega$ and $T$. The results of $n(\omega)$ and $\alpha(\omega)$ were used in analysis of the data for the films.

The upper and middle panels of Fig. 40 show the reflectance and transmittance of a 1800-Å YBa$_2$Cu$_3$O$_7$ film on MgO. The reflectance is well below unity in the normal state at all frequencies. It is greatly enhanced in the superconducting state and very nearly 100% for frequencies below 150 cm$^{-1}$. Unlike the La$_{2-z}$Sr$_z$CuO$_4$ film discussed, the $a$-$b$-plane YBa$_2$Cu$_3$O$_{7-\delta}$ phonons, strongly screened by free carriers, are not visible in the spectra and the $c$-axis phonons are not probed since we are sensing solely $a$-$b$-plane response.$^{45,46}$ The $T$ spectra, with overall levels of less than 0.5%, are complicated by the MgO substrate which must be dealt with properly to extract the frequency-dependent optical conductivity. However, the transmittance approaches zero at low frequencies for $T < T_c$, as expected for a superconductor.

The bottom panel of Fig. 40 is the conductivity derived from $R$ and $T$ using the technique described on p. 20–24. In the normal state, the conductivity is nearly
equal to the dc conductivity at low frequencies but has a non-Drude (midinfrared) contribution at higher frequencies. Below $T_c$, when the Drude part condenses, the remaining conductivity—with overall level of 1500 ($\Omega \text{ cm}$)$^{-1}$—can be attributed to the low-frequency part of the midinfrared absorption. These results are similar to those previously obtained by Kramers-Kronig analysis of reflectance.$^{31-35,40-44}$

Figure 41 presents the complex conductivity of a 1560-Å thick YBa$_2$Cu$_3$O$_{7-\delta}$ film. The real part, $\sigma_1$, has similar features to the 1800-Å film discussed above. The imaginary part, $\sigma_2$, increase monotonically with decreasing temperatures, similar to that show in Fig. 25. At $T < T_c$, $\sigma_2$ exhibits a $A/\omega$ dependence for $\omega \leq 100$ cm$^{-1}$, where $A$ is a constant. This behavior agree with the prediction of Eq. (47). The constant $A$ is associated to the strength of superconducting condensate and the London penetration depth. However, at $\omega > 100$ cm$^{-1}$, $\sigma_2$ falls off much slowly and deviates significantly from the $1/\omega$ dependence.

The real conductivity, $\sigma_1$, obtained for all three films in the superconducting state has large errors below 150 cm$^{-1}$, because the reflectance is nearly 100%. The conductivity is

$$\sigma_1 = \frac{cn}{4\pi d} \frac{1 - \mathcal{R}_f - \mathcal{I}_f}{\mathcal{I}_f}.$$ 

As $\mathcal{R}_f \rightarrow 1 \pm$ noise, the accuracy of the conductivity becomes small, with systematic error in the reflectance level becoming dominant in the conductivity extraction. Once the errors in $\mathcal{R}$ are comparable to the magnitude of $\mathcal{I}$, the method breaks down completely. This is the case below $T_c$ for most of our measurements. (A similar problem occurs in Kramers-Kronig analysis of highly reflecting bulk samples.$^{35}$) The use of $\mathcal{R}$ and $\mathcal{I}$ to find $\sigma_1$ is most accurate when $\mathcal{R} \approx \mathcal{I} < 0.5$. For this condition to hold, we would need $\sim$ 50-Å films. (Such ultra-thin films are available recently, and the spectra of which will be presented in Appendix A.) We note that transmittance is more reliable than reflectance because very high accuracy in $\mathcal{I}$ is not required and
the propagated errors to $\sigma_1(\omega)$ from $\mathcal{I}(\omega)$ are generally much smaller than that from $\mathcal{R}(\omega)$. Furthermore, transmittance is more sensitive to the changes in $\sigma_1$ and $\sigma_2$ because it probes the entire sample thickness. Thus in the remainder of this paper we will emphasize transmittance data.

**Free-Standing Transmittance $\mathcal{I}_f$**

Figure 42 shows the “free-standing” transmittance, calculated from Eq. (24) for three films at temperatures between 20 and 200 K. The absorption and dispersion in the substrate have been removed in these curves; the refractive index has been set to $n = 1$. Note that the data below $T_c$ extrapolate to zero, indicating that the inductive response of the superconductor dominates at these frequencies, as expected and shown in Fig. 41. At the higher temperatures, the slope of $\mathcal{I}_f$ changes sign; the transmittance decreases with increasing frequency. This behavior is consistent with a two-component (Drude plus midinfrared) infrared conductivity but is inconsistent with either simple Drude behavior or with a generalized Drude conductivity having a frequency-dependent scattering rate of the form $1/\tau = \max(\omega, k_B T/\hbar)$, as suggested by models of marginal Fermi liquids$^{37}$ and nested Fermi liquids.$^{39}$ If the admittance is large (the case here, where $\mathcal{I}_f \ll \mathcal{I}_{\text{sub}}$), then $\mathcal{I}_f \propto (1/|\sigma|^2)$ or

$$\mathcal{I}_f = 4n(c/d)^2 \frac{1/\tau^2 + \omega^2}{\omega_p^4},$$

where $\omega_p$ is the plasma frequency and $1/\tau$ is the free-carrier scattering rate. Whether $1/\tau$ is constant or increasing with $\omega$, the transmittance will increase with $\omega$, in disagreement with the higher-temperature data of Fig. 42.

In a two-component picture, the decreasing transmittance is a consequence of the midinfrared absorption. At high temperatures, the Drude absorption is quite broad and overlaps the midinfrared band. Thus, as $\omega$ increases, the total conductivity $\sigma_1$ (Drude plus midinfrared), as seen in Figs 40 and 41, increases thus $\mathcal{I}_f$ decreases.
Two-Fluid Model Fit

We have used simple models\textsuperscript{31,34,35,40,47} for the two components in order to fit the transmittance data. In the normal state, the dielectric function is a sum of a narrow Drude band, broad midinfrared Lorentzians, and high-frequency contribution as discussed in chapter III:

\[ \epsilon(\omega) = \epsilon_{Drude} + \epsilon_{mid-ir} + \epsilon_{\infty} \quad (T > T_c), \quad (101) \]

where \( \epsilon_{mid-ir} \) accounts for the absorption described by oscillators centered at midinfrared region, and \( \epsilon_{\infty} \) is the contributions from excitations at frequencies above \( \sim 1000 \text{ cm}^{-1} \).

In the superconducting state, to accommodate temperatures near \( T_c \), we assumed the Drude contribution remains due to some fraction of nonsuperconducting carriers. Thus, we tried a two-fluid model:

\[ \epsilon(\omega) = (1 - f_s)\epsilon_{Drude} + f_s\epsilon_{sup} + \epsilon_{mid-ir} + \epsilon_{\infty} \quad (T < T_c), \quad (102) \]

where \( \epsilon_{Drude}, \epsilon_{mid-ir}, \) and \( \epsilon_{\infty} \) are the same as those in Eq. (101), \( f_s \) is the fraction of the free-carrier electron density in the superfluid, and

\[ \epsilon_{sup} = \frac{\omega_p^2}{\omega^2} + i \frac{\pi \omega_p^2}{2\omega} \delta(\omega). \quad (103) \]

The details of the fit are rather complicated because of the many parameters. We have tried to reduce these to as few as possible, particularly the temperature-dependent ones. Because the data extend only to 350 cm\(^{-1}\), we fixed the parameters (of all three films) for the higher mid-ir oscillator at center frequency \( \omega_2 = 720 \text{ cm}^{-1} \), strength \( \omega_p^2 = 10\,000 \text{ cm}^{-1} \), and width \( \gamma_2 = 1400 \text{ cm}^{-1} \) as suggested by Ref. 35. In
Table 6. The nearly temperature independent oscillator parameters obtained from a two-fluid model fit to the measured transmittance of three YBa$_2$Cu$_3$O$_{7-\delta}$ films for all temperatures.

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>$\omega_p$ (cm$^{-1}$)</th>
<th>$\omega_{p1}$ (cm$^{-1}$)</th>
<th>$\omega_1$ (cm$^{-1}$)</th>
<th>$\gamma$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>7700</td>
<td>9900</td>
<td>200</td>
<td>750</td>
</tr>
<tr>
<td>1560</td>
<td>10000</td>
<td>9700</td>
<td>280</td>
<td>700</td>
</tr>
<tr>
<td>1800</td>
<td>9400</td>
<td>7800</td>
<td>200</td>
<td>700</td>
</tr>
</tbody>
</table>

In addition, we fixed $\epsilon_{\infty} = 25$. Then we varied the Drude parameters $\omega_p$ and $1/\tau$ as well as the fraction $f_s$ and the lower mid-IR oscillator, at $\omega_1 \approx 200$ cm$^{-1}$. In other words, we varied six parameters ($\omega_p$, $1/\tau$, $f_s$, $\omega_1$, $\omega_{p1}$, and $\gamma_1$). However, we found that we could obtain good fits by making $\omega_p$, $\omega_{p1}$, $\omega_1$, and $\gamma_1$ temperature independent. Table 6 lists these $T$-independent parameters.

We attribute the difference in oscillator strengths among the films in part to uncertainties in the film thickness. Because the transmittance is governed by $y = Z_0 d \sigma$, errors in $d$ gives equal errors in $\omega_p^2$ and $\omega_{p1}^2$.

Figure 43 shows the transmittance raw data (as dots, with a symbol on very 20th point for identification purposes) of a 480-Å film at selected temperatures. The solid curves are model fits. It appears the models give excellent fits to the experimental data both in the normal and superconducting states.
Relaxation Rate and Superfluid Condensate

Like the La$_{2-x}$Sr$_x$CuO$_4$ film described in the previous chapter, we also found that the relaxation rate for YBa$_2$Cu$_3$O$_{7-\delta}$ at $T > T_c$ was linear in temperature, $1/\tau \approx 2.8 \, k_B T$, with a nearly zero intercept. Below $T_c$ the two-fluid model gave a rather sudden drop in $1/\tau$ near $T_c$, with saturation at $T \simeq 50$ K and below. It suggests a strong suppression of the scattering channel upon superconducting transition in response to a gap opening. The possible dumping mechanism below $T_c$ has been discussed on p. 82. This striking feature seems a unique properties of high temperature superconductors, as the ordinary phonon scattering is not expected to change the quasiparticle lifetime dramatically at $T_c$.

Figure 44(a) shows the temperature dependence of $1/\tau$. This is compared with $(1/\tau)_{dc}$ determined from the measured four-probe dc resistivity $\rho_{dc}$ according to

$$
(1/\tau)_{dc} = \frac{\omega_p^2}{4\pi} \rho_{dc},
$$

where $\omega_p$ is the plasma frequency from the fit to $\mathcal{S}$. The magnitude of $(1/\tau)_{dc}$ is about 30% higher than that of the far-infrared (FIR) relaxation rate $(1/\tau)_{FIR}$. We note that the slopes of the two determinations are the same; it is the $T = 0$ intercept which is higher in the dc case. Taking $v_F = 2 \times 10^7$ cm/sec, and using our relaxation rate of $1/\tau \approx 180$ cm$^{-1}$ at 100 K, we can estimate the mean free path $l = v_F \tau = 60$ Å.

Figure 44(b) shows the temperature dependence of the superfluid electron density fraction $f_s(T)$. This quantity dominates and is determined by the low-frequency behavior of the transmittance. As can be seen in Fig. 43, $\mathcal{S}$ changes substantially through the superconducting transition with even a sign change in the slope of the curve. Thus, despite the relatively large number of parameters in our model, the quantity $f_s$ is well determined by the data. Note that $f_s = 0$ above $T_c$. Below $T_c$, the normal carriers condense rapidly into the superfluid; hence, $f_s$ increases as
temperature drops. The curves in Fig. 44(b) correspond to the behavior of $f_s(T)$ in BCS theory,

$$f_s = f_{s0} \left[ \frac{\Delta(T)}{\Delta_0} \right]^2,$$  \hspace{1cm} (105)

where $f_{s0}$ is the zero-temperature value, $\Delta(T)$ is the temperature-dependent BCS order parameters, and $\Delta_0$ its $T = 0$ value. Although $f_s$ never reaches 1, it appears that this two-fluid model gives otherwise a good description of the temperature dependence of the order parameter. We are unable to determine whether the $\sim 30-50\%$ remaining Drude oscillator strength in the two thinner films is due to a defective layer or is intrinsic to the material. However, the superconducting fraction for the thickest film (1800 Å) at $T \ll T_c$ approaches $f_s \approx 0.87$, which is extremely close to the value (85%) obtained previously from the La$_2$-zSr$_z$CuO$_4$ film (see Fig. 33 and the discussion on p. 86). This surprising agreement is a further confirmation that a small part of the free carriers do not condense into pairs at $T \ll T_c$, and the spectral weight responsible for this part shifts to higher energy region. From the values of $f_s$ and $\omega_p$ for this film, the penetration depth is estimated to be 1800 Å.

"Coherence Peak"

One of the interesting results found in this work was that the conductivity at low frequencies exhibited a peak below $T_c$, shown in Fig. 45. The data in the figure were obtained directly from the experimental conductivity derived from $\mathcal{R}(\omega)$ and $\mathcal{I}(\omega)$ of the films. This feature resembled the case II coherence effect found in classical superconductors. We note that the actual coherence peak predicted and observed was not in $\sigma_{1s}(T)$, but in the ratio of the superconducting-to-normal state conductivity.$^{71}$

In order to see how this peak in $\sigma_{1s}(T)/\sigma_{1n}(T)$ occurs, we use a simplistic model and ignore the coherence effect in a Drude formula at $\omega = 0$:

$$\sigma_1 = \omega_p^2 \tau / 4\pi.$$  \hspace{1cm} (106)
In the superconducting state, the quasi-particle plasma frequency is given by \( \omega^2_{pq} = (1 - f_s)\omega^2_p \) (taking the quasi-particles to be a normal fluid in the superconducting state), thus the ratio can be estimated to be

\[
\frac{\sigma_{1s}(T)}{\sigma_{1n}(T)} = \frac{(1 - f_s)\tau_s}{\tau_n}.
\] (107)

At \( T > T_c \), the ratio in Eq. (107) is unity because \( f_s = 0 \) and \( \tau_s = \tau_n \). To remove the \( T \)-linear dependence of the "normal-state" dc resistivity below \( T_c \), we can make a linear extrapolation of \( 1/\tau \), shown in Fig. 44(a), to obtain \( \tau_n \) for \( T < T_c \). The \( 1/\tau \) data below \( T_c \) in Fig. 44(a) can be used as the "superconducting-state" scattering rate, \( 1/\tau_s \), and \( f_s \) is taken from the results of Fig. 44(b). The calculated result based in this simple model is shown in Fig. 46, in which a peak is seen just below \( T_c \), resembling the picture of Fig. 4. However, since such a peak is absent in the nuclear relaxation rate of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) as reported by Hammel et al.,\(^{119} \) it naturally can not be associated with the BCS case II coherence effect. Rather, the peak is due to the dramatic decrease in the quasiparticle damping rate below \( T_c \), and is a result of the competition between the decreased plasma frequency (\( \omega_{pq} \)) and the increased relaxation time (\( \tau_s \)) of the quasiparticles with decreasing temperature.

**Mid-Infrared Band and Superconducting Gap**

In contrast to \( 1/\tau \), the midinfrared band has very little temperature dependence, in agreement with the similar results reported from reflectance measurements.\(^3^5 \) We noticed that the overall size and shape of the midinfrared contribution to the conductivity remained almost unchanged at all temperatures.

Finally, there is no evidence in our spectra for a superconducting gap in the 50–30 cm\(^{-1} \) region at any temperature. This is illustrated in Fig. 47, which shows the free-standing transmittance for our 480-Å film for four temperatures below \( T_c \). In an ordinary superconducting film,\(^6^9,^{12}0 \) the transmission increases up to the gap energy
2\Delta$, where there is a maximum followed by a drop at higher frequencies, due to the increasing $\sigma_1(\omega)$ above the gap. No such structure is seen in our data. This can be understood within a "clean-limit" picture;\textsuperscript{35} the relaxation rate of the free carriers is $\sim 200$ cm$^{-1}$ at 100 K, smaller than the gap expected for a BCS superconductor with $T_c = 90$ K. Thus most of the free-carrier oscillator strength is at frequencies below $2\Delta$, leaving little strength for transition across the gap. Any remaining structure is masked by the tail of the midinfrared absorption.

To show the effect of a gap in the intermediate limit, we have calculated the transmittance within the Leplae\textsuperscript{121} model for our 480-Å film. The Mattis-Bardeen theory described by Eq. (59) has the assumption of either the extremely dirty or the extremely clean limit; whereas the Leplae theory does not have this restriction and the conductivity at $T = 0$ is given by\textsuperscript{121}

$$
\sigma_{1s}(\omega) = \begin{cases} 
0, & \hbar\omega \leq 2\Delta \\
\frac{1}{2\hbar\omega} \int_{\Delta}^{\hbar\omega-\Delta} \{ [g(E, E') - 1]\sigma_{1n}(|\varepsilon'| - |\varepsilon|) \\
+ [g(E, E') + 1]\sigma_{1n}(|\varepsilon'| + |\varepsilon|) \} dE. & \hbar\omega \geq 2\Delta
\end{cases}
$$

(108)

where

$$
g(E, E') = (EE' - \Delta^2)/|\varepsilon\varepsilon' - \Delta^2|,$$

$$
\varepsilon = (E^2 - \Delta^2)^{1/2},$$

$$
\varepsilon' = (E'^2 - \Delta^2)^{1/2},$$

$$
E' = \hbar\omega - E.
$$

(109)

The imaginary part of the conductivity can be obtained by the Kramers-Kronig relation:

$$
\sigma_{2s}(\omega) = \frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\sigma_{1s}(\omega')}{\omega^2 - \omega'^2} d\omega' + \frac{2}{\pi\omega} \int_0^\infty \left[ \sigma_{1n}(\omega') - \sigma_{1s}(\omega') \right] d\omega'.
$$

(110)

Once $\sigma_{1s}$ and $\sigma_{2s}$ are determined, the free-standing transmittance can be computed according to Eq. (24). The calculated result is shown as the solid line in
Fig. 47. The parameters used in the calculation were $\omega_p = 7700 \text{ cm}^{-1}$ (from the two-component model fit discussed above), $2\Delta = 225 \text{ cm}^{-1}$, and $1/\tau = 100 \text{ cm}^{-1}$. With these parameters, the calculated transmittance is systematically higher than the measurement. In the intermediate limit, oscillator strength is removed from the zero-frequency $\delta$ function and put into the gap transition. This reduces $\sigma_2$ and increases the calculated transmittance. The calculation could be brought back down to the measured transmittance with an increasing $\omega_p$; however, this would lead to a significant difference in free-carrier oscillator strength above and below $T_c$.

The calculation shows a sharp upwards cusp in the transmittance which is reproduced neither in these data nor in the results of others. As temperature is increased, the cusp in the calculation would weaken and shift to lower frequencies as the value of the $T$-dependent gap is decreased. No such shift is observed in our measurement. Thus our transmission data are more consistent with a clean-limit picture than an intermediate or dirty-limit picture.

**Summary**

Far-infrared transmittance and reflectance spectra for YBa$_2$Cu$_3$O$_{7-\delta}$ thin films show a Drude response and midinfrared absorption in the frequency range below 350 cm$^{-1}$. In the transmittance fits, the plasma frequency is essentially constant, whereas the Drude relaxation rate is linear in $T$ in the normal state and has a dramatic decrease just below $T_c$. The mid-ir absorption, in contrast, is nearly temperature independent both for $T > T_c$ and for $T < T_c$. The two-fluid model works for our samples and implies a BCS-like temperature dependence of the condensate fraction; however, $f_s < 1$ in our samples. A peak is observed in the temperature dependence of the low-frequency conductivity near $T_c$. This behavior is closely related to the observed dramatic decrease of the quasi-particle damping rate upon superconducting
transition. The films are near the clear limit and no distinct gap feature has been found in frequency range below 350 cm$^{-1}$. 
Fig. 38. Reflectance and transmittance of MgO at selected temperatures between 300 K and 7 K.
Fig. 39. Dispersion $n(\omega)$ and absorption $\alpha(\omega)$ of MgO.
Fig. 40. (a) Measured far-infrared reflectance, (b) transmittance, (c) and optical conductivity obtained from $R$ and $I$ of a 1800-Å-thick YBa$_2$Cu$_3$O$_{7-\delta}$ film deposited on a 1-mm-thick MgO substrate.
Figure 41. The real part (upper panel) and imaginary part (lower panel) of the optical conductivity obtained from $\mathcal{R}$ and $\mathcal{I}$ of a 1560-Å-thick $\text{YBa}_2\text{Cu}_3\text{O}_7$ film deposited on a 1-mm-thick MgO substrate.
Fig. 42. Free-standing far-infrared transmittance of three YBa₂Cu₃O₇₋ₓ films at temperatures between 20 and 200 K.
Fig. 43. Measured transmittance (in solid dots and symbols) of a 480-Å $\text{YBa}_2\text{Cu}_3\text{O}_7$ film deposited on a 1-mm-thick MgO substrate at selected temperatures above and below $T_c$. The solid curves are fits to the data using a two-component model for the dielectric function.
Fig. 44. (a) Temperature dependence of Drude scattering rate, $1/\tau$, obtained from fits to the transmittance (in symbols) and estimated from dc resistivity (in solid and dash-dotted lines). (b) Superfluid density, $f_s(T) \equiv n_s(T)/n$, vs. temperature. The curves are $f_s(T)$ as predicted by the BCS theory, taking $f_s(0) = 0.68$ (480 Å), 0.47 (1560 Å), and 0.90 (1800 Å).
Fig. 45. Temperature dependent conductivity at low frequencies for two YBa$_2$Cu$_3$O$_{7-\delta}$ films.
Fig. 46. Conductivity ratio showing a peak near $T_c$. The results are obtained as described in the text. (p. 123)
Fig. 47. Free-standing transmittance of the 480-Å film below $T_c$. The solid curve is a calculation from the Leplae model.
CHAPTER IX
YBa$_2$Cu$_3$O$_{7-\delta}$ POLYCRYSTALLINE SAMPLES

In the early studies of high-$T_c$ superconductors, most of the optical measurements, including ours, were restricted to polycrystalline ceramic samples, in which the spectra show a complicated mixture of in-plane and out-of-plane response. The infrared phonons of these samples showed, however, many interesting features which were distinguished from the behaviors of the $c$-axis phonons in oriented single crystals. Since the optical response of an anisotropic oxide superconductor is characterized by an effective average contribution from the superconducting $ab$-plane and $c$-axis directions, the temperature dependence of the infrared phonon spectra can provide an indirect probe to the electron-phonon interaction, which may relate to the superconductivity.

It is the purpose of this chapter to present and discuss the results of our early work on the fully oxygenated YBa$_2$Cu$_3$O$_{7-\delta}$ ceramic samples ($T_c = 90$ K), and to compare the experimental data with theoretical calculation predicted by a few models of effective medium approximation.

Infrared Spectra and Analysis

Sample characteristics and reannealing treatments have been detailed previously in chapter V, and the optical measurement has been described in chapter VI. The YBa$_{2-x}$Sr$_x$Cu$_3$O$_{7-\delta}$ pellets with $x > 0$ are ignored in this chapter.

Figure 48 shows the far-infrared reflectance $\mathcal{R}(\omega)$ and conductivity $\sigma_1(\omega)$ of a YBa$_2$Cu$_3$O$_{7-\delta}$ polycrystalline pellet at selected temperatures below and above $T_c$, and Fig. 49 displays the entire measured range in logarithmic frequency scale at two temperatures. We can see a systematic variation of $\mathcal{R}(\omega)$ and $\sigma_1(\omega)$ with $T$ in both the normal and superconducting states, but the $T$-dependence at $\omega > 500$ cm$^{-1}$ is
much weaker. The rest of this chapter will concentrate on analysis of the far-infrared spectra below 700 cm\(^{-1}\), within which all vibrational features are visible.

The spectra of the YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) polycrystalline shown in Fig. 48 are analogous in several ways to that of the La\(_{2-x}\)Sr\(_x\)CuO\(_4\) and YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) films discussed in the previous two chapters:

1. \(\mathcal{R}(\omega, T)\) increases with decreasing \(\omega\) and \(T\),
2. \(\mathcal{R}(\omega)\to 1\) at low \(\omega\) for \(T\) below the superconducting transition,
3. \(\sigma_1(\omega)\) consists of an electronic Drude absorption in the normal state at low \(\omega\) and a smooth background at \(\omega > 200\) cm\(^{-1}\) which is attributed to the midinfrared tail.

However, there are some definite differences compared with the oriented films. First, the overall levels of \(\mathcal{R}(\omega)\) and \(\sigma_1(\omega)\) are much lower. Second, the vibrational structures are more distinct and are strongly temperature dependent. The low reflectance or low conductivity of a randomly oriented cuprate superconductor can be easily understood because we are seeing an effective average contribution from the conducting CuO\(_2\) planes and the almost insulating \(c\)-axis directions. As the sample becomes superconducting, the Drude background is suppressed and the phonon lines observed are sharply narrowed.

**Superconducting Condensate**

For the electronic part, we can subtract the contributions from the phonon and midinfrared absorption to estimate the superconducting order parameter by applying the partial sum rule and calculating the missing area, \(A(T)\), below \(T_c\):

\[
A(T) = \int_0^{\omega_c} [\sigma_1(\omega, T) - \sigma_1(\omega, T_c)] \, d\omega \quad T \leq T_c. \tag{111}
\]

Here \(\omega_c\) (\(\sim 5000\) cm\(^{-1}\)) is an arbitrary cut off frequency at which the \(\sigma_1(\omega)\) is essentially \(T\)-independent. The order parameter, shown in Fig. 50, is then given by
\[ \eta(T) = \frac{A(T)}{A(6\text{K})} \propto \left[ \frac{\Delta(T)}{\Delta(0)} \right]^2. \]  

(112)

The superconducting plasma frequency extracted is \( \omega_{ps} \approx 1600 \text{ cm}^{-1} \), significantly lower than that for the oriented YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) films, as expected for a randomly oriented sample.

**Phonon Frequency and Linewidth**

The vibrational features are the major interest of this chapter. As can been seen in Fig. 48, there are three pairs of infrared phonons (at 6 K) centered near 149 and 190 cm\(^{-1}\), 265 and 298 cm\(^{-1}\), 560 and 610 cm\(^{-1}\). All these phonon modes have been assigned as vibrations along the \( c \) axis.\(^{89} \) The first doublet represents an in-phase motion of O(1)-Cu(1) and an Y-vibration. The second pair corresponds to O(2)-Cu(2)-O(3) bond bending modes. And the 560 cm\(^{-1}\) mode is assigned to the Cu(1)-O(4)-Cu(2) stretching along \( c \)-direction. We note that there is completely different temperature dependence between the first two doublets.

First, there is hardly any shift with temperature in the vibrational eigenfrequencies illustrated in Fig. 51 for the lowest doublet at 149 and 190 cm\(^{-1}\); whereas both peaks in the second doublet soften (red shift) by \( \sim 10 \text{ cm}^{-1} \) below \( T_c \). Secondly, as shown in Fig. 52, the linewidths of the lowest pair narrow rapidly upon entering superconducting state, particularly between 90 K and 40 K and then saturate; whereas the variations in linewidths for the second pair is much less dramatic. The highest doublet at 560 and 610 cm\(^{-1}\), on the other hand, are essentially insensible to \( T \).

The dramatic \( T \)-dependence of the phonon spectra which is apparently associated with the occurrence of superconductivity can be interpreted as a consequence of the electron-phonon (\( e-p \)) interaction. The frequency shift has been explained within the framework of conventional strong-coupling theory.\(^{124} \) Phonon linewidths are associated with the scattering caused by impurities, anharmonicity and the \( e-p \)
interaction. As $T$ is lowered below $T_c$, a superconducting gap develops and the number of quasiparticles decreases rapidly as a result of superconducting condensation. Phonons with energy $\hbar \omega_{ph} < 2\Delta$ can interact only with the thermally excited quasiparticles near the Fermi surface because they do not have sufficient energy to break Cooper pairs; consequently, their lifetimes increase (or linewidths decrease) rapidly as the number of quasiparticles decreases.

Phonons with $\hbar \omega_{ph} > 2\Delta$, however, can interact not only with the thermally excited quasiparticles but also with the superconducting electrons by breaking up the Cooper pairs. Furthermore, the $e-p$ interaction for phonons of energies close to $2\Delta$ is enhanced due to an increased density of state (DOS) near the gap. The latter two factors (pair breaking and enhanced DOS) will broaden the phonon linewidth, compensating for the narrowing due to the first factor (superconducting condensation). Thus, phonons of $\hbar \omega_{ph} > 2\Delta$ have much less dramatic $T$-dependence than those of $\hbar \omega_{ph} < 2\Delta$ do.

From this argument it is concluded that the electron-phonon interaction still plays an important role in high-$T_c$ superconductivity and that the energy gap might be deduced indirectly. Our data in Fig. 48 and Fig. 52 show that phonons at 149 and 190 cm$^{-1}$ narrow rapidly below $T_c$, while phonons above 265 cm$^{-1}$ do not, suggesting that the gap lies between 190 and 265 cm$^{-1}$ or $3.0 < \frac{2\Delta}{k_B T_c} < 4.2$. The highest phonon pair at 560 and 610 cm$^{-1}$ does not change upon superconducting transition because their energies are much higher than $2\Delta$.

It is interesting that the narrowing observed in YBa$_2$Cu$_3$O$_{7-\delta}$ ceramic samples has not been seen in single crystals. Note in both cases the observed phonons are the $c$-axis modes, because the $ab$-plane phonon modes are screened by the strong plasmon background. For comparison, Fig. 53 illustrates the spectra for the $c$-axis of a YBa$_2$Cu$_3$O$_{7-\delta}$ crystal. The figure shows there is finite conductivity at low frequencies, but much less than for the $ab$-plane. This is probably intrinsic, but may
be an indication of less than 100% orientation in sample growth or an effect due to a finite incidence angle in the reflectance measurement, hence a small fraction of the conducting CuO$_2$ plane response has been probed. In any event, here we only see a moderate narrowing in phonon linewidths as $T$ is lowered below $T_c$, and the variations are much less dramatic than in the case of the randomly oriented ceramic sample discussed above. The difference between these two cases may be attributed to the fact that YBa$_2$Cu$_3$O$_7$ is almost insulating along $c$-direction; hence, the $c$-axis modes in the oriented samples do not sense the change when the free carriers condense into superfluid, whereas the same $c$-axis phonons in the randomly oriented samples may be affected by the $ab$-plane carriers due to intergrain hopping or wavefunction overlapping.

The spectra of polycrystalline samples are very much dependent on factors such as material preparation techniques,$^{127}$ surface treatments$^{95}$ and degree of orientation. To illustrate this, Fig. 54 and Fig. 55 display the spectra measured by Bonn et al.$^{128}$ and Kamarás et al.$^{129}$ for a randomly oriented and a textured YBa$_2$Cu$_3$O$_{7-\delta}$ polycrystalline samples. Although the spectra of Figs. 54 and 55 differ quantitatively, from the samples shown in Figs. 48, 54 and 55, they do have similar $T$-dependence qualitatively in phonon lines as described above.

**Effective Medium Approximation**

The layered copper oxide superconductors are highly anisotropic: metallic when electrons move along the two-dimensional $ab$-plane but almost insulating along the $c$-direction. Such crystals are optically uniaxial, that is, $\epsilon_a \approx \epsilon_b \neq \epsilon_c$. Therefore the infrared spectra of a polycrystalline sample can be regarded as an effective response averaged over the randomly oriented crystallites. To analyze this phenomenon, we have tried to use several models to find the effective dielectric function using the measured reflectance of a single crystal along the $c$-axis and of an oriented film along
the \(ab\)-plane, (the spectra of these two samples are shown as solid lines in Fig. 56 and will be discussed below), and to compare the calculated \textit{effective} reflectance using the modeled \textit{effective} dielectric function with the experimental data of the ceramic samples. The oriented samples mentioned above are thick enough so that single bounce reflectance may safely be assumed.

Strictly speaking, a polycrystalline superconductor is an inhomogeneous medium whose physical properties vary spatially due to crystal-to-crystal orientation. In our samples, a local response can be justified because the grain size \((d \sim 15 \ \mu \text{m})\)—a scale over which the dielectric function fluctuates—is much greater than the electronic mean free path \(l\) \((\sim 100 \ \AA)\). Further more, the wavelength \(\lambda\) in the range of our interest is much greater than the grain size, thus we can treat the medium as if it were uniform using an effective dielectric function \(\varepsilon_{\text{eff}}(\omega)\) to describe its average response to the applied fields. The software for the calculations based on all of the following models are presented in Appendix B.

\textbf{Anisotropic Medium}

Suppose the light is propagating in an anisotropic superconductor, which can be taken as a uniaxial crystal, and the wave vector \(\mathbf{q}\) makes an angle \(\theta\) with the \(c\) axis. The dielectric function is then given by\textsuperscript{130,131}

\[
\varepsilon_{\text{eff}}(\theta) = \frac{\varepsilon_{||}\varepsilon_{\perp}}{\varepsilon_{\perp} \cos^2 \theta + \varepsilon_{||} \sin^2 \theta},
\]

or

\[
\frac{1}{\varepsilon_{\text{eff}}(\theta)} = \frac{\cos^2 \theta}{\varepsilon_{||}} + \frac{\sin^2 \theta}{\varepsilon_{\perp}},
\]

where \(\varepsilon_{||} = \varepsilon_{a,b}\) is the \(ab\)-plane dielectric function, and \(\varepsilon_{\perp} = \varepsilon_{c}\) is for the \(c\)-axis. At \(\theta = 0\) (or \(\mathbf{q} \parallel \mathbf{c}\)), the propagation is along the \(c\)-axis and the \(\mathbf{E}\) field is polarized in the \(ab\)-plane thus \(\varepsilon_{\text{eff}} = \varepsilon_{||}\); when \(\theta = \pi/2\) (\(\mathbf{q} \perp \mathbf{c}\)), the propagation is perpendicular to the \(c\)-axis and \(\mathbf{E}\) is polarized in the \(c\)-axis or perpendicular to the \(ab\)-plane, thus \(\varepsilon_{\text{eff}} = \varepsilon_{\perp}\).
A ceramic superconductor can be considered as a collection of large number of crystallites. The $c$ axis of the $i$\textsuperscript{th} crystallite makes an angle $\theta_i$ with the wave vector $\mathbf{q}$. Doll \textit{et al.}\textsuperscript{132} have evaluated the reflectance of polycrystalline $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4-\delta$ by averaging the individual reflectivities of the grains. For simplicity, here we assume that the response of the system can be characterized by an ensemble average angle $\theta$, from which the dielectric function can be calculated from Eq. (113) and the reflectance is then determined by

$$R_{\text{eff}} (\theta) = \left| \frac{1 - \sqrt{\varepsilon_{\text{eff}}}}{1 + \sqrt{\varepsilon_{\text{eff}}}} \right|^2 .$$

(114)

We have used the experimental $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ derived from the Kramers-Kronig (KK) transformations of the $ab$-plane ($R_{\parallel}$) and $c$-axis ($R_{\perp}$) reflectance data. It has also been found the resulting $R_{\text{eff}}$ calculated from Eqs. (113)–(114) satisfied the KK relations, which ensured the credibility of this approach. In other words, the dielectric function, $\varepsilon'_{\text{eff}}$, derived from the KK transformation of $R_{\text{eff}}$ agrees well with the initial determination of $\varepsilon_{\text{eff}}$ from Eq. (113). The algorithm of this method is summarized as follows:

1. $\epsilon_{\parallel}, \epsilon_{\perp} \leftarrow R_{\parallel}, R_{\perp}$, KK
2. $\epsilon_{\text{eff}} \leftarrow \epsilon_{\parallel}, \epsilon_{\perp}$, Eq. (113)
3. $R_{\text{eff}} \leftarrow \epsilon_{\text{eff}}$, Eq. (114)
4. $\varepsilon'_{\text{eff}} \leftarrow R_{\text{eff}}$, KK
5. Compare $\epsilon_{\text{eff}}$ and $\varepsilon'_{\text{eff}}$.

Fig. 56 shows the calculated reflectance at different values of $\theta$ according to Eqs. (113) and (114) at two temperatures, above and below $T_c$. Also shown in the figure is the experimental reflectance data for the $ab$-plane ($R_{\parallel}$) and $c$-axis ($R_{\perp}$) crystals as well as a textured ceramic sample. Note here $R_{\parallel}$ means $\mathbf{q} \parallel c$-axis or $\mathbf{E} \parallel ab$-plane, and $R_{\perp}$ means $\mathbf{q} \perp c$-axis or $\mathbf{E} \perp ab$-plane. It turns out that the calculated
results at $\theta = 20^\circ$ give a reasonable good fit throughout the far-infrared region to the textured ceramic data (dotted curves) at both temperatures. It is expected that the effective response of a randomly oriented sample is characterized by an average angle $\theta = \arccos(1/\sqrt{3}) = 55^\circ$ (recall that in 3-D space $(\cos^2 \theta) = 1/3$). However, according to our calculations shown in Fig. 57, no particular value of $\theta$ can give a good fit to the data of our ceramic sample (labeled as Gao) and the sample of Bonn et al. (labeled as Bonn). The approach discussed above is appropriate if $\lambda < d$, which is not the case for the latter two samples. The coincidence of the calculated result at $\theta = 20^\circ$ with the data of Kamarás et al. is perhaps because their sample is highly textured with a smoother surface hence a larger value of $d$. The degree of orientation for their sample can therefore be estimated to be $\sim 88\% \ (\cos^2 20^\circ)$.

**EMA and MGT Approaches**

Two other methods to describe the effective response of a mixture are the "effective medium approximation" (EMA)$^{133,134}$ introduced by Bruggeman, and "Maxwell-Garnett theory" (MGT)$^{135}$ due to Garnett. These two models are in principle appropriate if $l < d < \lambda$, the case of our sample, so that the dielectric functions of the individual crystallites can be averaged. The results are the simplest if the inhomogeneous system can be regarded as a two-component composite. Taking the dielectric functions of these two constituents be $\epsilon_\parallel$ and $\epsilon_\perp$ and assuming the volume fraction of $\epsilon_\parallel$ be $f$, the dielectric functions in these two models are then given by$^{136}$

$$
\epsilon_{MGT} = \epsilon_\perp + \epsilon_\perp \frac{3f(\epsilon_\parallel - \epsilon_\perp)}{(1 - f)(\epsilon_\parallel - \epsilon_\perp) + 3\epsilon_\perp},
$$

and

$$
\epsilon_{EMA} = \frac{B}{4} \pm \frac{1}{4} \sqrt{B^2 + 8\epsilon_\parallel \epsilon_\perp},
$$

where
\[ B = (3f - 1)\epsilon_{\parallel} + (2 - 3f)\epsilon_{\perp}, \]

and we have chosen the sign in Eq. (116) such that \( \text{Im}(\epsilon_{EMA}) \geq 0 \). The EMA approach treats each constituents in the medium on an equal way thus the solution is symmetric, namely, \( \epsilon_{\parallel} \) and \( \epsilon_{\perp} \) play equal role in the equation hence there is no restriction to the value of concentration \( f \). In contrast, the MGT approach treats the two constituents in different way and the equation is asymmetric. One will obtain different results depending on which constituent is the host and which one is the inclusion.

The calculated results are shown in Fig. 58 and Fig. 59. Here \( f_{ab} \) is the fraction of \( ab \)-planes probed by the incident electric field \( \mathbf{E} \). This fraction is presumably \( \sim 2/3 \) for randomly oriented (uniaxial) samples and has higher value for textured samples. As can be seen from these two figures, both approaches appear underestimate this fraction and the calculated reflectance with reasonable values of \( f_{ab} \) is essentially higher than the experimental data. The MGT model appears to fit the data of the textured sample well with a fraction \( f_{ab} = 2/3 \), a value expected for randomly oriented samples. A textured sample is expected to have a higher \( f_{ab} \). In contrast, the EMA model can give a good fit to the textured sample in the long wavelength limit (\( \omega < 400 \text{ cm}^{-1} \)) for \( T = 10 \text{ K} \) with \( f_{ab} = 1/3 \), a value significantly lower than expected.

A major distinction between the data of the two randomly oriented samples (labeled as Gao and Bonn in the figures) and the calculated results based on MGT or EMA theory is that the experimental data at 10 K show a plasma-like edge around 100 cm\(^{-1}\), but non of the calculations give this effect. The edge is postulated to be associated with the condensation of the superconducting carriers which causes a zero crossing of the real dielectric function.

One thing that should be aware, however, is that the \( c \)-axis data we have used seem to have considerable amount of metallic conductivity as seen in Fig. 53. The
appropriate approach which should have been done is to subtract the finite Drude contribution from the $c$-axis data, assuming the $c$-direction is totally insulating, before using Eqs. (115) and (116). This may have matched the experimental data.

**Weighted Average**

Another approach is also carried out with a simple assumption:

$$R_{\text{eff}}(\omega) = \frac{1}{3} R_{\perp} + \frac{2}{3} R_{\parallel}.$$  \hspace{1cm} (117)

This expression usually assumes that $\lambda \ll d$, namely, the wavelength is less than the crystallite dimensions. The effective total reflectance is then approximated by averaging over the individual reflectivities of the randomly orientated grains. As seen in the results shown in Fig. 60, this approach gives a quite good coincidence with the measured data of the textured sample. We have also carried out the Kramers-Kronig analysis of $R_{\text{eff}}(\omega)$ and found the derived optical constants were also in good agreement with the corresponding experimental data of the textured sample. However, this approach did not give satisfactory fit to the other two randomly oriented samples (not shown). This is not surprising because apparently the latter two samples do not meet the condition $\lambda \ll d$ in the far-infrared region.

**Summary**

Measurements of the randomly oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ polycrystalline superconductors show a complicated mixture of the conducting CuO-plane and the almost insulating $c$-axis response. The rich vibrational featured observed are dominated by the $c$-axis response. However, in contrast to the pure $c$-axis response, these vibrational phonons in ceramics are strongly affected by the conducting electrons in the CuO plane due to the wavefunction overlapping or intergrain hopping. The results imply an important role of the electron-phonon interaction in this system.
The lowest pair of phonons has dramatic temperature dependence in linewidths but not in the eigenfrequencies, whereas phonons of higher energies show opposite behavior. These anomalous effects allows an estimate of the energy gap: a lower bound 190 cm\(^{-1}\)—phonons of energy below which lose widths rapidly at \(T < T_c\), and an upper bound 265 cm\(^{-1}\)—phonons above which do not.

The textured polycrystalline superconductor, for both \(T > T_c\) and \(T < T_c\), can be well described by an anisotropic medium approximation using an effective dielectric function characterized by an ensemble average angle that the incidence wave vector makes with the \(c\)-axis. This approach allows an estimate of the degree of texture, and it explains the \(T\)-dependence of the infrared phonons in ceramic samples. The weighted reflectance average approach also fits well the textured sample. The agreement indicates that the effective response of this sample can be approximated by averaging the reflectivities of the grains in different directions.

In contrast, the theory of MGT or EMA is less successful in description of the polycrystalline ceramics. Further more, none of the effective medium models can describe well the randomly oriented samples. Some problems should be considered are the inhomogeneity and surface quality of these samples, which would significantly affect the quantitative response of these materials.
Fig. 48. Far-infrared Reflectance and conductivity of a polycrystalline YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor studied in this work.
Fig. 49. Reflectance and conductivity in the entire measured range. Note the logarithmic frequency scale.
Fig. 50. Missing area in the conductivity curve, $\sigma_1(\omega)$, at $T < T_c$. 

**Diagram Description:**
- **YBa$_2$Cu$_3$O$_7$**
- Ceramic polycrystalline pellet
- **Axes:**
  - Y-axis: $A(T) / A(6K)$
  - X-axis: Temperature (K)
- **Legend:**
  - Missing Area in Superconducting state
Fig. 51. Vibrational frequency as a function of temperature. The lines are guides for the eye.
Fig. 52. Temperature dependence of the phonon linewidths for the lowest doublet. (The 149 cm\(^{-1}\) phonon width at \(T > 100\) K is not shown here because of difficulties in fitting the highly asymmetric peaks in the normal state.)
Fig. 53. Reflectance and conductivity data, provided by Homes et al., (Ref. 126) for light polarized along the insulating c-axis.
Fig. 54. Reflectance and conductivity spectra, measured by Bonn et al., (Ref. 128) for an randomly oriented YBa$_2$Cu$_3$O$_{7-\delta}$ ceramic sample.
Fig. 55. Reflectance and conductivity data, provided by Kamarás et al. (Ref. 129) for a textured YBa$_2$Cu$_3$O$_{7-δ}$ sample.
Fig. 56. Comparison between the calculated reflectance using Eqs. (113), (114) and the measured data for a textured samples (dotted lines). The agreement is excellent for $\theta = 20^\circ$. 
Fig. 57. Comparison between the calculated reflectance using Eqs. (113), (114) and the measured data for two randomly oriented ceramic samples. No particular values for $\theta$ can fit the experimental data.
Fig. 58. Comparison between the calculated reflectance using the MGT theory and the measured data for ceramic samples.
Fig. 59. Comparison between the calculated reflectance using the EMA theory and the measured data for ceramic samples.
Fig. 60. Comparison between the calculated reflectance, an weighted average of the $ab$-plane and $c$-axis reflectance, and the measured data for a textured sample.
CHAPTER X
SUMMARY AND CONCLUSIONS

This dissertation has been devoted to an extensive study of the infrared and optical properties of various high temperature superconducting samples. The experimental spectra were measured as a function of photon energy and sample temperature over a wide range. The results of the studies indicate that these copper oxide materials have extremely anomalous behaviors both in the normal and superconducting states.

Normal State

An usually behavior that common for both the oriented La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$ films is that the normal state conductivity contains a strong non-Drude contribution throughout much of the far- and mid-infrared region. We concentrated on the two-component analysis and tried to identify the free carrier (Drude) and the bound carrier (mid-infrared and interband) contributions to the optical conductivity $\sigma(\omega,T)$. The Drude component has a narrow peak (with width of order $k_BT_c$) centered at $\omega = 0$. The conductivity of this component at the extrapolated zero frequency, $\sigma_{1D}(0,T)$, compares well with the values of the measured dc conductivity $\sigma_{dc}(T)$, thus it is associated with the free-carrier contribution. This agreement indicates that there are no low frequency excitations below the far-infrared frequencies. The Drude oscillator strengths:

$$\omega_{pD} \simeq \begin{cases} 6300 \text{ cm}^{-1} & \text{ (for La$_{2-x}$Sr$_x$CuO$_4$)}, \\ 10000 \text{ cm}^{-1} & \text{ (for YBa$_2$Cu$_3$O$_{7-\delta}$)} \end{cases}$$
are related to a fixed number of carrier concentration and are temperature independent, whereas the scattering rate, constant in $\omega$, is liner in $T$ in a form of

$$\frac{\hbar}{\tau} = 2\pi \lambda k_B T,$$

and

$$\lambda \simeq \begin{cases} 
0.25 & \text{for La}_{2-x}\text{Sr}_x\text{CuO}_4, \\
0.45 & \text{for YBa}_2\text{Cu}_3\text{O}_{7-\delta}.
\end{cases}$$

This result shows that the linear $T$-dependence of the dc resistivity is primarily due to a $T$-linear scattering rate at low frequencies. The small value of the coupling constant $\lambda$ implies a weak coupling picture and is consistent with the observed absence of saturation up to $\sim 1000$ K for the dc resistivity. The second component called MIR band is centered at finite frequency in the mid-infrared region ($\sim 50$ meV) and it is associated with bound carrier excitation. In contrast with the Drude component, the MIR component is a broad, only weakly $T$-dependent (inert), band throughout the midinfrared. The origin of this residual absorption still remains a mystery.

Another approach based on the single-component analysis gives a very strong frequency dependent, rather than a constant, scattering rate and effective mass. The low frequency experimental data has some qualitative features predicted by this approach in a marginal or nested Fermi liquid theory. However, a major difficulty with this model is that the coupling strength is significantly large which would lead to a deviation in the observed linearity of the dc resistivity. Therefore, we conclude that the midinfrared absorption cannot be accounted for entirely by the the frequency dependent scattering rate and effective mass, nor by the Holstein absorption process.

**Superconducting State**

Below $T_c$, a substantial amount of free carrier oscillator strength is removed rapidly from the low frequency conductivity to the superconducting condensate. The temperature dependence of the superfluid density for all our samples is similar and resembles the behavior of the BCS order parameter as illustrated in Figs. 33, 44, and 50. The features of the second component in $\sigma_1(\omega, T)$ become distinct and fully
revealed below $T_c$, resembling the normal state mid-infrared band but is enhanced slightly in the 150–1500 cm$^{-1}$ range. The threshold of this absorption appears to be coincident with the value of a conventional BCS gap. However, for one thing, this threshold is extremely sensitive to the reflectance accuracy and is within our detection limit; for the other, the absorption onset is independent of temperature and can even be seen in the normal state when the free carrier absorption is subtracted, making it unlikely the superconducting gap.

In contrast to its $T$-linear dependence above $T_c$, the quasiparticle damping rate decreases dramatically in the superconducting state. This behavior is not expected in phonon scattering of conventional superconductors. It may suggests that the excitation responsible for the $T$-linear scattering rate in the normal state is strongly suppressed below $T_c$ as the superconducting gap opens. Furthermore, this anomalous $T$-dependence in $1/\tau$ below $T_c$ causes a peak observed in $\sigma_{1s}(T)/\sigma_{1n}(T)$ below $T_c$, which is not associated with the conventional BCS case II coherence effect. Finally, there are similarities in the $T$-dependence of $1/\tau$ for the oriented films (see Figs. 27 and 44) and of the phonon linewidths for the YBa$_2$Cu$_3$O$_{7-\delta}$ polycrystalline sample (see Fig. 52), which may suggest that they are closely interrelated.

Although the gap may perhaps be inferred indirectly from the far-infrared phonon spectra (with a wide bound) of the randomly oriented YBa$_2$Cu$_3$O$_{7-\delta}$ crystals, there is no direct and convincing evidence for absorptions across the superconducting gap in the conductivity spectra of the CuO$_2$ planes. Because of the short coherence length, the high temperature superconductors are in the clean limit, $2\Delta \gg 1/\tau$. Most of the free carriers condense into pairs, leaving little strength for transition across the gap. Any remaining feature due to the gap is masked by the strong midinfrared absorption.
APPENDIX A

DATA FOR OTHER SAMPLES

This appendix presents a few plots of the optical spectra measured by the author for other high-$T_c$ superconducting samples that were not presented in the text of this dissertation. Data were collected using a fast-scanning Bruker Fourier interferometer and a Pekin-Elemer monochromator. These samples include: an ultra-thin YBa$_2$Cu$_3$O$_{7-\delta}$ film prepared at Bell Communication Research, a 2500-Å thick granular YBa$_{2.1}$Cu$_{3.4}$O$_{7-\delta}$ film prepared at Naval Research Laboratory, and a YBa$_2$Cu$_4$O$_8$ polycrystalline sample prepared at Lawrence Berkeley Laboratory.
Fig. A-1. \(\mathcal{R}(\omega)\) and \(\mathcal{S}(\omega)\) of an ultra-thin YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) trilayer film: 250 Å PrBa\(_2\)Cu\(_3\)O\(_7\)/96 Å YBa\(_2\)Cu\(_3\)O\(_7\)/250 Å PrBa\(_2\)Cu\(_3\)O\(_7\) \((T_c = 53\ \text{K})\), grown on a 0.5-mm MgO (100) substrate. The insets show the interference effect due to the substrate in higher resolution measurement \((2\ \text{cm}^{-1})\). The fringes can be averaged out in lower resolution measurement \((4\ \text{cm}^{-1})\). Note that the optical constants extracted from the direct determination technique introduced on p. 20–24 will be most accurate when \(\mathcal{R} \approx \mathcal{S} \leq 0.5\).
Fig. A-2. Reflectance of a 96-Å YBa$_2$Cu$_3$O$_{7-\delta}$ film. The sample and data are the same as shown in the previous figure, except here it shows a wider frequency range up to 600 cm$^{-1}$. The peak near 400 cm$^{-1}$ is caused by the TO phonon of the MgO substrate.
Fig. A-3. Far-infrared reflectance and transmittance of a 2500-Å thick granular YBa$_{2.1}$Cu$_{3.4}$O$_{7-\delta}$ film on a 1-mm MgO. The superconducting transition of grains is at 82 K, and the entire film is nearly zero resistance at $T \leq 20$ K. The far-infrared photoresponse of this film has been reported previously.(Ref. 137)
Fig. A-4. Reflectance and conductivity of a YBa$_2$Cu$_4$O$_8$ polycrystalline sample. The insets show the entire measured frequency range in logarithmic frequency scale. This material has double copper chains between the planes.
APPENDIX B

COMPUTER PROGRAMS

This appendix presents some of the computer software programs (in Fortran language) used for data analysis and to generate results according to the theoretical models. The program GTFILM in combination of MGONA evaluates the frequency dependent complex conductivity and free-standing transmission using the Glover-Tinkham expression for the YBa$_2$Cu$_3$O$_{7-\delta}$ films deposited on MgO substrates. The routine was written for the PDP-11 computers. WMASS is a program to compute the $\omega$-dependence of the effective mass enhancement and quasi-particle self energy for the La$_{2-x}$Sr$_x$CuO$_4$ films using the phenomenologically generalized one-component model. YBEMA is a routine to calculate the effective reflectance and conductivity using anisotropic medium approach of Eq. (113), MGT theory of Eq. (115), EMA theory of Eq. (116), and weighted average of Eq. (117). The latter two programs were written for use on PC computers.
Program GTFILM

C ************************************************************************

C Frank Gao and Larry Carr

C Program to compute surface admittance (Y1 and Y2) for a film on an
C absorbing substrate. Inputs are film/sub transmission, front surface
C reflectance, substrate absorption coefficient, and substrate index.

C Transmission and Reflectance in absolute units (not percentages).
C Substrate absorption coefficient (alpha) in 1/cm.
C Film and substrate thicknesses (FLMTHK, SUBTHK) in cm.
C All frequencies in wave-number (1/cm).
C Output conductivities in l/(ohm-cm).

C Input files for Tfile (transmission), Rfile (reflectance) and
C Afile (absorption coeff.) must have first line = '/*

C Input parameters from file TY.PRM (no /* here!)

C ************************************************************************

CHARACTER TFILE*32,RFILE*32,AFILE*32,0FILE*32,HEAD*64,Y0N*32

1 FORMAT (' The film thickness (in nm) is', F7.1)
5 FORMAT (A32)
6 FORMAT (' ',A64)
7 FORMAT (A64)
OPEN (UNIT=1,FILE='TY.PRM',STATUS='OLD')
READ (1,* ) SUBTHK
read (1.*) FLMTHK
WRITE(5,1) 1E+07*FLMTHK
TYPE 20

Accept 25, YON

25 FORMAT (A1)
30 READ (1,5, END=299) TFILE
READ (1,5) RFILE
READ (1,5) AFFILE
READ (1,5) OFFILE
IF (OFFILE.EQ.' ') GO TO 199
OPEN (UNIT=2,FILE=TFILE,STATUS='OLD')
OPEN (UNIT=3,FILE=RFFILE,STATUS='OLD')
OPEN (UNIT=4,FILE=AFFILE,STATUS='OLD')
OPEN (UNIT=8,FILE=OFFILE,STATUS='NEW')

C - Get rid of that /* business, print filenames and headers on screen
C
WRITE (5,*) 'Transmission file => ',TFILE
50 READ (2,7) HEAD
WRITE (5,6) HEAD
if (HEAD(1:2) .NE. '/*') GO TO 50
WRITE (5,*) 'Reflectance file => ',RFFILE
60 READ (3,7) HEAD
WRITE (5,6) HEAD
IF (HEAD(1:2) .NE. '/*') GO TO 60
WRITE (5,*) 'MgO absorption file => ', AFILE

READ (4,7) HEAD
WRITE (5,6) HEAD
IF (HEAD(1:2).NE. '/*') GO TO 70
If (YON.EQ. 'Y') WRITE (5,*) 'W, Rint, TG-T, Y1, Y2'
C - But put a /* in the output file so pdp-11 plot routines can read it!

C write (8,5) Ofile
WRITE (8,*) 'Frequency, Sigma1, Sigma2, T(G-T), Tfilm, Rfilm'
WRITE (8,89) '/*

89 FORMAT (A2)
C Starting calculation and set the initial value of Y2=0 for the first point.
C When the counter I = 1, the initial point is assumed. Y2 is not 0 for I > 1.
Y20 = 0.
I=0
K=0
100 I=I+1
READ (2,*,END=199) WT, TRANS
READ (3,*,END=199) WR, REFL
READ (4,*,END=199) WA, ALPHA, Sindex, Rsub

C - Check that data from files is "synchronized"
C
WD1=ABS(WT-WR)
WD2=ABS(WT-WA)
IF (((WD1.LT.0.5).AND.(WD2.LT.0.5)) GO TO 150
WRITE (5,*) 'Frequencies do not coincide, aborting '
WRITE (5,*) 'T-file is ', TFILE
GO TO 199

150 W=WT
C
C - Compute Y1 from external reflectance, assuming Y2=Y20 (previous Y2 as J=1)
C
J=1
UMT=1.-TRANS
If (YON.EQ. 'Y') WRITE (5,*) 'R=',REFL,' TFS=',TRANS, 'TGT=',TGTT
C
C - Compute absorption and its square
C
if (alpha.LT. 0.) alpha=0.
A=EXP(-ALPHA*SUBTHK)
A2=A*A
C ** Find the self consistent Rinter by iteration for the first points
If (I.EQ. 1) then
RINTER = REFL
152 TGT=TRANS* (1.-RSUB*RINTER*A2)/((1.-RSUB)*A)
Y1=SINDEX*((1.-REFL)/TGT-1.)
RP = RINTER
K = K + 1
WRITE (6,154) K, W, RINTER, TGT, Y1
154 FORMAT (' ', I2, F7.1, ' Rin=',F8.4, ' TGT=',G12.4, ' Y1=',G12.4)
Rinter = Refl - Y1*TGT*(SINDEX - 1.)/SINDEX
IF (ABS(RINTER - RP) .GT. 1E-04*ABS(RP)) GOTO 152
GOTO 165
END IF
C IF (YON .EQ. 'Y') WRITE (5,*), 'UMT=',UMT,'SR=',SR, 'Y1=',Y1
C - Compute internal film reflectance (from inside substrate)
C 160 Y2SQ=Y2*Y2
RINTER=((Y1+1.-SINDEX)**2+Y2SQ)/((Y1+1.+SINDEX)**2+Y2SQ)
C - Extract G-T transmission (from vacuum into the substrate)
C 165 TP = TGT
Y1P = Y1
Y2P = Y2
TGT=TRANS*(1.-RSUB*RINTER*A2)/((1.-RSUB)*A)
C - Compute Y1 and Y2 from G-T transmission and external reflectance
C Y1=SINDEX*((1.-REFL)/TGT-1.)
if (Y1 .LT. 0.) Y1=0.
SARG=(4.*SINDEX/TGT-(Y1+SINDEX+1.)**2)
IF (SARG.LT.0.) WRITE (5,*), W, SARG
IF (SARG.LT.0.) GO TO 170
Y2=SQRST(SARG)
IF (YON .EQ. 'Y') WRITE (5,*), W, Rinter, TGT, Y1,Y2
170 J=J+1
C - Test if this was first or second pass (J=2 => first so do it again)
C IF(ABS(TGT-TP).GT.1E-04*TGT. AND.ABS(Y1-Y1P).GT.1E-04*Y1)GOTO 160
C - Convert to conductivity (in 1/(ohm-cm)) and save Y1 into Y10 and Y2 into Y20 as initial values for next frequency point because of continuation.
S1=Y1/(377.+FLMTHK)
S2=Y2/(377.+FLMTHK)
C Y10 = Y1
C Y20 = Y2
C - Calculate the Transmission and Reflectance of a free standing film by setting n = 1 in Glover Tinkham expression TO get free standing film R&T
TFLM = 4./((Y1+2.)*Y1+2+Y2*Y2)
RFLM = (Y1*Y1+Y2*Y2)/((Y1+2.)*Y1+2+Y2*Y2)
RGT=((Y1+SINDEX-1.)**2+Y2*Y2)/((Y1+SINDEX+1.)*Y1+2+Y2*Y2)
C -- Output results
C WRITE (8,99) W,S1,S2,TGT,TFLM, RFLM
C - Go back to repeat the calculation for the next frequency point
GO TO 100
99 FORMAT (',F9.2, 5(',G11.4))
199 WRITE (5,*) 'Output file is ', OFILE
Write (5,*)
CLOSE (UNIT=2)
CLOSE (UNIT=3)
CLOSE (UNIT=4)
CLOSE (UNIT=8)
C - Computation is done for this file and go back to do the next file.
GO TO 30
299 STOP ' All done!' END

Program MGONA
C **************************************************************
C Frank Gao and Larry Carr
C Program to compute the index of refraction N and the
C absorption coefficient A for a substrate
C **************************************************************
COMPLEX ZSM, ZLG
C WRITE (5,*),'enter the values of A, B and C'
C READ (5,*), A, B, C
C CALL ZQADR (A, B, C, ZSM, ZLG, IER)
C WRITE (5,*), ZSM = ', ZSM
C WRITE (5,*), ZLG = ', ZLG
C
C Input parameters from SUB.PRM
CHARACTER*14 MGOTRN, mgorfl, MGOALP, YON
CHARACTER*60 HEAD
TYPE 2
2 FORMAT ('Program to calculate the index and absorption ',/'
1' coefficient of the substrate from reflection and transmission'/
2' Must have a edited parameter file SUB.PRM '/
3' '/
3' Input parameters in SUB.PRM as follows:/
4' substrate thickness (in cm)/
5' name of input file with measured Substrate transmission'/
6' name of input file with measured substrate reflectance'/
7' name of output file for storing absorption coefficient'/)
C
C Open SUB.PRM input parameter file
C
OPEN (UNIT=1, FILE='SUB.PRM', STATUS='OLD')
C
Input parameters as follows:
substrate thickness (in cm)
name of input file with measured MgO transmission
name of input file with measured MgO reflectance
name of output file for storing computed absorption coefficient
C
READ (1,*), THICK
Write(5,5) 10*Thick
5 FORMAT(' The sample thickness (in mm) is ', F6.3)
WRITE (5,*)
Type 6

FORMAT(' Do you want to see the data on the screen (Y/N)? '$)
Accept 8,YON

WRITE(5,*)

READ (1,20,end=999) MGOTRM
Read (1,20) Mgorfl
READ (1,20) MGOALP

WRITE (5,*)

OPEN (UNIT=2, FILE=MGOTRM, STATUS='OLD')
OPEN (UNIT=3, FILE=MGORFL, STATUS='OLD')
OPEN (UNIT=4, FILE=MGOALP, STATUS='NEW')

C Write the name and the header into the file

C Write (4,20) mgoalp
WRITE (4,*), ' Frequency, Alpha, Index, Rs'
WRITE (4,30)

FORMAT ('/')

C Begin loop over frequencies (defined in input file)
C Next read gets thru /* in input file. Print the file name and its
C Header on screen.
WRITE (5,*) 'Transmission file => ',MGOTRM

READ (2,20) HEAD
WRITE (5,25) HEAD
IF (HEAD(1:2) NE. '/*') GO TO 50
WRITE (5,*)
WRITE (5,*) 'Reflectance file => ',MGORFL

READ (3,20) HEAD
WRITE (5,25) HEAD
IF (HEAD(1:2) NE. '/*') GO TO 60
WRITE (5,*)
IF (YON .EQ. 'Y') Write (5,*) ' Frequency, R, Rs, '

10 J = 1
READ (2,*,END=499) WT, T
Read (3,*,END=499) WR, R

C Check that data from files is "synchronized"
IF (ABS(WT-WR) GT 0.5) STOP ' Frequencies do not coincide.'
W = WT

C Begin loop for iteration
A = AO

110 Rs = R/(T*A+1.)
Sindex = (1.+SQRT(RS))/(1.-SQRT(RS))
A1 = (Rs**2)*T
B1 = (1-RS)**2

Invert T = (1-Rs)**2*A/(1-(R*A)**2) And R = Rs*(T*A+1) to find
Rs and A=Exp(-Alpha*Thick) by iterations, assuming the first
data point gives A=AO=1. The number of iteration is J.
C1 = -T
If (YON .EQ. 'Y') Write(5,*); W, R, Rs, Sindex, A
C IF (500*ABS(4.*A1*C1) .LT. B1**2) THEN
C A = 2*C1/(-B1 - SQRT(B1**2-4.*A1*C1))
C ELSE
C A =(-B1 + SQRT(B1**2-4.*A1*C1))/(2*A1)
C END IF
CALL ZQADR (A1, B1, C1, ZSM, ZLG, IER)
A = REAL(ZSM)
J = J+1
if (J .LE. 3) go to 110
C Protect from negative argument for logarithm.
C A value for alpha = 999 means there was a problem
C Compute absorption coefficient in normal fashion
C
300 ALP = -1*ALOG(A)/THICK
C Output the results
C
400 WRITE (4,410) W, ALP, Sindex, Rs
410 FORMAT (' ',F9.2,' ',G10.4, 2(F7.3))
C Loop for next data point until end of transmission file is reached
C and save the current value of A into A0 as the initial(J=1) iteration
C value for the next freq data point because of continuation
A0 = A
GO TO 100
499 CLOSE (UNIT=4)
Close (unit=3)
CLOSE (UNIT=2)
Write (5,*); 'Output file is ',MGOALP
Write (5,*)
C Loop until no more entries in MGO.PRM (will do more than one)
C
GO TO 10
C All done.
C
999 CLOSE (UNIT=1)
STOP
END
PROGRAM WMASS
C **********************************************************************
C Frank Gao
C Program to compute frequency-dependent scattering parameters
C using the Marginal Fermi Liquid, Thomas-Millis and Memory function
C notations.
C Input parameter file for BATCH MODE should be arranged as:
c L1: Input file for dielectric function Epsilon(1) and Epsilon(2)
c L2: Output file for storing the other optical constants
C L3: Starting and ending frequencies (WL, WH) in wave numbers
C L4: Normal Plasma freq(WPN), Super-plasma freq (WPS)
c L5: Epsilon high contribution freq dependent? (Y or N)
c L6: Parameter file for Epsilon(high) if L5 is Y, or enter by hand if N
C Can be repeated to process more files.
C **********************************************************************
REAL W[FAR](3000), E1[FAR](3000), E2[FAR](3000)
Real IMSENG, MEFF, WP(20), WRES(20), DAMP(20)
Character*12 Sfile, Ofile, FILE, ID*79, IDENT*5, YN*1, FILPRM
COMPLEX E, SENGY, EPSLON, EHI, EPSHI[FAR](3000)
C DATA NDIM /4000/
C 10 Format (A)
15 Format (A2)
20 PRINT *, 'Program to compute the frequency dependent self-energy',
   * ' and mass enhancement.'
C  READ (*,5) YN
35 FORMAT ('1Input file for E1, E2: (/ ->', A, ' ) ')$
22 FORMAT (' Enter freq range (WL, WH): (/ ->',2F8.1,') ')$
25 FORMAT (' Enter WpN, WpS (1/cm): (/ ->',2F8.1,') ')$
30 Format ( 'WpN =', F8.1, ' WpS =', F8.1 $ )
32 Format (13, ', 3F12.1)
C ---
40 WRITE (*, 35) SFILE
 READ (*, 10) FILE
 IF (FILE .EQ. ' ') STOP 'No input file. All done'
 IF (FILE(1:1) .NE. '/') SFILE = FILE
 WRITE (*, '(1X,3A \') 'Output file for OPTCs: (/ ->',OFILE, ' ) '
 READ (*, 10) FILE
 IF (FILE(1:1) .NE. '/') OFILE = FILE
 WRITE (*, 22) WL, WH
 READ (*, *) WL, WH
 WRITE (*, 25) WPN, WPS
 READ (*, *) WPN, WPS
 WPN2 = WPN*WPN
 WPS2 = WPS*WPS
 Open (unit = 2, File = Sfile, Status = 'old')
 Open (unit = 3, File = Ofile, Status = 'UNKNOWN')
C —- Copy the first line information from the input file into the outfile
 Read (2, 10) ID
 Write (3, 10) ID
C — Find the wildcard */ before reading the data
50 Read (2, 10) ID
If (ID(1:2) .NE. '/*') GO TO 50
C Now query for constants to write out into file
C Loop for computing parameters
C -- GM -> Imaginary memory function or effective 1/tau
C WPI2 -> effective plasma frequency
C MW -> effective mass (enhancible)
C
K = 1
100 Read (2, *, End = 110) W(K), E1(K), E2(K)
   IF (W(K) .LT. WL) GO TO 100
   IF (W(K) .GT. WH) GO TO 110
   K = K + 1
   GO TO 100
110 N = K - 1
   WRITE (*, '(lx, A)') 'Is Epsilon infinity freq dependent? (N)'
   READ (*, 10) IDENT
   IF ((IDENT(1:1).EQ.'Y').OR.(IDENT(1:1).EQ.'y')) THEN
      CALL ESLINF(W, N, EPSHI, EINF, WP, WRES, DAMP, NOSC, FILPRM)
      WRITE (3, 10) 'Osc. parameters for Epsilon high contributions'
      WRITE (3, '(2A)') FILPRM, WP WRES Gamma'
      WRITE (3,32) (I, WP(I), WRES(I), DAMP(I), I = 1, NOSC )
   ELSE
      WRITE (*, '(1X, A, F7.1, A \)')
      * 'Enter constant Einf: (/ ->', EINF, ')
      READ (*, *) EINF
   END IF
   WRITE (3, '(A, F6.1)') 'EINF = ', EINF
   Write(3,30) WPW, Wps
   Write(3,15) 'Freq WPeff 1/Teff Self-E1 ',
   * 'Self-E2 Meff Ehi(1) Ehi(2)'
   Write(3,15) '/*',
C Epsl is the effective quantity including the superfluid effect.
DO 250 K = 1, N
   EPSLON = CMPLX (E1(K), E2(K))
   WK = W(K)
   EHI = CMPLX (EINF, 0.)
   IF (((IDENT(:1).EQ.'Y').OR.(IDENT(:1).EQ.'y'))) THEN
      E = EHI - EPSLON - WPS2/WK**2
      SENGY = WPW2/(WK+E) - WK
      RESENG = REAL (SENGY)
      IMSENG = AIMAG (SENGY)
      Meff = 1. + RESENG/WK
      WPEFF2 = WPW2/Meff
      GAMEFF = IMSENG/Meff
      IF (WPEFF2 .LE. 0.) THEN
         WPEFF = - SQRT(- WPEFF2)
      ELSE
         WPEFF = SQRT(WPEFF2)
      END IF
   ELSE
      IF(YN.EQ.'Y') Write (*,200) WK, GM, WPI2, S1, S2, MW, Meff
      IF((IDENT(:1).NE.'Y').and.(IDENT(:1).NE.'y').and.(K.GT.3)) Then
         Write (3,200) WK, INT(WPEFF), GAMEEFF, SENGY, Meff
      ELSE

Write (3,200) WK, INT(WPEFF), GAMEFF, SENGY, Meff, EHI
END IF
250 CONTINUE
199 Write (', '(2A)') ' Outputfile => ', Ofile
Close (unit = 2)
Close (unit = 3)
C Computation is done for the current file return to do the next one
Go TO 40
C -- 200 Format ( F8.1, 2F9.1, 2F9.2, F10.3, 2F11.2)
200 Format ( F8.1, I8, F11.1, 2F12.2, F8.3, 2F8.2)
105 FORMAT (' Input filespec for Epsilon? ')
115 FORMAT (' Input filespec for Sigma? ')
125 FORMAT (' Output filespec? ')
137 FORMAT (' Enter no. of function to be written into file:'/
1 ' (Enter <0> to Stop)''/
2 ' 1 ==> 1/Teff'/ 2 ==> Weff-2'/
3 ' 3 ==> Real G(w)'/ 4 ==> Imag G(w)'/
4 ' 5 ==> Real Self-energy'/ 6 ==> Imag Self-energy'/
5 ' 7 ==> Meff/Mband'/ 8 ==> MIR Gamma(w)''$)
140 FORMAT (' ',A1,'?-W-Can"t find file — re-enter filespec:')
Stop 'All done!'
END
C
C
SUBROUTINE ESLINF(W, NW, EPSL, EPSINF, WP,WRES,DAMP,HUMOSC,FILPRM)
C ******************************************************************************
C Routine to compute complex optical constants for parameter resultting
C from the least squares fitting program (LSTSQR). Parameter can be
C entered from an existing file or from keyboard.
C
COMPLEX*8 LORENT, EPSL(NW), CDIEL
REAL WRES(20),WP(20),DAMP(20), W(NW)
CHARACTER*12 FILPRM, FILE
2 FORMAT (A)
5 FORMAT ('0Parameter file for Einf? ( < > -> Non, / -> ',A,' ) '
20 FORMAT ('0Input number of oscillators ( / -> ', I3, ' ) '
30 FORMAT (' Number',I3, ': ( / -> ',3F10.1,') ' ) '$)
31 FORMAT ( I2, ': ', 3F12.1 )
35 FORMAT (' Enter Epsinf: ( / -> ',F6.1,') ' ) '$)
C - Input parameter and output files. If entered as "/", keep the previous
C - file names. If param. entered as < >, get param. from keyboard.
40 WRITE (*,5) FILPRM
READ (*,2) FILE
IF ( FILE(1:1) .NE. '/') FILPRM = FILE
C Input the oscillator parameters from keyboard if par file entered as "0"
IF ( FILPRM .EQ. ' ) THEN
WRITE(*, 20) NUMOSC
READ (*, *) NUMOSC
WRITE (*, '(1X, A /)') 'Enter Wp, Wres, WDAMP in 1/cm:'
DO 50 I = 1, NUMOSC
WRITE (*, 30) I, Wp(I), Wres(I), DAMP(I)
READ (*, *) Wp(I), Wres(I), DAMP(I)
50 CONTINUE
WRITE (*, 35) EPSINF
READ (*, *) EPSINF
ELSE
C Input the oscillator parameters from FILPRM if the filename entered
OPEN (UNIT = 1, FILE = FILPRM, STATUS = 'OLD')
READ (1,*) DUMMY, NUMOSC
DO 100 I=1,NUMOSC
READ (1,*) DUMMY, Wp(I)
READ (1,*) DUMMY, WRES(I)
100 READ (1,*) DUMMY, DAMP(I)
READ (1,*) DUMMY, EPSINF
CLOSE (UNIT=1)
END IF
C - Write the oscillator parameters in to the output file
WRITE (2, 2) 'Optical constants obtained from Lorentz oscillators'
WRITE (2,10) 'Wp  WRES  GAMMA'
WRITE (2,31) ( I, WP(I), WRES(I), DAMP(I), I = 1, NUMOSC)
WRITE (2, '(A, F6.1)') 'EPSINF = ', EPSINF
WRITE (2,*) ' EPSIHF
CLOSE (UNIT=2)
RETURN
END
FUNCTION LORENT(W,WRES,WPLASM,DAMP)
COMPLEX*8 LORENT
LORENT=WPLASM**2/(WRES**2-W**2-CMPLX(0.,1.)*W*DAMP)
RETURN
END
**PROGRAM YBEMA**

C *********************************************************************
C  Frank Gao
C Program to compute the effective complex dielectric function
C using the HTSC's ab-plane and c-axis dielectric function data.
C
C  Input parameter file for BATCH MODE should be arranged as:
C L1: Input file for ab-plane dielectric function Epsilon 1 and Epsilon 2
C L2: Input file for c-axis dielectric function Epsilon 1 and Epsilon 2
C L3: Output file for storing the effective optical constants
C L4: Model to be used
C L5: Starting and ending frequencies (WL, WH) in wave numbers
C L6: Angle of incident electric field with respect to the ab-plane
C or fraction of ab-plane
C
C Can be repeated to process more files.
C *********************************************************************

REAL Wab [FAR](3000), Wc [FAR](3000)
REAL Elab[FAR](3000), E2ab[FAR](3000)
REAL Elc [FAR](3000), E2c [FAR](3000)
Character*12 Fileab, Filec, 0FILE, FILE, ID*79
COMPLEX R, INDEX, EPS, SIGMA, EPSab, EPSc
DATA PI /3.1415926/

C 10 Format (A)
15 Format (A2)
20 WRITE (*, 25)
25 FORMAT ('OProgram to compute the effective complex dielectric',
1 ' function using the HTSC/
2 ' ab-plane and c-axis dielectric function data.')
30 FORMAT ('0Input file for ab-plane E1, E2: (/ ->', A, ' )' ' $)
31 FORMAT ('0Input file for c-axis E1, E2: (/ ->', A, ' )' ' $)
32 FORMAT (' Enter freq range (WL, WH): (/ ->',2F8.1, ' )' ' $)
33 FORMAT(' Model to be used? (1 => EMA, 2 => MGT, 3 => EFF).',
1 ' ( / -> ',12,' )' ' $)
C ###
C input files for ab-plane and c-axis dielectric functions
C entering '/ means the filename is unchanged (same as previous one)
C otherwise the filename is replaced by the one being entered.
40 WRITE (*, 30) FILEab
READ (*, 10) FILE
IF (FILE .EQ. ' ') STOP 'No input file. All done'
IF (FILE(1:1) .NE. '/') FILEab = FILE
WRITE (*, 31) FILEc
READ (*, 10) FILE
IF (FILE(1:1) .NE. '/') FILEc = FILE
WRITE (*,'(IX,3A \)') 'Output file for OPTCs: (/ ->',0FILE, ' )
READ (*, 10) FILE
IF (FILE(1:1) .NE. '/') OFILE = FILE
WRITE (*, 32) WL, WH
READ (*, *) WL, WH
WRITE (*, 33) MODEL
READ (*, *) MODEL
Open (unit = 2, File = FILEab, Status = 'old')
Open (unit = 3, File = FILEc, Status = 'old')
Open (unit = 4, File = Ofile, Status = 'UNKNOWN')

C -- Record the input filenames into the outfile
Write (4, '(2A)') 'ab-plane file:', FILEAB
Write (4, '(2A)') 'c-plane file:', FILEC

C -- Find the wildcard /* before reading the data
50  Read (2, 10) ID
   If (ID(1:2) .NE. '/*') GO TO 50
55  Read (3, 10) ID
   If (ID(1:2) .NE. '/*') GO TO 55

C
C Now query for constants to write out into file
C Loop for computing parameters
C -- EPS -> effective complex dielectric function
C -- SIGMA -> effective complex conductivity
C -- INDEX -> effective complex index of refraction
C -- R -> effective complex reflection coefficient
C -- PHASE -> effective phase shift of the reflected electric field
C -- REFL -> effective reflectance
C
N, M -> number of data points

C
C Now read the data of the ab-plane dielectric function
WRITE (*, *) 'Reading data ...'
K = 1
60  Read (2, *, End = 70) Wab(K), Elab(K), E2ab(K)
   If (Wab(K) .LT. WL) GO TO 60
   If (Wab(K) .GT. WH) GO TO 70
   K = K +1
   GO TO 60
70  N = K -1
C
C Now read the data of the c-axis dielectric function
K = 1
100 Read (3, *, End = 110) Wc(K), E1c(K), E2c(K)
   If (Wc(K) .LT. WL) GO TO 100
   If (Wc(K) .GT. WH) GO TO 110
   K = K +1
   Go TO 100
110 M = K -1
   N = MINO (N, M)
C ## get the parameter (Metal fraction or incident angle).
   If ( (MODEL .EQ. 1) .OR. (MODEL .EQ. 2) ) THEN
      WRITE (*, 120) Fab
120 FORMAT ('Enter the fraction for ab-plane: (/ -> ,F5.2, ) ')$
      READ (*, *) Fab
      WRITE (4, '(A, F4.2)') 'Fraction of ab-plane f = ', Fab
      If (MODEL .EQ. 1) WRITE (4, *) 'EMA approximation'
      If (MODEL .EQ. 2) WRITE (4, *) 'MGT approximation'
   ELSE
      ## Model 3: Effective 1/EPS = Cos2/Eab + Sin2/Ec
      WRITE (*, 130) ANGLE
130 FORMAT ('Enter the angle of (k,c) or (E,ab) in degree: '),
READ (*,*) ANGLE

C  ## Convert the angle into radian unit  ##

THETA = ANGLE*PI/180.0
COS2 = COS(THETA) * COS(THETA)
SIN2 = 1.0 - COS2

WRITE (4, '(F5.1,1E6)') 'Angle of (E, ab) = ', ANGLE

END IF

WRITE (4, '(7I5,F7.2)') 'l:Freq, 2:Eps 1, 3:Eps 2, 4:Refl, 5:Sigma 1, 6:Phase'

C -- loop to compute the effective optical constants

WRITE (*,*) 'Now computing ...'

DO 250 K = 1, N

IF (ABS(Wab(K) - Wc(K)).GE.1.0) THEN

WRITE (*, '(*,2(4X,A,F8.2))') K, 'Wab =', Wab(K), 'Wc =', Wc(K)

Stop 'Frequencies are not synchronized!'

END IF

WK = Wc(K)
EPSab = CMPLX(E1ab(K), E2ab(K))
EPSc  = CMPLX(E1c(K), E2c(K))

IF (MODEL .EQ. 1) CALL EMA (WK, Fab, EPSab, EPSc, EPS)
IF (MODEL .EQ. 2) CALL MGT (Fab, EPSab, EPSc, EPS)
IF((MODEL .NE. 1).AND.(MODEL .NE. 2))

CALL EFF (COS2, SIN2, EPSab, EPSc, EPS)

SIGMA = CMPLX(0., 1.0) * (1. - EPS) * WK/60.
INDEX = CSQRT(EPS)
R = (1. - INDEX)/(1. + INDEX)
REFL = CABS (R*R)
PHASE = ATAN (AIMAG(R)/REAL(R))

WRITE (4,300) WK, EPS, REFL, REAL(SIGMA), PHASE

250 CONTINUE

300 Format (F8.1, 2F10.2, F8.5, F9.2, F9.6)
400 Write (*, '(2A)') 'Outputfile => ', Ofile
Close (unit = 2)
Close (unit = 3)
Close (unit = 4)

C Computation is done for the current file return to do the next one

Go TO 40

500 FORMAT ('Enter no. of function to be written into file:'/
1 ' (Enter <0> to Stop)'/
2 ' 1 ==> 1/Teff' '/ 2 == Weff^2'/
3 ' 3 ==> Real G(w)'/ 4 ==> Imag G(w)'/
4 ' 5 ==> Real Self-energy'/ 6 ==> Imag Self-energy'/
5 ' 7 ==> Mef/MBand'/ 8 ==> Gamma(w)'/ 9 ==> MIR Gamma(w)'/

600 FORMAT ('A1,'?-W-Can"t find file -- re-enter filespec:')

END

C

SUBROUTINE EMA (W, F, EMET, EINS, EEMA)

C Parameters are grouped as follows:
C For EMA:
C
C F Volume fraction of metal.
C EMET Complex dielectric function for metallic
C EINS Complex dielectric function for insulating

COMPLEX EMET,EINS,EEMA
COMPLEX A,B,C,ZSM,ZLG

C Step 1: Compute EMA dielectric function.
A = 2.0
B = -(2.0-3.0*F)*EINS - (3.0*F-1.0)*EMET
C = -EMET*EINS
CALL ZQADC (A,B,C,ZSM,ZLG,IER)
EEMA = ZSM
IF ( (AIMAG (ZSM) .GT. 0.0) .and. (AIMAG (ZLG) .GT. 0.0) )
* write (*,*),'Warning!! Both roots positive. at \( W = \) ',W
IF (AIMAG (ZSM) .LT. 0.0) EEMA = ZLG
C Write (*,*), W, ZSM, ZLG, EEMA
RETURN
END

C SUBROUTINE MGT (F, Ea, Eb, EMGT)

C Parameters are grouped as follows:
C For MGT:
C
C F Volume fraction of metal.
C Ea Complex dielectric function for metallic
C Eb Complex dielectric function for insulating

COMPLEX EMGT, Ea, Eb
EMGT = Eb + 3*f*(Ea-Eb)*Eb / ( (1-f)*(Ea-Eb) + 3*Eb )
RETURN
END

C SUBROUTINE EFF (COS2, SIN2, Ea, Eb, EPS)

C Parameters are grouped as follows:
C
C EPS = 1./(COS2/Ea + SIN2/Eb)
C
C F Volume fraction of metal.
C Ea Complex dielectric function for metallic
C Eb Complex dielectric function for insulating

COMPLEX EPS, Ea, Eb
EPS = Ea*Eb / (Ea*SIN2 + Eb*COS2)
RETURN
END
REFERENCES


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Feng Gao, also known as Frank, was born, raised, and educated in Canton (Guangzhou), Guangdong Province, of the People’s Republic of China. He is the son of Chouwa Gao and Xiuzhen Lee. His education was interrupted by the “cultural revolution” when he was a first-year secondary school student. In 1978, he was admitted, through the national entrance examinations, into Jinan University in Canton, where he was awarded a physics B.S. in 1982. He then worked as a physics instructor at Jinan university. In 1984, he accepted an offer to enter the master program in physics at the California State University, Northridge, where he was awarded a M.S. degree in 1986. He then transferred to the University of Florida to pursue a Ph.D. program in physics and began his research in optical properties of high T_c superconductors under professor David Tanner since 1987. He accepted an offer in 1992 as a postdoctoral research associate to join the research at the Science Technology Center for Superconductivity and the physics department at the University of Illinois.

He married to Zequn (Sandy) Yu in 1983 and had a daughter, Shan Gao, in 1985, and a son, Peter Gao, in 1989.
I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

David B. Tanner, Chairman
Professor of Physics

I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Neil S. Sullivan
Professor of Physics

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Mark W. Meisel
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James W. Dufty
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I certify that I have read this study and that in my opinion it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Physics in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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